MANUAL OF CHEMICAL METHODS FOR PESTICIDES AND DEVICES

U.S. Environmental Protection Agency

OFFICE OF PESTICIDE PROGRAMS
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Preface

The EPA Manual of Chemical Methods for Pesticides and Devices is a compendium of analytical procedures for technical and commercial pesticide formulations. It is an example of federal and state cooperation which developed through the professional concern of scientists and scientific groups who recognized that uniform, reliable, standardized analytical chemical methods will help regulatory officials better serve the public as well as the regulated industries.

The initial plan to publish a manual originated with the EPA's Beltsville, Maryland laboratory scientists. The idea was proposed to the Methods Clearing House Committee of the Association of American Pest Control Official (AAPCO) for their consideration. In August 1974, at their 28th Annual Meeting, AAPCO passed a resolution requesting EPA's Technical Services Division (TSD) to prepare and maintain a manual of methods for pesticide formulation analysis. In October of the same year, EPA, TSD's Methods Development Coordination chemists (Beltsville, Maryland) and AAPCO's Methods Clearing House Committee (AAPPCO's official body designed to work with EPA) held a meeting to decide on the general format and contents of the proposed manual. In July of 1976, the first edition of the manual was published.

Continuing with the aim of providing analytical methods which can be used to support enforcement actions, the editors decided to reprint the original manual (July 1976); the updates of 1977 and 1979; and 55 additional methods. This 2nd edition EPA Manual of Chemical Methods for Pesticides and Devices contains 317 analytical methods for 162 chemicals which may be found in commercial pesticide formulations.

Although the procedures in this manual have not achieved official AOAC status through collaborative testing, most have been partially validated in the EPA and state laboratories. In many instances, the procedures are believed to be the best and, in some cases, the only methods available for a particular formulation.

It is hoped that these methods will eventually achieve official AOAC status by collaborative study under the direction of AOAC associate referees. If a method achieves official status, it will be published in the AOAC Methods of Analysis and deleted from this manual. All methods will be reviewed by a committee of AOAC referees and AAPCO Clearing House Committee members. The committee will recommend to the editors appropriate actions with respect to corrections, modification, and deletions.

The AOAC recognizes the method gap which exists because of the limited number of applicable official analyses available for analyzing the many pesticide products sold to the public. Therefore, it is pleased to join the EPA and AAPCO through the publication and sale of this manual in making available to industry, states, other nations, academic and scientific institutions, libraries, and the general public these analytical methods currently being used by EPA and state laboratories in pesticide regulatory programs. Where an official AOAC method does exist it is, of course, the method of choice.

The editors wish to thank those people who have contributed in making this manual possible. The editors would also appreciate receiving methods and suggestions for making the manual a viable and continuing source of methodology.

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Preface

This EPA Manual of Chemical Methods for Pesticides and Devices is a compendium of over 200 analytical procedures for commercial pesticide formulations. It also contains 350 infrared curves and a bibliography of books, manuals, and periodicals relating to pesticides.

The initial plan to publish a manual originated within EPA and the idea was proposed to the Methods Clearing House Committee of the Association of American Pesticide Control Officials (AAPCO) for their consideration. In August 1974, at their 28th Annual Meeting, AAPCO passed a resolution requesting EPA's Technical Services Division (TSD) to prepare and maintain a manual of methods for pesticide formulation analysis. In October of the same year, EPA, TSD's Methods Development Coordination chemists, and AAPCO's Methods Clearing House Committee (AAPCO's official body designated to work with EPA) held a meeting to decide on the general format and content of the proposed manual. Also at that time two committees were formed: (1) an Editorial Committee (consisting of 4 EPA pesticide formulation chemists and 2 state chemists recognized by AAPCO as having experience and expertise in formulation analysis) whose task would be to standardize the method format and edit all related material to be included in the manual; (2) a Method Review Committee (comprised of a majority of experienced state chemists and a minority of experienced EPA formulation chemists) having the responsibility for accepting or rejecting analytical methods submitted for inclusion in the manual. The present members of these committees are listed at the end of this preface.

Many of the methods in the manual have been reviewed and accepted by the committee. Some were not reviewed but were accepted because of their wide use (e.g. Virginia Department of Agriculture Methods and Mississippi

State Chemical Laboratory Methods). This procedure was agreed to by AAPCO and EPA in October 1975. Also, it was agreed that certain methods be designated as "Tentative." This designation was chosen for new techniques or experimental methods and for those methods not widely used. However, after one year in the manual, these tentative methods will be submitted to the Method Review Committee for a final decision of full acceptance (removal of "Tentative" designation) or rejection.

Analytical methods are currently being developed at a rapid pace, and procedures and data are being generated at a rate much faster than they can be validated. Although the procedures in this manual have not achieved official AOAC status through collaborative testing, most of them have been partially validated in the EPA and state laboratories. In many instances, the procedures are believed to be the best--in some cases the only--methods available for a particular formulation. It is hoped that the manual methods will eventually achieve official AOAC status by collaborative study under the direction of AOAC Associate Referees. When a method does receive official status, it will be deleted from the manual. The loose-leaf format was chosen to facilitate both this deletion and the addition of new or improved methods and data. Semiannual updates will be issued to keep the manual current and as free from error as possible. The "devices" mentioned in the title of this volume, although not included in the original issue, will appear in future updates.

This manual is an example of Federal and state cooperation that developed through the professional concern of individuals and groups for standardizing chemical analyses used by Federal and state pesticide

regulatory laboratories, and the recognition that uniform, reliable chemical methods will help regulatory officials better serve the public as well as the regulated industries.

The AOAC has recognized the gap that exists because of the limited number of applicable official methods; therefore, it is pleased to join with EPA and AAPCO through the publication and sale of this manual to make available to industry, academic and scientific institutions, libraries, and the public these analytical procedures currently being used by EPA and state laboratories in enforcing the law. Where an official AOAC procedure does exist, it is, of course, the method of choice.

The Editorial Chairman would appreciate receiving corrections, suggestions, and new and improved methods or data for inclusion in this manual. He will forward the methods (after conversion to standard format) and pertinent comments to the chairman of the AAPCO-EPA Review Committee for appropriate action.

The compilers of this manual take this opportunity to thank those who have helped collect the information presented in this volume and to request their help and the help of others in maintaining the manual as a viable and current source of methodology.

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Chairman of the Editorial Committee

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O,O-dimethyl O-p-nitrophenol phosphorothioate	Methyl Parathion EPA-1, 2, 3, 4, & 5
O,O-dimethyl S-(4-oxo-1,2,3-benzo-triazin-3(4H)-ylmethyl) phosphorodithioate	Azinphos-methyl EPA-1
cis-3-(dimethoxyphosphinyloxy)-N-methylcrotonamide	Monocrotophos EPA-1 & 2
dimethyl parathion	Methyl Parathion EPA-1, 2, 3, 4, & 5
dimethyl phosphate of 3-hydroxy-N-methyl-cis-crotonamide	Monocrotophos EPA-1 & 2
1,1-dimethyl-3-(α,α,α-trifluoro-m-tolyl)urea	Fluometuron EPA-1
m-(3,3-dimethylureido)phenyl tert-butylcarbamate	Karbutilate EPA-1
Dinitro	Dinoseb EPA-1 & 2
4,6-dinitro-o-cresol	Nitrophenols EPA-1 & 2
2,4-dinitro-6-octylphenyl crotonate	Dinocap EPA-1 & 2
2,6-dinitro-4-octylphenyl crotonate	Dinocap EPA-1 & 2
Dinocap EPA-1	total nitrogen
Dinocap EPA-2 (tentative)	IR
Dinoseb EPA-1 (tentative)	IR

Dinoseb EPA-2 (tentative)	GLC-TCD
dinoseb methacrylate	Binapacryl EPA-1
dinosebe (France)	Dinoseb EPA-1 & 2
Di-on	Diuron EPA-1, 2, 3, & 4
Diphacin	Diphacinone EPA-1
diphacin (Turkey)	Diphacinone EPA-1
Diphacinone EPA-1	UV
diphenadione	Diphacinone EPA-1
2-(diphenylacetyl)-1,3-indandione	Diphacinone EPA-1
Direz	Anilazine EPA-1 & 2
disodium methanearsonate	Arsenic Compounds EPA-3 & 4
Disulfoton EPA-1 (tentative)	IR
Disulfoton EPA-2 (tentative)	GLC-FID-IS
Disyston	Disulfoton EPA-1 & 2
Di-Syston (US)	Disulfoton EPA-1 & 2
ditranil	Dicloran EPA-1
Dithio-systox	Disulfoton EPA-1 & 2
Diurex	Diuron EPA-1, 2, 3, & 4
Diuron EPA-1	alkaline hydrolysis & titration
Diuron EPA-2 (tentative)	HPLC
Diuron EPA-3 (tentative)	UV
Diuron EPA-4 (tentative)	IR
Dolmix	BHC, gamma isomer EPA-1
DN 289	Dinoseb EPA-1 & 2
DNBP	Dinoseb EPA-1 & 2
DNOC	Nitrophenols EPA-1 & 2
DO14	Propargite EPA-1 & 2

2,4-DP	dichlorprop
Dormone	2,4-D
Dowcide 1	o-phenylphenol
Dowco 132	Crufomate EPA-1 & 2
Dowpon	Dalapon EPA-1
Draza	Methiocarb EPA-1
Drinox	Heptachlor EPA-1
Drop-Leaf	Sodium Chlorate EPA-1
DSMA	Arsenic Compounds EPA-3 & 4
Dyrene	Anilazine EPA-1 & 2
E 601	Methyl Parathion EPA-1, 2, 3, 4, & 5
E 605	Parathion EPA-1 & 2
E 3314	Heptachlor EPA-1
Ectoral	Ronnel EPA-1 & 2
EI 4049	Malathion EPA-1 & 2
Emmatos	Malathion EPA-1 & 2
Embutox	2,4-DB
Endosan	Binapacryl EPA-1
Endosulfan EPA-1	alkaline hydrolysis
Endosulfan EPA-2 (tentative)	IR
Endosulfan EPA-3 (tentative)	GLC-TCD-IS
Endosulfan EPA-4 (tentative)	GLC-FID-IS
Endothal	Endothall EPA-1 & 2
endothal (Europe except Italy)	Endothall EPA-1 & 2
Endothall EPA-1	oxidation & titration
Endothall EPA-2 (tentative)	GLC-FID

ephirsulfonate	Ovex EPA-1
Eptam	EPTC EPA-1, 2, 3, 4, & 5
EPTC EPA-1 (tentative)	GLC-TCD-IS
EPTC EPA-2 (tentative)	HPLC
EPTC EPA-3	GLC-FID-IS
EPTC EPA-4 (tentative)	GLC-FID-IS
EPTC EPA-5 (tentative)	GLC-TCD-IS
Eradicane	EPTC EPA-1, 2, 3, 4, & 5
erbon	Chlorophenoxy Herbicides EPA-1, 2, & 3
Erbon (Dow)	erbon
Esteron	2,4-D
Estone	2,4-D
Estonmite	Ovex EPA-1
Estron 245	2,4,5-T
Ethion EPA-1	IR
Ethion EPA-2 (tentative)	GLC-TCD
Ethodan	Ethion EPA-1 & 2
ethohexadiol	Ethyl Hexanediol EPA-1 & 2
Ethoprop EPA-1 (tentative)	IR
Ethoprop EPA-2 (tentative)	GLC-TCD-IS
Ethoprop EPA-3 (tentative)	GLC-FID-IS
S-ethyl cyclohexylethylthiocarbamate	Cycloate EPA-1
S-ethyl diisobutylthiocarbamate	Butylate EPA-1, 2, 3, 4, & 5
O-ethyl-S,S-dipropyl phosphorodithioate	Ethoprop EPA-1, 2, & 3
S-ethyl dipropylthiocarbamate	EPTC EPA-1, 2, 3, 4, & 5

Ethyl Hexanediol EPA-1	acetylation & titration
Ethyl Hexanediol EPA-2 (tentative)	GLC-TCD-IS
2-ethyl-1,3-hexanediol	Ethyl Hexanediol EPA-1 & 2
ethylhexylene glycol	Ethyl Hexanediol EPA-1 & 2
Ethyl Parathion	Parathion EPA-1 & 2
Etilon	Parathion EPA-1 & 2
Etrolene	Ronnel EPA-1 & 2
Eurex	Cycloate EPA-1, 2, & 3
Fall	Sodium Chlorate EPA-1
Falone	2,4-DEP
FBHC	BHC, gamma isomer EPA-1
Fence Rider	2,4,5-T
fenchlorphos (ISO and BSI)	Ronnel EPA-1 & 2
Fermide	Thiram EPA-1 & 2
Fernesta	2,4-D
Fernimine	2,4-D
Fernoxone	2,4-D
ferroprop	silvex
Ferxone	2,4-D
flour sulfur	Sulfur EPA-1, 2, & 3
flowers of sulfur	Sulfur EPA-1, 2, & 3
Fluometuron EPA-1	IR
FMC 5273	Piperonyl Butoxide EPA-1 & 2
FMC 5462	Endosulfan EPA-1, 2, 3, & 4
FMC 9044	Binapacryl EPA-1
FMC 10242	Carbofuran EPA-1

FMC 17370	Resmethrin EPA-1, 2, 3, 4, & 5
Folcid	Captafol EPA-1
Folidol	Parathion EPA-1 & 2
Folidol M	Methyl Parathion EPA-1, 2, 3, 4, & 5
Folpan	Folpet EPA-1
Folpet EPA-1	IR
For-mal	Malathion EPA-1 & 2
Forron	2,4,5-T
Fortrol	Cyanazine EPA-1
Fosferno	Parathion EPA-1 & 2
Fosferno M50	Methyl Parathion EPA-1, 2, 3, 4, & 5
Fosfono	Parathion EPA-1 & 2
Fruitone A	2,4,5-T
Fruitone T	silvex
Frumin AL	Disulfoton EPA-1 & 2
Fumarin	Coumafuryl EPA-1 & 2
fumarin (Great Britain, New Zealand)	Coumafuryl EPA-1 & 2
Fumazone	Dibromochloropropane EPA-1 & 2
Furadan	Carbofuran EPA-1
Fylanon	Malathion EPA-1 & 2
G-24480	Diazinon EPA-1, 2, 3, & 4
G-30027	Atrazine EPA-1 & 2
G-41435	Prometone EPA-1 & 2
Gammexane	BHC, gamma isomer EPA-1
Gardentox	Diazinon EPA-1, 2, 3, & 4

Garlon	silvex
Gearphos	Methyl Parathion EPA-1, 2, 3, 4, & 5
Gebutox	Dinoseb EPA-1 & 2
Genitox	DDT EPA-1
Gesafram	Prometone EPA-1 & 2
Gesapon	DDT EPA-1
Gesaprim	Atrazine EPA-1 & 2
Gesarex	DDT EPA-1
Gesarol	DDT EPA-1
Gesatop	Simazine EPA-1
Gramevin	Dalapon EPA-1
Guesarol	DDT EPA-1
Gusathion	Azinphos-methyl EPA-1
Guthion	Azinphos-methyl EPA-1
Gyron	DDT EPA-1
H 119	Pyrazon EPA-1
H 133	Dichlobenil EPA-1
H 321	Methiocarb EPA-1
Haiari (British Guiana)	Rotenone EPA-1
HCCH	BHC, gamma isomer EPA-1
HCH	BHC, gamma isomer EPA-1
Hedonal	2,4-D
Hedonal MCPP	mecoprop
Heptachlor EPA-1	IR
1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	Heptachlor EPA-1

Heptachlorotetrahydro-4,7-methano-indene (and related compounds)	Heptachlor EPA-1
Heptamul	Heptachlor EPA-1
Herbicide 273	Endothall EPA-1 & 2
Herbicide 283	Endothall EPA-1 & 2
Herbizole	Amitrole EPA-1
Hercules 9573	Terbutol EPA-1 & 2
hexachlor	BHC, gamma isomer EPA-1
hexachloran	BHC, gamma isomer EPA-1
1,2,3,4,5,6-hexachlorocyclohexane	BHC, gamma isomer EPA-1
Hexachlorohexahydromethano-2,3,4-benzodioxathiepin-3-oxide	Endosulfan EPA-1, 2, 3, & 4
Hexafor	BHC, gamma isomer EPA-1
Hexathir	Thiram EPA-1 & 2
Hexavin	Carbaryl EPA-1 & 2
Hexyclan	BHC, gamma isomer EPA-1
Hibor	Bromacil EPA-1
HOE 2671	Endosulfan EPA-1, 2, 3, & 4
HOE 2784	Binapacryl EPA-1
HOE 2810	Linuron EPA-1 & 2
Hormodin	Indolebutyric acid EPA-1
Hormotuho	MCPA
Hydout	Endothall EPA-1 & 2
o-hydrodiphenyl	o-phenylphenol
Hydrothol	Endothall EPA-1 & 2
6-hydroxy-3-(2H)-pyridazinone	MH EPA-1
5-(alpha-hydroxy-alpha-2-pyridyl-benzyl)-7-(alpha-2-pyridylbenzyl-idene-5-norborene-2,3-dicarboximide	Norbormide EPA-1
Hyvar	Bromacil EPA-1

Indolebutyric acid EPA-1	UV
indole-3-butyric acid	Indolebutyric acid EPA-1
3-indolebutyric acid	Indolebutyric acid EPA-1
4-(3-indolyl)-butyric acid	Indolebutyric acid EPA-1
Inorganic phosphorus compounds	Phosphorus Compounds EPA-1
6-12 Insect Repellent	Ethyl Hexanediol EPA-1 & 2
Insectophene	Endosulfan EPA-1, 2, 3, & 4
Inverton 245	2,4,5-T
Iso-Comox	mecoprop
Isocothan	Dinocap EPA-1 & 2
2-isovaleryl-1,3-indandione	PMP EPA-1, 2, & 3
Ixodex	DDT EPA-1
jasmolins	Pyrethrins EPA-1
Karathane	Dinocap EPA-1 & 2
Karbaspray	Carbaryl EPA-1 & 2
Karbofos	Malathion EPA-1 & 2
Karbutilate EPA-1	IR
Karmex	Diuron EPA-1, 2, 3, & 4
Kemate	Anilazine EPA-1 & 2
Kiloseb	Dinoseb EPA-1 & 2
Kilprop	mecoprop
Kilrat	Zinc Phosphide EPA-1 & 2
Kilsem	MCPA
Kloben	Neburon EPA-1
KMH	MH EPA-1
Knoxweed	EPTC EPA-1, 2, 3, 4, & 5

Kopsol	DDT EPA-1
Kop-Thiodan	Endosulfan EPA-1, 2, 3, & 4
Kop-thion	Malathion EPA-1 & 2
Korlan	Ronnel EPA-1 & 2
Klorex	Sodium Chlorate EPA-1
Krovar	Bromacil EPA-1
Kuron	silvex
Kurosal	silvex
Kwik-kil	Strychnine EPA-1 & 2
Kypfarin	Warfarin EPA-1, 2, & 3
Kyphos	Malathion EPA-1 & 2
Lanex	Fluometuron EPA-1
Lasso	Alachlor EPA-1 & 2
Lazo	Alachlor EPA-1 & 2
lead arsenate	Arsenic Compounds EPA-1 & 2
lemongrass oil	Oil of Lemongrass EPA-1
Line Rider	2,4,5-T
Linuron EPA-1 (tentative)	HPLC
Linuron EPA-2	IR
Lonchocarpus	Rotenone EPA-1
Lorox	Linuron EPA-1 & 2
M-74 (USSR)	Disulfoton EPA-1 & 2
MAA	Arsenic Compounds EPA-3 & 4
Maintain 3	MH EPA-1
Malamar	Malathion EPA-1 & 2
Malaspray	Malathion EPA-1 & 2

Malathion EPA-1 (tentative)	HPLC
Malathion EPA-2	IR
maleic hydrazide	MH EPA-1
Malix	Endosulfan EPA-1, 2, 3, & 4
Maloran	Chlorbromuron EPA-1
MAMA	Arsenic Compounds EPA-3 & 4
Marlate	Methoxychlor EPA-1 & 2
MB 2878	2,4-DB
MB 3046	MCPB
MCP	MCPA
MCPA	Chlorophenoxy Herbicides EPA-1, 2, & 3
MCPB	Chlorophenoxy Herbicides EPA-1, 2, & 3
2,4-MCPB	MCPB
MCPP	mecoprop
mecoprop	Chlorophenoxy Herbicides EPA-1, 2, & 3
Meldane	Coumaphos EPA-1, 2, & 3
Mephanac	MCPA
Mepro	mecoprop
mercaptodimethur	Methiocarb EPA-1
mercaptothion	Malathion EPA-1 & 2
Mercuram	Thiram EPA-1 & 2
Merpan	Captan EPA-1 & 2
Mesurol	Methiocarb EPA-1
Meta	Metaldehyde EPA-1, 2, 3, & 4
metacetaldehyde	Metaldehyde EPA-1, 2, 3, & 4
Metacide	Methyl Parathion EPA-1, 2, 3, 4, & 5

Metadelphene	Deet EPA-1, 2, & 3
Metaldehyde EPA-1	iodimetric titration
Metaldehyde EPA-2 (tentative)	GLC-TCD-IS
Metaldehyde EPA-3 (tentative)	IR
Metaldehyde EPA-4 (tentative)	GLC-TCD
Metaphos	Methyl Parathion EPA-1, 2, 3, 4, & 5
metaxon	MCPA
methanearsonic acid	Arsenic Compounds EPA-3 & 4
Methiocarb EPA-1 (tentative)	IR
Methoxone	mecoprop
Methoxychlor EPA-1 (tentative)	IR
Methoxychlor EPA-2 (tentative)	GLC-FID-IS
2,2-bis(p-methoxyphenyl)-1,1,1-trichloroethane 88% and related compounds 12%	Methoxychlor EPA-1 & 2
methyl-1-(butylcarbamoyl)-2-benzimidazolecarbamate	Benomyl EPA-1 & 2
O-methyl O-2-chloro-4-tert-butyl-phenol N-methylamidophosphate	Crufomate EPA-1 & 2
4-(2-methyl-4-chlorophenoxy) acetic acid	MCPA
4-(2-methyl-4-chlorophenoxy) butyric acid	MCPB
2-(2-methyl-4-chlorophenoxy) propionic acid	mecoprop
1-(2-methylcyclohexyl)-3-phenylurea	Siduron EPA-1
2,2'-methylenebis(4-chlorophenol)	Phenols & Chlorophenols EPA-1, 3, & 8
2,2'-methylenebis(3,4,6-trichloro-phenol)	Phenols & Chlorophenols EPA-1, 3, & 8
Methyl Parathion EPA-1 (tentative)	HPLC

Methyl Parathion EPA-2	IR
Methyl Parathion EPA-3	colorimetric (visible) spectroscopy
Methyl Parathion EPA-4	GLC-FID-IS
Methyl Parathion EPA-5	GLC-FID-IS
4-(methylthio)-3,5-xylyl N-methylcarbamate	Methiocarb EPA-1
Metiltriazotion	Azinphos-methyl EPA-1
metmercapturon	Methiocarb EPA-1
Metobromuron EPA-1 (tentative)	IR
Metobromuron EPA-2 (tentative)	GLC-FID
Metobromuron EPA-3 (tentative)	GLC-TCD-IS
Metron	Methyl Parathion EPA-1, 2, 3, 4, & 5
MH EPA-1	UV
MH-30	MH EPA-1
Mildex	Dinocap EPA-1 & 2
2M-4Kh-M	MCPB
MLT	Malathion EPA-1 & 2
Mocap	Ethoprop EPA-1, 2, & 3
monoammonium methanearsonate	Arsenic Compounds EPA-3 & 4
Monocron	Monocrotophos EPA-1 & 2
Monocrotophos EPA-1	IR
Monocrotophos EPA-2	GLC-FID-IS
monosodium methanearsonate	Arsenic Compounds EPA-3 & 4
Monurex	Monuron EPA-1, 2, & 3
Monuron EPA-1	alkaline hydrolysis & titration
Monuron EPA-2	UV
Monuron EPA-3	IR

Morocide	Binapacryl EPA-1
Mous-con	Zinc Phosphide
Mouse-tox	Strychnine EPA-1 & 2
Moxie	Methoxychlor EPA-1 & 2
MSMA	Arsenic Compounds EPA-3 & 4
Muscatox	Coumaphos EPA-1, 2, & 3
Nankor	Ronnel EPA-1 & 2
1-naphthyl methylcarbamate	Carbaryl EPA-1
neburea	Neburon EPA-1
Neburex	Neburon EPA-1
Neburon EPA-1 (tentative)	IR
Nekos (Dutch Guiana)	Rotenone EPA-1
Nemafume	Dibromochloropropane EPA-1 & 2
Nemagon	Dibromochloropropane EPA-1 & 2
Neocid	DDT EPA-1
Neocidol	Diazinon EPA-1, 2, 3, & 4
NIA 1240	Ethion EPA-1 & 2
NIA 5273	Piperonyl Butoxide EPA-1 & 2
NIA 5462	Endosulfan EPA-1, 2, 3, & 4
NIA 9044	Binapacryl EPA-1
NIA 10242	Carbofuran EPA-1
NIA 11092	Karbutilate EPA-1
NIA 17370	Resmethrin EPA-1, 2, 3, 4, & 5
Niagaratran	Ovex EPA-1
Nialate	Ethion EPA-1 & 2
Nicouline	Rotenone EPA-1
Nivan	Parathion EPA-1 & 2

Nitrophenols EPA-1	stannous chloride reduction
Nitrophenols EPA-2	total nitrogen
Nitropone	Dinoseb EPA-1 & 2
Nitrox 80	Methyl Parathion EPA-1, 2, 3, 4, & 5
Nomersan	Thiram EPA-1 & 2
Nor-Am	Chloroxuron EPA-1 & 2
Norbormide EPA-1	UV
Norex	Chloroxuron EPA-1 & 2
NRDC 104	Resmethrin EPA-1, 2, 3, 4, & 5
Nucidol	Diazinon EPA-1, 2, 3, & 4
Nuvacron	Monocrotophos EPA-1 & 2
Off	Deet EPA-1, 2, & 3
Oil of Lemongrass EPA-1 (tentative)	GLC-TCD
oil of verbena (Indian)	Oil of Lemongrass EPA-1
Omite	Propargite EPA-1 & 2
Organophosphorus compounds	Phosphorus Compounds EPA-1
Organotin Compounds EPA-1	oxidation, reduction, titration
orthoboric acid	Boron Compounds EPA-1
Orthocide	Captan EPA-1 & 2
Orthophos	Parathion EPA-1 & 2
orthoxenol	o-phenylphenol
OS 1898	Dibromochloropropane EPA-1 & 2
ovatran (Argentina)	Ovex EPA-1
Ovex EPA-1	IR
ovochlor	Ovex EPA-1
Ovotran	Ovex EPA-1

Outrack	Prometone EPA-1 & 2
7-oxabicyclo(2,2,1)heptane-2,3-dicarboxylic acid	Endothall EPA-1 & 2
PCA	Pyrazon EPA-1
PCP	pentachlorophenol
PDB	p-Dichlorobenzene EPA-1 & 2
PDQ	MCPB
Panthion	Parathion EPA-1 & 2
Paracide	p-Dichlorobenzene EPA-1 & 2
paradichlorobenzene	p-Dichlorobenzene EPA-1 & 2
Paradow	p-Dichlorobenzene EPA-1 & 2
Paramar	Parathion EPA-1 & 2
Paraphos	Parathion EPA-1 & 2
Parathene	Parathion EPA-1 & 2
Parathion EPA-1 (tentative)	HPLC
Parathion EPA-2 (tentative)	GLC-FID-IS
parathion-methyl (ISO and BSI)	Methyl Parathion EPA-1, 2, 3, 4, & 5
Parawet	Parathion EPA-1 & 2
Paris green	Arsenic Compounds EPA-1 & 2
Partron M	Methyl Parathion EPA-1, 2, 3, 4, & 5
Patoran	Metobromuron EPA-1, 2, & 3
Pebulate EPA-1 (tentative)	GLC-TCD
Pebulate EPA-2 (tentative)	GLC-FID-IS
Pebulate EPA-3 (tentative)	GLC-FID-IS
Pennamine D	2,4-D
Penta	pentachlorophenol

Pentachlorin	DDT EPA-1
pentachlorophenol	Phenols & Chlorophenols EPA-1, 3, & 5
Pentaphen	p-tert-amylphenol
p-tert-pentylphenol	p-tert-amylphenol
Phaltan	Folpet EPA-1
Phenols & Chlorophenols EPA-1	Definition, Structure, and Technical Data
Phenols & Chlorophenols EPA-2	UV
Phenols & Chlorophenols EPA-3	lime fusion
Phenols & Chlorophenols EPA-4	bromination & titration
Phenols & Chlorophenols EPA-5 (tentative)	HPLC
Phenols & Chlorophenols EPA-6 (tentative)	GLC-TCD
Phenols & Chlorophenols EPA-7 (tentative)	GLC-TCD-FID
Phenols & Chlorophenols EPA-8 (tentative)	GLC-TCD-IS
Phenothiazine EPA-1 (tentative)	IR
o-phenylphenol	Phenols & Chlorophenols EPA-1, 2, 4, 6, & 8
Phorate EPA-1	IR
Phoskil	Parathion EPA-1 & 2
Phosphorus Compounds EPA-1	acid digestion and gravimetric procedure
Phygon	Dichlone EPA-1
Picloram EPA-1 (tentative)	HPLC
Pindone EPA-1	UV (ether extraction)
Pindone EPA-2	UV (pyrophosphate extraction)
Pindone EPA-3	UV (water-soluble formulations)

Piperonyl Butoxide EPA-1	qualitative test
Piperonyl Butoxide EPA-2	GLC-FID-IS
Pival	Pindone EPA-1, 2, & 3
pival (Portugal, Turkey)	Pindone EPA-1, 2, & 3
pivaldione	Pindone EPA-1, 2, & 3
2-pivalyl-1,3-indandione	Pindone EPA-1, 2, & 3
Pivalyl valone	Pindone EPA-1, 2, & 3
Pivalyn	Pindone EPA-1, 2, & 3
PMP EPA-1	UV (ether extraction)
PMP EPA-2	UV (pyrophosphate extraction)
PMP EPA-3	UV (water-soluble formulation)
Pomarsol	Thiram EPA-1 & 2
Pramitol	Prometone EPA-1 & 2
precipitated sulfur	Sulfur EPA-1, 2, & 3
Prefar	Bensulide EPA-1
Premerge	Dinoseb EPA-1 & 2
Primatol	Prometone EPA-1 & 2
Primatol A	Atrazine EPA-1 & 2
Primatol S	Simazine EPA-1
Princep	Simazine EPA-1
Printop	Simazine EPA-1
prometon (ISO)	Prometone EPA-1 & 2
Prometone EPA-1 (tentative)	GLC-TCD-IS
Prometone EPA-2 (tentative)	GLC-FID-IS
Propargite EPA-1 (tentative)	IR
Propargite EPA-2 (tentative)	GLC-TCD-IS
propazine	Chloro-Triazine Herbicides EPA-1

prophos	Ethoprop EPA-1, 2, & 3
S-propyl butylethylthiocarbamate	Pebulate EPA-1, 2, & 3
S-propyl dipropylthiocarbamate	Vernolate EPA-1, 2, & 3
S-propyl N,N-dipropyl thiocarbamate	Vernolate EPA-1, 2, & 3
Protex	Rotenone EPA-1
Pyramin	Pyrazon EPA-1
Pyrazon EPA-1 (tentative)	IR
Pyrethrins EPA-1	Description, Structure, and Technical Data
Pyrethrins EPA-2	GLC-FID
Pyrethrins EPA-3	steam distillation & titration (Seil method)
Quaternary Ammonium Compounds EPA-1	Definition, Structure, Technical Data Halogen and Nitrogen Conversion Factors
Quaternary Ammonium Compounds EPA-2	qualitative (Auerbach) tests
Quaternary Ammonium Compounds EPA-3	ferricyanide method
Quaternary Ammonium Compounds EPA-4	Epton titration method
Quaternary Ammonium Compounds EPA-5	potentiometric titration
Quilan	Benefin EPA-1 & 2
R 1582	Azinphos-methyl EPA-1
R 1607	Vernolate EPA-1, 2, & 3
R 1910	Butylate EPA-1, 2, 3, 4, & 5
R 2061	Pebulate EPA-1, 2, & 3
R 2063	Cycloate EPA-1, 2, & 3
Radapon	Dalapon EPA-1
Ramik	Diphacinone EPA-1
Rampart	Phorate EPA-1

Ranyon	Carbaryl EPA-1 & 2
Rasikal	Sodium Chlorate EPA-1
Raticate	Norbormide EPA-1
RD 406	dichlorprop
RD 4593	mecoprop
Reddon	2,4,5-T
Regulox	MH EPA-1
Resitox	Coumaphos EPA-1, 2, & 3
Resmethrin EPA-1 (tentative)	IR
Resmethrin EPA-2 (tentative)	GLC-TCD
Resmethrin EPA-3 (tentative)	GLC-TCD-IS
Resmethrin EPA-4 (tentative)	HPLC
Resmethrin EPA-5 (tentative)	GLC-FID-IS
Retard	MH EPA-1
Rhodiatox	Parathion EPA-1 & 2
Rhomene	MCPA
Rhonox	MCPA
rock sulfur, ground	Sulfur EPA-1, 2, & 3
Ro-Dec	Strychnine EPA-1 & 2
Ro-Neet	Cycloate EPA-1, 2, & 3
Ronnel EPA-1	IR
Ronnel EPA-2	GLC-FID-IS
Rotenone EPA-1	qualitative tests
Royal MH-30	MH EPA-1
Ruelene	Crufomate EPA-1 & 2
Rukseam	DDT EPA-1
Rumetan	Zinc Phosphide EPA-1 & 2
Rutgers 6-12	Ethyl Hexanediol EPA-1 & 2

S-276	Disulfoton EPA-1 & 2
666	BHC, gamma isomer EPA-1
Salicylanilide EPA-1	UV
Salvo	2,4-D
Santochlor	p-Dichlorobenzene EPA-1 & 2
Santophen 1	o-benzyl-p-chlorophenol
Santophen 20	pentachlorophenol
Sappiran	Ovex EPA-1
Sarclex	Linuron EPA-1 & 2
Sarolex	Diazinon EPA-1, 2, 3, & 4
SBP 1382	Resmethrin EPA-1, 2, 3, 4, & 5
SD 15418	Cyanazine EPA-1
Septene	Carbaryl EPA-1 & 2
Septiphene	o-benzyl-p-chlorophenol
Seradix	Indolebutyric acid EPA-1
Sevin	Carbaryl EPA-1 & 2
sevin (USSR)	Carbaryl EPA-1 & 2
Shed-a-Leaf	Sodium Chlorate EPA-1
Shirlan	Salicylanilide EPA-1
Shoxin	Norbormide EPA-1
Siduron EPA-1 (tentative)	UV
silvex	Chlorophenoxy Herbicides EPA-1, 2, 3, & 5
Simanex	Simazine EPA-1
simazine	Chloro-Triazine Herbicides EPA-1
Simazine EPA-1 (tentative)	UV
Sinox	Dinoseb EPA-1 & 2

Slo-Gro	MH EPA-1
sodium arsenate	Arsenic Compounds EPA-1 & 2
sodium arsenite	Arsenic Compounds EPA-1 & 2
sodium biborate	Boron Compounds EPA-1
Sodium Chlorate EPA-1	reduction and titration
sodium pyroborate	Boron Compounds EPA-1
sodium tetraborate decahydrate	Boron Compounds EPA-1
Solvirex	Disulfoton EPA-1 & 2
Soprathion	Parathion EPA-1 & 2
Soprocide	BHC, gamma isomer EPA-1
Spectracide	Diazinon EPA-1, 2, 3, & 4
Spotrete	Thiram EPA-1 & 2
Sprout-Stop	MH EPA-1
Strathion	Parathion EPA-1 & 2
Streptomycin EPA-1	UV or colorimetric spectroscopy
streptomycine (France)	Streptomycin EPA-1
streptomycin hydrochloride	Streptomycin EPA-1
streptomycin nitrate	Streptomycin EPA-1
streptomycin sulfate	Streptomycin EPA-1
Strychnine EPA-1	picric acid precipitation
Strychnine EPA-2	UV
Stuntman	MH EPA-1
sublimed sulfur	Sulfur EPA-1, 2, & 3
Suckerstuff	MH EPA-1
Sulfur EPA-1	CS_2 extraction
Sulfur EPA-2	barium sulfate precipitation
Sulfur EPA-3	CS_2 extraction (presence acetone-soluble pesticides)

Sulfur Dioxide EPA-1	iodine titration
sulfurous acid anhydride	Sulfur Dioxide EPA-1
sulfurous oxide	Sulfur Dioxide EPA-1
Su Seguro Carpidor	Trifluralin EPA-1 & 2
Sutan	Butylate EPA-1, 2, 3, 4, & 5
Synthrin	Resmethrin EPA-1, 2, 3, 4, & 5
2,4,5-T	Chlorophenoxy Herbicides EPA-1, 2, 3, 4, & 5
2,4,5-TB	Chlorophenoxy Herbicides EPA-1, 2, & 3
4-2,4,5-TB	2,4,5-TB
Tabatrex	Dibutyl Succinate EPA-1
Tabutrex	Dibutyl Succinate EPA-1
Tandex	Karbutilate EPA-1
TCC	Trichlorocarbanilide EPA-1
Tekwaisa	Methyl Parathion EPA-1, 2, 3, 4, & 5
Telvar	Monuron EPA-1, 2, & 3
Temasept	Brominated Salicylanilides EPA-1
Tenoran	Chloroxuron EPA-1 & 2
Terbucarb	Terbutol EPA-1 & 2
Terbutol EPA-1 (tentative)	IR
Terbutol EPA-2 (tentative)	GLC-FID-IS
Termil	Chlorothalonil EPA-1
Tersan	Thiram EPA-1 & 2
Tersan 1991	Benomyl EPA-1 & 2
2,4,5,6-tetrachloro-3-cyanobenzonitrile	Chlorothalonil EPA-1

2,4,5,6-tetrachloro-1,3-dicyanobenzene	Chlorothalonil EPA-1
cis-N-[(1,1,2,2-tetrachloroethyl)thio]-4-cyclohexene-1,2-dicarboximide	Captafol EPA-1
tetrachloroisophthalonitrile	Chlorothalonil EPA-1
O,O,O',O'-tetraethyl S,S'-methylene bisphosphorodithioate	Ethion EPA-1 & 2
1,2,3,6-tetrahydro-3,6-dioxo-pyridazine	MH EPA-1
tetramethylthiuram disulfide	Thiram EPA-1 & 2
Thifor	Endosulfan EPA-1, 2, 3, & 4
Thimar	Thiram EPA-1 & 2
Thimet	Phorate EPA-1
Thimul	Endosulfan EPA-1, 2, 3, & 4
Thiodan	Endosulfan EPA-1, 2, 3, & 4
thiodemeton	Disulfoton EPA-1 & 2
thiodiphenylamine	Phenothiazine EPA-1
Thionex	Endosulfan EPA-1, 2, 3, & 4
thiophal	Folpet EPA-1
thiophos	Parathion EPA-1 & 2
Thiram EPA-1	UV
Thiram EPA-2	IR
Thistrol	MCPB
Thylate	Thiram EPA-1 & 2
Tillam	Pebulate EPA-1, 2, & 3
Timbo (Brazil)	Rotenone EPA-1
timet	Phorate EPA-1
tin, organic compounds	Organotin Compounds EPA-1
TMTD	Thiram EPA-1 & 2

tomarin	Coumafuryl EPA-1 & 2
Tordon	Picloram EPA-1
Tormona	2,4,5-T
2,4,5-TP	silvex
Trefanocide	Trifluralin EPA-1 & 2
Treficon	Trifluralin EPA-1 & 2
Treflan	Trifluralin EPA-1 & 2
Triasyn	Anilazine EPA-1 & 2
3,4',5-tribromosalicylanilides	Brominated Salicylanilides EPA-1
Tributon	2,4-D or 2,4,5-T
tributyltin compounds	Organotin Compounds EPA-1
Tricarnam	Carbaryl EPA-1 & 2
trichlorfension	Ovex EPA-1
1,1,1-trichloro-2,2-bis (p-chlorophenyl)ethane	DDT EPA-1
1,1,1-trichloro-2,2-bis (p-methoxyphenyl)ethane	Methoxychlor EPA-1 & 2
Trichlorocarbanilide EPA-1	UV
3,4,4'-trichlorocarbanilide	Trichlorocarbanilide EPA-1
N-trichloromethylthio-4-cyclo-hexene-1,2-dicarboximide	Captan EPA-1
N-(trichloromethylthio)phthalimide	Folpet EPA-1
2,4,5-trichlorophenoxy acetic acid	2,4,5-T
4-(2,4,5-trichlorophenoxy)butyric acid	2,4,5-TB
2-(2,4,5-trichlorophenoxy)ethyl-2,2-dichloropropionate	erbon
2-(2,4,5-trichlorophenoxy)propionic acid	silvex
Tri-Endothal	Endothall EPA-1 & 2
α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine	Trifluralin EPA-1 & 2

Trifluralin EPA-1	GLC-FID-IS
Trifluralin EPA-2	IR
Triflurex	Trifluralin EPA-1 & 2
Trioxone	2,4,5-T
triphenyltin compounds	Organotin Compounds EPA-1
tris[2-(2,4-dichlorophenoxy)ethyl] phosphite	2,4-DEP
Trolene	Ronnel EPA-1 & 2
Tropotox	MCPB
Tuads	Thiram EPA-1 & 2
tubatoxin	Rotenone EPA-1
Tupersan	Siduron EPA-1
UC 7744	Carbaryl EPA-1 & 2
Unipon	Dalapon EPA-1
Uniroyal	Diclone EPA-1
Ureabor	Bromacil EPA-1
USR 604	Dichlone 604
Valone	PMP EPA-1, 2, & 3
Vancide	Thiram EPA-1 & 2
VC 9-104	Ethoprop EPA-1, 2, & 3
Velsicol 104	Heptachlor EPA-1
Vergemaster	2,4-D
Vernam	Vernolate EPA-1, 2, & 3
Vernolate EPA-1	IR
Vernolate EPA-2	GLC-FID-IS
Vernolate EPA-3 (tentative)	GLC-TCD-IS
Vertron 2D	2,4-D

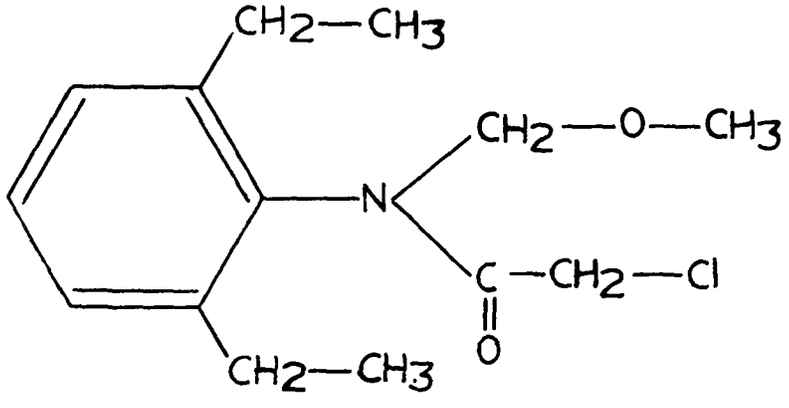
Viozene	Ronnel EPA-1 & 2
Visko-Rhop	2,4-D
Vitavax	Carboxin EPA-1
Vonaldehyde	MH EPA-1
Voncaptan	Captan EPA-1 & 2
Vondrax	MH EPA-1
Vonduron	Diuron EPA-1, 2, 3, & 4
WARF	Warfarin EPA-1, 2, & 3
Warfarin EPA-1 (tentative)	HPLC
Warfarin EPA-2	UV
Warfarin EPA-3 (tentative)	HPLC (sodium salt)
Weedar	2,4-D or 2,4,5-T
Weedazole	Amitrole EPA-1
Weedone	2,4-D
Weedone 170	dichlorprop
Weedone 2,4-DP	dichlorprop
Weedone 2,4,5-T	2,4,5-T
Weedone 2,4,5-TP	silvex
WL 19805	Cyanazine EPA-1
Wolfatox	Methyl Parathion EPA-1, 2, 3, 4, & 5
3Y9	2,4-DEP
Zelan	MCPA
Zerdane	DDT EPA-1
Zinc Phosphide EPA-1	phosphine evolution
Zinc Phosphide EPA-2	GLC-FPD
Zithiol	Malathion EPA-1 & 2
Zoocoumarin	Warfarin EPA-1, 2, & 3

December 1975

Alachlor EPA-1
(Tentative)

Determination of Alachlor by Gas-Liquid Chromatography (TCD - Internal Standard)

Alachlor is the common name for 2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide, a registered herbicide having the chemical structure:



Molecular formula: $C_{14}H_{20}ClNO_2$

Molecular weight: 269.8

Melting point: 39.5 to 41.5°C

Physical state, color, and odor: odorless, cream-colored crystalline solid (at RT)

Solubility: 242 ppm in water at 25°C; soluble in acetone, benzene, chloroform, ethanol, ethyl acetate; slightly soluble in heptane

Stability: hydrolyzed under strongly acid or alkaline conditions; good resistance to decomposition by UV irradiation

Other names: Lasso (Monsanto), CP 50144, Lazo

Reagents:

1. Alachlor standard of known % purity
2. Benzyl benzoate standard of known % purity
3. Chloroform, pesticide or spectro grade
4. Internal Standard solution - weigh 0.625 gram benzyl benzoate into a 50 ml volumetric flask, dissolve in, and make to volume with chloroform. (conc 12.5 mg benzyl benzoate/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 6' x 1/8" stainless steel, packed with 10% SE-30 on 80/100 Diatoport S (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	225°C
Injection temperature:	235°C
Detector temperature:	235°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas flow:	25 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.2 gram alachlor standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 20 mg alachlor and 12.5 mg benzyl benzoate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.2 gram alachlor into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the alachlor. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 20 mg alachlor and 12.5 mg benzyl benzoate/ml)

Determination:

Inject 2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is benzyl benzoate, then alachlor.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of alachlor and benzyl benzoate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

I.S. = internal standard = benzyl benzoate

$$RF = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area alachlor})}{(\text{wt. alachlor})(\%\text{ purity alachlor})(\text{pk. ht. or area I.S.})}$$

Determine the percent alachlor for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area alachlor})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area I.S.})(RF)} \quad U\text{-}1$$

Method submitted by Stelios Gerazounis, EPA, Region II, New York, N.Y.

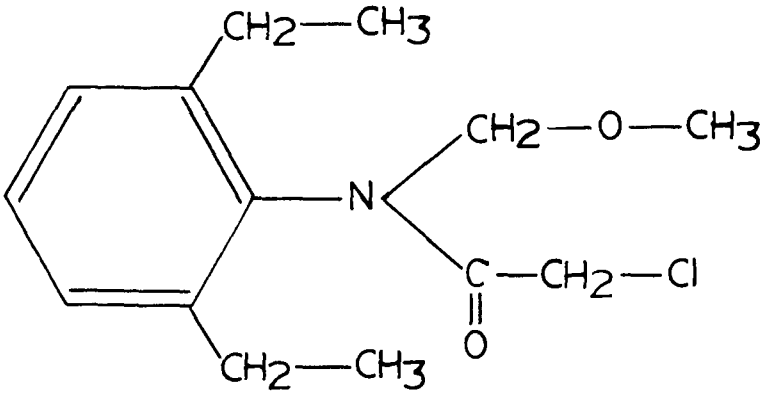
Note! It has been suggested to cut down on the concentration of internal standard, standard, and sample solutions by a factor of 5 and increase the amount injected by a factor of 5. This would use less standards.

December 1975

Alachlor EPA-2
(Tentative)

Determination of Alachlor by Gas-Liquid Chromatography (FID - Internal Standard)

Alachlor is the common name for 2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide, a registered herbicide having the chemical structure:



Molecular formula: $C_{14}H_{20}ClNO_2$

Molecular weight: 269.8

Melting point: 39.5 to 41.5°C

Physical state, color, and odor: odorless, cream-colored crystalline solid (at RT)

Solubility: 242 ppm in water at 25°C; soluble in acetone, benzene, chloroform, ethanol, ethyl acetate; slightly soluble in heptane

Stability: hydrolyzed under strongly acid or alkaline conditions; good resistance to decomposition by UV irradiation

Other names: Lasso (Monsanto), CP 50144, Lazo

Reagents:

1. Alachlor standard of known % purity
2. Triphenylmethane standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.15 gram triphenylmethane into a 50 ml volumetric flask, dissolve in, and make to volume with acetone. (conc 3 mg triphenylmethane/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm glass column packed with 5% SE-30 on 80/100 Chromosorb W HP (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	190°C
Injection temperature:	240°C
Detector temperature:	240°C
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi (adjusted for specific GC)
Hydrogen pressure:	20 psi (adjusted for specific GC)
Air pressure:	30 psi (adjusted for specific GC)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.08 gram alachlor standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 8 mg alachlor and 3 mg triphenylmethane/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.08 gram alachlor into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the alachlor. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 8 mg alachlor and 3 mg triphenylmethane/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is alachlor, then triphenylmethane.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of alachlor and triphenylmethane from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

I.S. = internal standard = triphenylmethane

$$RF = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area alachlor})}{(\text{wt. alachlor})(\%\text{ purity alachlor})(\text{pk. ht. or area I.S.})}$$

Determine the percent alachlor for each injection of the sample-internal standard solution as follows and calculate the average:

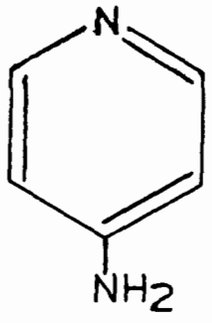
$$\% = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area alachlor})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area I.S.})(RF)} \qquad (4\text{-}1)$$

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Note! This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Chemistry Lab. Any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated.

Determination of 4-Aminopyridine in Solid Formulations by Ultraviolet Spectroscopy

4-Aminopyridine is a registered avicide and repellant having the chemical structure:



Molecular formula: $C_5H_6N_2$

Molecular weight: 94.11

Melting point: 158°C

Physical state and color: white crystalline solid

Solubility: soluble in water, alcohol, and ether

Stability:

Other names: Avitrol (Avitrol Corp.), 4-AP

Reagents:

1. 4-aminopyridine of known % purity
2. Distilled water

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.06 gram 4-aminopyridine standard into a 100 ml volumetric flask. Dissolve, make to volume with distilled water, and mix thoroughly. Pipette a 10 ml aliquot into a 200 ml volumetric flask and make to volume with water. Mix thoroughly and pipette a 10 ml aliquot into a 100 ml volumetric flask. Make to volume and again mix thoroughly. (final conc 3 µg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.003 gram of 4-aminopyridine into a 300 ml Erlenmeyer glass-stoppered flask. Add 100 ml distilled water by pipette and shake on a mechanical shaker for one hour. Filter and pipette 10 ml of the clear filtrate into a 100 ml volumetric flask. Make to volume with distilled water and mix thoroughly. (final conc 3 µg 4-aminopyridine/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at ~~302~~ 262 nm with distilled water in each cell. Scan both the standard and sample from 300 nm to 210 nm with distilled water in the reference cell. Measure the absorbance of both standard and sample at 302 nm.

Calculation:

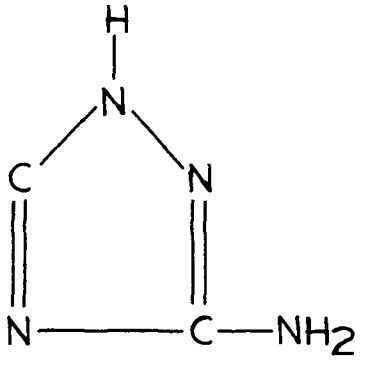
From the above absorbances and using the standard and sample concentrations, calculate the percent 4-aminopyridine as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

Method submitted by Stelios Gerazounis, EPA Product Analysis Lab, Region II, New York, N. Y.

Determination of Amitrole by Visible (Colorimetric) Spectroscopy

Amitrole is the accepted common name for 3-amino-1H-1,2,4-triazole, a registered herbicide having the chemical structure:



Molecular formula: $C_2H_4N_4$

Molecular weight: 84.1

Melting point: 159°C

Physical state, color, and odor: white crystalline powder; odorless when pure; bitter taste

Solubility: soluble in water (28 g/100 ml at 25°C); insoluble in non-polar solvents, acetone, ethyl ether, oils, carbon tetrachloride

Stability: reacts with most acids and bases to form salts, oxidizes to azotriazole; forms derivatives with aldehydes and ketones; strong chelating agent; somewhat corrosive to iron, aluminum, and copper

Other names: aminotriazole (France, Great Britain, New Zealand, USSR), 3-amino-s-triazole, Amerol, Amizol, ATA, Cytrol, Herbizole, Weedazol

Reagents:

1. Amitrole standard of known % purity
2. Sodium nitroferricyanide solution - weigh 5.96 grams $Na_2Fe(CN)_5NO.2H_2O$ into a 100 ml volumetric flask; dissolve and make to volume with water.
3. Potassium ferrocyanide solution - weigh 8.44 grams $K_4Fe(CN)_6.3H_2O$ into a 100 ml volumetric flask; dissolve and make to volume with water.
4. Sodium hydroxide solution, 10% w/v - dissolve 10 grams of NaOH in water and make to 100 ml.
5. Hydrogen peroxide solution 3% - dilute 30% solution 1:10.
6. Glacial acetic acid
7. Color reagent - mix 20 ml sodium nitroferricyanide solution, 20 ml potassium ferrocyanide solution, 10 ml sodium hydroxide solution, 50 ml hydrogen peroxide solution, and add 1.2 ml glacial acetic acid. This solution should not be mixed until needed because it is not stable for more than one hour.

Equipment:

1. UV-visible spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram amitrole standard into a one liter volumetric flask; dissolve and make to volume with water. (conc 100 µg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram amitrole into a one liter volumetric flask; dissolve and make to volume with water. (conc 100 µg amitrole/ml)

Color Formation:

Pipette 25 ml of standard into a 100 ml volumetric flask and dilute to about 70 ml with water. Pipette 25 ml of sample in a second flask, and, for a reagent blank, add 70 ml water to a third flask.

To each of the three flasks, add 0.15 ml of 10% sodium hydroxide solution and 10 ml of the color reagent. Make to volume with water, mix well, and allow to stand at room temperature for two hours. Filter if necessary to obtain clear solutions.

Spectrophotometric Determination:

With the spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 634 nm with the reagent blank in each cell. Scan both the standard and sample from 750 nm to 550 nm with the reagent blank in the reference cell.

Measure the absorbance of both standard and sample at 634 nm.

(Amitrole gives a deep green color which appears gradually. The blank is yellow, but absorbs very little at 634 nm. Beer's law is followed.)

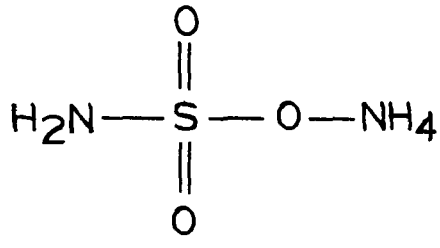
Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent amitrole as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

Determination of AMS by Sodium Nitrite Titration

AMS is the common name for ammonium sulfamate, a registered herbicide having the chemical structure:



Molecular formula: $H_6N_2O_3S$

Molecular weight: 114.1

Melting point: 130°C, decomposing at 160°C; the technical product is at least 97% pure and has a m.p. of 131 to 132°C.

Physical state, color, and odor: Colorless, odorless, crystalline solid (forms plates)

Solubility: 216 g/100 g water at 25°C; soluble in glycerol, glycols, and formamide; hygroscopic

Stability: decomposed by heat to non-flammable gases and hence has flame retardant properties; readily oxidized by bromine and chlorine; forms additional products with aldehydes; somewhat corrosive to mild steel and some other metals

Other names: Ammate (DuPont), Amcide (Albright and Wilson Ltd), Ammonium sulfamate

Reagents:

1. AMS of known % purity
2. Sodium nitrite, 0.2 N solution - dissolve 2.3 grams reagent grade sodium nitrite in water and dilute to 500 ml. Standardize against ammonium sulfamate using the same procedure as for the sample determination.
3. Starch iodide paper - impregnate strip of filter paper with a freshly prepared solution of 10 grams starch and 1 gram potassium iodide in 200 ml boiling water. Dry and store in airtight jars or bottles.
4. Sulfuric acid, 10% solution

Equipment:

1. Titration apparatus
2. Usual laboratory glassware

Procedure:

Weigh a portion of sample equivalent to 0.2 gram of AMS into a 300 ml glass-stoppered Erlenmeyer flask; add 100 ml distilled water and 10 ml 10% sulfuric acid. Titrate slowly with standard 0.2 N sodium nitrite solution. Shake flask vigorously after each addition of nitrite solution to aid in the removal of the nitrogen which is evolved. Near the end point, the titration must be done drop by drop with shaking after each addition.

The end point is determined by dipping a glass rod into the solution being titrated and touching it quickly to a piece of starch-iodide paper. An intense blue-black color must appear immediately and must be obtained repeatedly during a 1-minute period without further addition of nitrite solution.

Calculation:

$$\% \text{ AMS} = \frac{(\text{ml } NaNO_2)(\text{N } NaNO_2)(.03803)(100)}{(\text{grams sample})}$$

The milliequivalent weight of sodium nitrite for this determination is 0.0230.

$$\frac{(69.01)}{(3)(1000)} = 0.0230$$

Reactions:

$$NH_4SO_3NH_2 + NaNO_2 \longrightarrow NaNH_4SO_4 + N_2\uparrow + H_2O$$

$$2NaNO_2 + 2KI + 4HCl \longrightarrow I_2 + 2KCl + 2NaCl + 2NO + 2H_2O$$

$$I_2 + \text{starch} \longrightarrow \text{blue-black color}$$

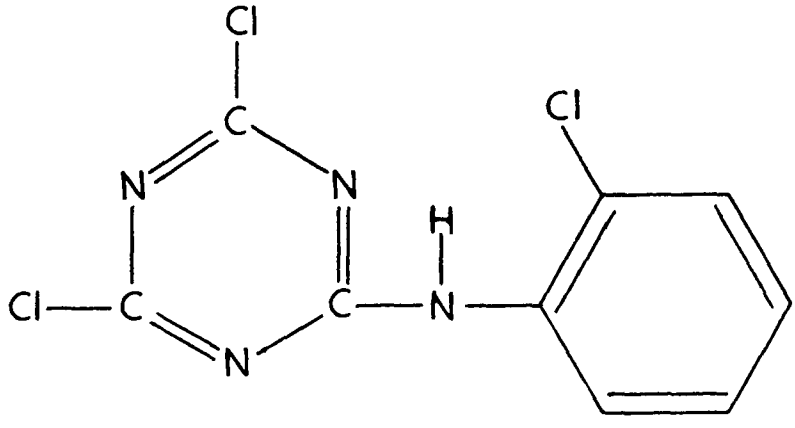
This method was adopted for use from "Comparison of Methods for Determination of Sulfamates," W.W. Bowler and E.A. Arnold, Anal. Chem. 19, 336 (1947) by Stelious Gerazounis, Chemist, PAL Region II, New York

October 1975

Anilazine **EPA-1**
(Tentative)

Determination of Anilazine by Infrared Spectroscopy

Anilazine is the common name for 2,4-dichloro-6-(o-chloroanilino)-s-triazine, a registered fungicide having the chemical structure:



Molecular formula: $C_9H_5Cl_3N_4$

Molecular weight: 275.5

Melting point: 159 to 160°C

Physical state and color: white to tan crystalline solid

Solubility: practically insoluble in water; soluble in hydrocarbons and most organic solvents

Stability: stable in neutral or slightly acid media; hydrolyzed by alkali on heating; compatible with most other pesticides

Other names: Dyrene (Chemagro); B-622 (Ethyl Corp.); Direz; Kemate; Triasyn; 4,6-dichloro-N-(2-chlorophenyl)-1,3,5-triazin-2-amine

Reagents:

1. Anilazine standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm NaCl or KBr cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.05 gram anilazine standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 5 mg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.5 gram anilazine into a glass-stoppered flask or screw-cap tube. Add 100 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precautions to prevent evaporation. (final conc 5 mg anilazine/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings, scan both the standard and sample from 1480 cm^{-1} to 1275 cm^{-1} (6.75 μ to 7.85 μ).

Determine the absorbance of standard and sample using the peak at 1375 cm^{-1} (7.27 μ) and basepoint 1333 cm^{-1} (7.5 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent anilazine as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

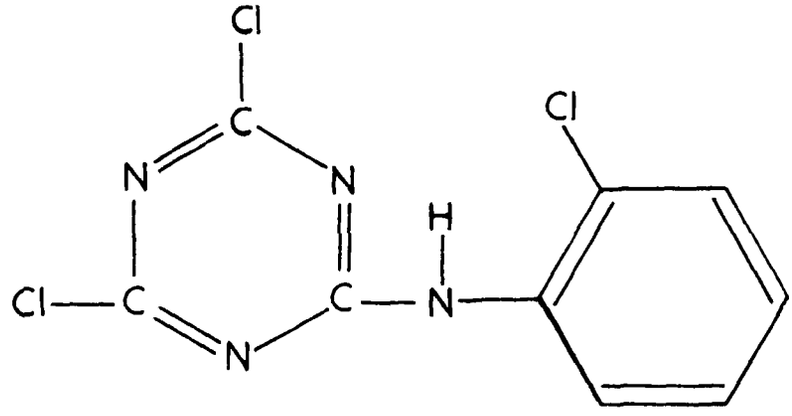
Method submitted by Eva Santos, EPA, Region IX, San Francisco, California.

November 1975

Anilazine EPA-2
(Tentative)

Determination of Anilazine by Gas-Liquid Chromatography (TCD - Internal Standard)

Anilazine is the common name for 2,4-dichloro-6-(o-chloroanilino)-s-triazine, a registered fungicide having the chemical structure:



Molecular formula: $C_9H_5Cl_3N_4$

Molecular weight: 275.5

Melting point: 159 to 160°C

Physical state and color: white to tan crystalline solid

Solubility: practically insoluble in water; soluble in hydrocarbons and most organic solvents

Stability: stable in neutral or slightly acid media; hydrolyzed by alkali on heating; compatible with most other pesticides

Other names: Dyrene (Chemagro); B-622 (Ethyl Corp.); Direz; Kemate; Triasyn; 4,6-dichloro-N-(2-chlorophenyl)-1,3,5-triazin-2-amine

Reagents:

1. Anilazine standard of known % purity
2. Dieldrin standard of known HEOD content
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh an amount of dieldrin equivalent to 0.25 gram HEOD into a 25 ml volumetric flask, dissolve in, and make to volume with acetone. (conc 10 mg HEOD/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. 6' x 1/8" SS column packed with 10% SE-30 on 80/100 mesh Diatoport S (or equivalent column)
3. Precision liquid syringe - 50 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	215°C
Injection temperature:	230°C
Detector temperature:	230°C
Filament current:	200 ma
Carrier gas:	Helium
Flow rate:	30 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.08 gram anilazine standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 8 mg anilazine and 10 mg HEOD/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.08 gram anilazine into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the anilazine. For coarse or granular materials, shake mechanically for 10-15 minutes or shake by hand intermittently for 25-30 minutes. Filter if needed. (final conc 8 mg anilazine and 10 mg HEOD/ml)

Determination:

Inject 25-50 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is anilazine, then HEOD.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of anilazine and HEOD from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. HEOD})(\%\text{ purity HEOD})(\text{pk. ht. or area anilazine})}{(\text{wt. anilazine})(\%\text{ purity anilazine})(\text{pk. ht. or area HEOD})}$$

Determine the percent anilazine for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. HEOD})(\%\text{ purity HEOD})(\text{pk. ht. or area anilazine})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area HEOD})(RF)} \quad (4\text{-}1)$$

Method contributed by Arthur O. Schlosser, EPA, Region II, New York, N. Y.

Determination of Sodium Arsenite and Sodium Arsenate in Aqueous Formulations

Sodium arsenite and sodium arsenate have been registered for pesticide use both as insecticides and herbicides. These uses have been superseded or discontinued because of the hazard to man and animals.

Sodium arsenate:

Sodium arsenate, dibasic or disodium hydrogen arsenate - molecular formula $Na_2H\ AsO_4$; molecular weight 185.91; very soluble in water, slightly soluble in alcohol; forms heptahydrate ($7H_2O$), an odorless, crystalline solid that effloresces in warm air, loses water and becomes anhydrous at 100°C, forms pyroarsenate at 150°C or higher. POISONOUS!

Sodium arsenite:

Molecular formula approx. $NaAsO_2$; molecular weight 129.90; white or grayish-white powder; somewhat hygroscopic; absorbs CO_2 from air; freely soluble in water, slightly in alcohol; VERY POISONOUS!

Principle of the Method:

Arsenic in aqueous formulations containing no other oxidizable or reducible substances may be titrated directly with iodine (for arsenite) or indirectly with thiosulfate (for arsenate) without any special sample treatment.

The reaction:

$$AsO_3^{\equiv} + I_2 + H_2O \rightleftharpoons AsO_4^{\equiv} + 2I^- + 2H^+$$

may be made to go to completion in either direction; therefore, either arsenate, arsenite, or both in the same solution can be determined.

Sodium arsenite may be titrated directly with iodine in a neutral solution (acid solution plus excess sodium bicarbonate) as in the reaction:

$$NaAsO_2 + I_2 + 3NaHCO_3 \longrightarrow Na_2H\ AsO_4 + 2NaI + 3CO_2 + H_2O$$

Sodium arsenate may be titrated indirectly using thiosulfate to titrate the equivalent iodine liberated from KI in acid solution (fairly concentrated hydrochloric acid) as in the reactions:

$$H_3AsO_4 + 2HI \xrightarrow[HCl]{conc} H_3AsO_3 + I_2 + H_2O$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

Reagents:

1. Iodine, 0.05N standard solution
2. Sodium thiosulfate, 0.05N standard solution
3. Concentrated hydrochloric acid, ACS
4. Dilute hydrochloric acid
5. Sodium bicarbonate, ACS
6. Starch indicator solution
7. Potassium iodide, crystals, ACS
8. Distilled water, boiled and cooled to remove dissolved oxygen
9. Concentrated sulfuric acid, ACS

Equipment:

1. Titration apparatus
2. Hot plate
3. Usual laboratory glassware

Procedure:

Determination of Sodium Arsenite:

Weigh a portion of sample equivalent to 0.05 gram arsenic (0.087 gram $NaAsO_2$) into a 500 ml iodine flask, dilute with water to about 200 ml, add a few drops phenolphthalein, and acidify with dilute hydrochloric acid, adding an excess of 2-3 drops.

Neutralize with sodium bicarbonate (in small amounts to prevent excessive foaming) and add 4-5 grams in excess. Add 5 ml starch indicator solution and titrate with standard iodine solution to the first permanent blue color.

Correct for the quantity of iodine solution necessary to produce the same color using the same reagents in the same quantities as above. From the ml iodine used, calculate the percent sodium arsenite in the sample as follows:

$$\% \text{ arsenic} = \frac{(\text{ml iodine})(\text{N iodine})(.03746)(100)}{(\text{grams sample})}$$

(milliequivalent weight arsenic = 0.03746)

% sodium arsenite = % arsenic X 1.734

If the arsenite results are lower than expected, another portion of sample should be checked using the reduction procedure as under "Determination of total arsenic: Method B" below.

Determination of Sodium Arsenate:

Weigh a portion of sample equivalent to 0.05 gram arsenic (0.124 gram $Na_2H\ AsO_4$) into a 500 ml iodine flask, dilute with water to about 200 ml, add 5 grams potassium iodide, and shake until dissolved. Add 2 grams sodium carbonate, shake to dissolve, and add 7-8 ml concentrated hydrochloric acid. Cover and set in the dark for 5-10 minutes to allow completion of the reaction.

Titrate with 0.05N sodium thiosulfate solution. When the iodine color becomes faint, add 5 ml starch indicator solution and titrate until the blue starch-iodine color just disappears.

Calculate the percent sodium arsenate as follows:

$$\% \text{ arsenic} = \frac{(\text{ml thiosulfate})(\text{N thiosulfate})(.03746)(100)}{(\text{grams sample})}$$

(milliequivalent weight arsenic = 0.03746)

% sodium arsenate = % arsenic X 2.481

Determination of Total Arsenic (Arsenate + Arsenite):

Method A - Using a portion of sample equivalent to 0.05 gram arsenic, titrate the arsenite arsenic as above under determination of sodium arsenite. Calculate as percent arsenic and as percent sodium arsenite.

Adjust conditions and titrate the arsenate arsenic as above under determination of sodium arsenate. Calculate as percent total arsenic.

Subtract the percent arsenic obtained in the arsenite procedure from the percent total arsenic to get the percent arsenate arsenic. Calculate this as percent sodium arsenate.

Method B - Using a portion of sample equivalent to 0.05 gram of arsenic, reduce all the arsenic to arsenite as follows: make to about 100 ml volume with water, add 3 ml sulfuric acid and one gram

potassium iodide, and boil until volume is approximately 40 ml. Cool, dilute to 200 ml, and add sodium thiosulfate solution dropwise until the iodine color just disappears (do not use starch indicator at this point). Neutralize with sodium bicarbonate and add 4-5 grams excess. Add 5 ml starch indicator solution and titrate with standard iodine solution to the first permanent blue color. Calculate the percent total arsenic as follows:

$$\% \text{ total arsenic} = \frac{(\text{ml iodine})(\text{N iodine})(.03746)(100)}{(\text{grams sample})}$$

Determination of Inorganic Arsenic Compounds in Formulations by Digestion, Reduction, and Titration

Inorganic arsenic compounds have been registered for pesticide use. Examples include the following:

insecticides - copper acetoarsenate (Paris green), lead arsenate, calcium arsenate and arsenite, sodium arsenate (ant syrups)

herbicides - sodium arsenite, arsenic acid

rodenticides - arsenic trioxide

Some of these uses have been superseded or discontinued because of the hazard to man and animals.

Arsenic is a silver gray or tin-white brittle, crystalline metal that turns black in air: atomic symbol, As; atomic weight, 74.92; m.p. 818°C at 36 atm.; sublimes at 760 mm at 615° without melting; insoluble in water; not attacked by cold H_2SO_4 or HCl; converted by HNO_3 or hot H_2SO_4 into arsenous or arsenic acid; forms inorganic and organic compounds, valence numbers: -3, +3, and +5

This method is primarily for sodium arsenite or sodium arsenate in ant bait syrups. For inorganic arsenicals containing calcium, copper, lead, etc., refer to the methods of the AOAC.

Principle of the Method:

A portion of sample is digested with concentrated nitric and sulfuric acids; the resulting arsenate is reduced to arsenite and titrated with standard iodine in neutral solution. Other compounds reducible or oxidizable by iodine will interfere.

Reagents:

1. Concentrated sulfuric acid, ACS
2. Concentrated nitric acid, ACS
3. Fuming nitric acid, ACS
4. Potassium iodide, crystals, ACS
5. Sodium thiosulfate solution, 0.05N (approx.)
6. Sodium bicarbonate, powder, ACS
7. Iodine, 0.05N standard solution
8. Starch indicator solution

Equipment:

1. 500 ml Kjeldahl flask
2. Digestion apparatus: Meker burner, asbestos board with a 1.5-2 inch diameter hole, fume hood
3. Hot plate
4. Titration apparatus
5. Usual laboratory glassware

Procedure:

Digestion:

Weigh a portion of sample equivalent to 0.05 gram arsenic and transfer to a 500 ml Kjeldahl flask (avoid getting any sample on the neck of the flask). Cautiously add 6-8 ml concentrated sulfuric acid and 2 ml concentrated nitric acid. Heat over a low flame until the mixture begins to darken; then add a few drops of fuming nitric acid (or a few ml of concentrated nitric acid). Continue heating (adding a little nitric acid when mixture darkens) until all the organic matter is destroyed (solution no longer darkens). Continue heating to dense white fumes of sulfur trioxide.

Cool, add 15-20 ml water, pouring down the side of the flask, and heat to fumes of sulfur trioxide (to decompose any nitrosylsulfuric acid). Repeat with two more additions of 10-15 ml of water until all the nitric oxide fumes are expelled. Cool.

Reduction:

Transfer the contents of the Kjeldahl flask to a 500 ml Erlenmeyer flask and dilute with water to about 100 ml. Add one gram potassium iodide, heat to boiling, and boil until a pale straw color develops, but do not go below 40 ml. If heating is continued too long after the proper color is reached, the solution will darken and the analysis is ruined. Cool, dilute to 150-200 ml, and remove excess free iodine by adding approx. 0.05N thiosulfate solution dropwise until the iodine color is gone. Starch indicator should be avoided; however, if the solution is slightly colored from organic matter or other cause than free iodine, it may be necessary to use a few drops at this time.

Titration:

Neutralize the solution with sodium bicarbonate added in small portions to prevent excessive foaming, and then add 4-5 grams excess. Add 5 ml starch indicator solution and titrate with 0.05N standard iodine solution to the first permanent blue color.

Calculation:

Calculate the percent arsenic as follows:

$$\% \text{ arsenic} = \frac{(\text{ml iodine})(\text{N iodine})(0.03746)(100)}{(\text{grams sample})}$$

milliequivalent arsenic = 0.03746

% sodium arsenite = % arsenic X 1.734

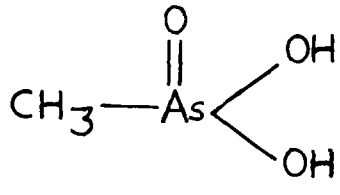
% sodium arsenate = % arsenic X 2.481

Determination of Organic Arsenic Compounds in Formulations by Digestion, Reduction, and Titration

Organic arsenic compounds have been registered for pesticide use. Examples include the following: ammonium methanearsonate (Ansar), cacodylic acid, disodium methanearsonate (DSMA), monoammonium methanearsonate (MAMA), monosodium methanearsonate (MSMA). All of these compounds are herbicides.

The following data on methanearsonic acid (MAA) will give an idea of the general characteristics of this group of compounds:

Structural formula:



Molecular formula: CH_5AsO_3

Molecular weight: 140.0

Physical state, color, and odor: odorless, white, crystalline solid

Melting point: 161°C

Solubility: very soluble in water and alcohol

Stability: nonflammable; mildly corrosive; stable on storage, although solid formulations are somewhat hygroscopic; calcium, magnesium, and iron tend to precipitate the water-insoluble methanearsonate salts of these ions

This method is intended particularly for formulations of disodium methanearsonate. It is not applicable in the presence of iron, copper, chromium, manganese, tin, etc. Also, it should not be used on entirely inorganic compounds such as arsenates or arsenites, although the addition of sucrose (0.1 gram) is supposed to make the method reliable.

Principle of the Method:

A portion of sample is digested for a definite period of time with concentrated sulfuric acid and fuming nitric acid in a Kjeldahl flask fitted with a cold finger. The arsenic is then reduced to arsenite by potassium iodide and titrated by standard iodine solution in the neutralized sample solution.

Reagents:

1. Concentrated sulfuric acid, ACS
2. Fuming nitric acid, ACS
3. Ammonium sulfamate, ACS
4. Potassium iodide, ACS, 10% solution
5. Sodium thiosulfate solution, approx. 0.1N
6. Sodium carbonate, ACS, approx. 4N (212 g/l)
7. Sodium bicarbonate, ACS, powder
8. Iodine, 0.1N standard solution

Equipment:

1. 500 ml Kjeldahl flask, fitted with a cold finger
2. Digestion apparatus: Meker burner, asbestos board with 1.5-2 inch diameter hole, stand to hold flask one inch above burner surface, fume hood
3. Titration apparatus
4. Usual laboratory glassware

Procedure:

Digestion:

Weigh a portion of sample equivalent to 0.08-0.10 gram arsenic and transfer to a 500 ml Kjeldahl flask, taking care that none adheres to the neck of the flask. Add 5.5 ml concentrated sulfuric acid and swirl gently to dissolve or to thoroughly wet the sample. Add 1-2 ml fuming nitric acid and place the flask on the digestion rack with the cold finger in place. Adjust so that the flask is one inch above the surface of the burner and digest for 55 minutes. There will be copious evolution of nitrogen oxide fumes which will escape past the cold finger. If evolution of these fumes ceases before the end of the digestion period, cautiously add a few more drops of nitric acid. After the 55 minute digestion, remove the cold finger and continue digestion to white fumes.

Remove the flask from the burner and let cool about 5 minutes. (The amount of cooling is best determined by experience. The flask and contents should cool just to the extent that the contents do not spatter badly when additional reagents are added.) Add 1.5 grams ammonium sulfate through a funnel so that it drops directly into the bottom of the flask. Mix vigorously for one minute, then cool under cold tap water.

Reduction:

Add 60 ml water and 10 ml potassium iodide solution and replace the flask on the burner with the cold finger in place. Boil until the solution is straw-colored from the iodine vapor which is evolved. (Do not boil after the proper color is reached or the solution will darken and the experiment is ruined because of the decomposition products formed.)

Remove the flask from the heat and add approx. 0.1N thiosulfate solution dropwise until the excess free iodine is gone as shown by the solution becoming colorless. Immediately add 70 ml water, mix

well, and carefully pour the solution into 50 ml of the sodium carbonate solution contained in a 500 ml Erlenmeyer flask. This should be done slowly to avoid loss of solutions caused by too vigorous an evolution of carbon dioxide. Rinse the Kjeldahl flask thoroughly, adding the washings to the Erlenmeyer flask.

Titration:

Complete the neutralization of the acid sample solution with sodium bicarbonate and add a slight excess. Add 5 ml starch solution and titrate with the 0.1N standard iodine solution to the first permanent blue color.

Calculation:

Calculate the percent arsenic as follows:

$$\% \text{ arsenic} = \frac{(\text{ml iodine})(\text{N iodine})(0.03746)(100)}{(\text{grams sample})}$$

milliequivalent weight arsenic = 0.03746

Calculate the percent organic compound by multiplying the percent arsenic by the factor arsenic to compound.

Example: for disodium methanearsonate (40.74% arsenic)

% = % arsenic X 2.455

This method is essentially that of the Vineland Chemical Co., Vineland, New Jersey.

The "tentative" designation has been placed on this method because reports from State and EPA chemists show: (1) some never use it, (2) some found it unsatisfactory, (3) some use it and find it satisfactory. Also, the method is originally for formulation of disodium methanearsonate, but it is suggested for all similar organic compounds. Any criticisms, suggestions, additions, deletions, or data are welcome.

Determination of Arsenic in Organic Compounds by Sulfuric Acid Digestion and Iodine Titration

For information on organic arsenic compounds of the type for which this method is suitable, see Arsenic Compounds EPA-3.

Principle of the Method:

A portion of sample is digested with sulfuric acid in the presence of some organic material either inherent in the sample or added (e.g., starch). The arsenic from the digested material is present in reduced form, and is titrated with standard iodine in the neutralized solution.

Reagents:

1. Concentrated sulfuric acid, ACS
2. Potassium sulfate, crystals, ACS
3. Starch powder
4. Sodium hydroxide, 25% solution
5. Phenolphthalein indicator solution
6. Sodium bicarbonate, powder, ACS
7. Starch indicator solution
8. Iodine, 0.1N standard solution

Equipment:

1. Kjeldahl flask, 500 or 800 ml
2. Digestion apparatus: Meker burner, asbestos board with 1.5-2 inch diameter hole, stand, fume hood
3. Titration apparatus
4. Usual laboratory glassware

Procedure:

Digestion:

Weigh a portion of sample equivalent to 0.08-0.10 gram arsenic and transfer to an 800 ml Kjeldahl flask, taking care that none adheres to the neck of the flask. Add 15 grams potassium sulfate, 20 ml sulfuric acid*, and about 0.3 gram of starch. Heat gently over a low flame until the initial frothing action subsides. Increase flame and digest at full heat for 3-4 hours or until the solution is colorless. The flask may be lifted from the digestion rack and swirled to dissolve any spatters of carbon adhering to the sides not in contact with the acid.

*There must be enough sulfuric acid in the flask to keep the sample wet during the digestion. In the case of large samples or particularly those containing vermiculite, more acid must be added at the beginning of the digestion. Additional acid may occasionally be needed during the digestion; if so, cautiously pour 5-10 ml down the neck of the flask and swirl gently to mix.

Neutralization and Titration:

Transfer the cooled contents of the Kjeldahl flask to a 500 ml Erlenmeyer or iodine flask, washing the Kjeldahl flask several times with water and adding the washings to the Erlenmeyer flask.

Add a few drops of phenolphthalein solution and neutralize the digest mixture to just alkaline. Cool to room temperature, make slightly acid, then neutralize with sodium bicarbonate,adding 4-5 grams excess.

Add 5 ml starch indicator solution and titrate with 0.1N standard iodine solution to the first permanent blue color.

For most accurate results, run a blank using the same procedure and same amounts of reagents. Subtract the blank titration from the sample titration.

Calculation:

Calculate the percent of arsenic as follows:

$$\% \text{ arsenic} = \frac{(\text{ml iodine})(\text{N iodine})(0.03746)(100)}{(\text{grams sample})}$$

milliequivalent weight arsenic = 0.03746

Calculate the percent organic arsenic compound by multiplying the percent arsenic by the factor arsenic to compound.

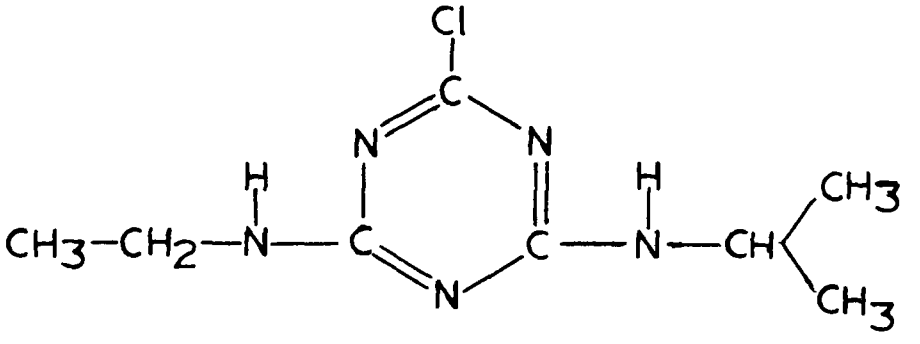
Example: for disodium methanearsonate (40.74% arsenic)

% = % arsenic X 2.455

This method is similar to the "Arsenic in Sodium Cacodylate" method, AOAC 12th Ed., 1975, 36.044. It is a method used by the State of Florida Pesticide Laboratory. Also it has been used for many years in the Beltsville Chemistry Laboratory, EPA, Beltsville, Maryland.

Determination of Atrazine by Infrared Spectroscopy

Atrazine is the common name for 2-chloro-4-ethylamino-6-isopropyl-amino-1,3,5-triazine, a registered herbicide having the chemical structure:



Molecular formula: $C_8H_{14}Cl\ N_5$

Molecular weight: 215.7

Melting point: 173 to 175°C

Physical state and color: white crystalline solid

Solubility: at 27°C solubility is 33 ppm in water, 360 ppm in n-pentane, 12,000 ppm in diethyl ether, 18,000 ppm in methanol, 28,000 ppm in ethyl acetate, and 52,000 ppm in chloroform

Stability: stable in neutral or slightly acidic or basic media, hydrolyzed by alkali or mineral acid at higher temperatures

Other names: Aatrex (Ciba-Geigy Corp.), G-30027, Atranex, Gesaprim, Primatol A

Reagents:

1. Atrazine standard of known % purity
2. Methylene chloride, pesticide or spectro grade
3. Anhydrous sodium sulfate, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.1 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps. These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.05 gram atrazine standard into a small glass-stoppered flask or screw-cap bottle, add 20 ml methylene chloride by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 2.5 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.125 gram atrazine into a glass-stoppered flask or screw-cap tube. Add 50 ml methylene chloride by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 2.5 mg atrazine/ml)

Determination:

With methylene chloride in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1755 cm^{-1} to 1410 cm^{-1} (5.7 μ to 7.1 μ).

Determine the absorbance of standard and sample using the peak at 1585 cm^{-1} (6.31 μ) and basepoint at 1675 cm^{-1} (5.97 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent atrazine as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg atrazine/ml methylene chloride gives an absorbance of approx. 0.149 in a 0.1 mm cell.)

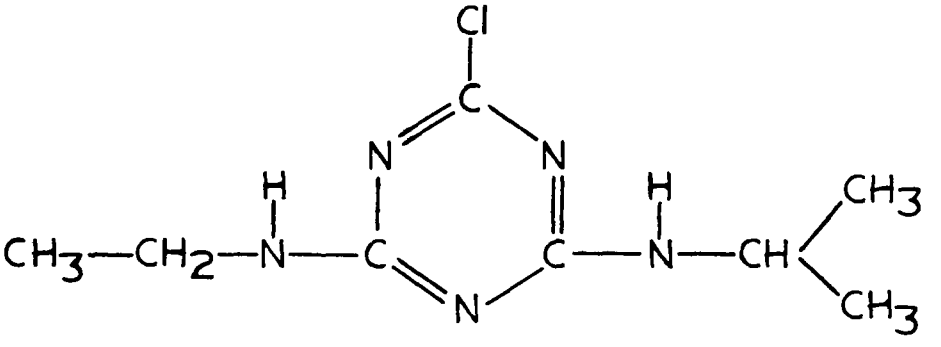
Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

October 1975

Atrazine **EPA-2**
(Tentative)

Determination of Atrazine by Gas-Liquid Chromatography (FID - Internal Standard)

Atrazine is the common name for 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine, a registered herbicide having the chemical structure:



Molecular formula: $C_8H_{14}Cl\ N_5$

Molecular weight: 215.7

Melting point: 173 to 175°C

Physical state and color: white crystalline solid

Solubility: at 27°C solubility is 33 ppm in water, 360 ppm in n-pentane, 12,000 ppm in diethyl ether, 18,000 ppm in methanol, 28,000 ppm in ethyl acetate, and 52,000 ppm in chloroform

Stability: stable in neutral or slightly acidic or basic media, hydrolyzed by alkali or mineral acid at higher temperatures

Other names: Aatrex (Ciba-Geigy Corp.), G-30027, Atranex, Gesaprim, Primatol A

Reagents:

1. Atrazine standard of known % purity
2. Alachlor standard of known % purity
3. Chloroform, pesticide or spectro grade (acetone could be used)
4. Internal Standard solution - weigh 0.2 gram alachlor into a 100 ml volumetric flask, dissolve in, and make to volume with chloroform. (conc 2 mg alachlor/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm ID glass column packed with 5% SE-30 on 80/100 mesh Chromosorb W HP (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	190°C
Injection temperature:	240°C
Detector temperature:	240°C
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi
Hydrogen pressure:	20 psi
Air pressure:	30 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram atrazine standard into a small glass-stoppered flask or screw-cap tube. Add by pipette 25 ml of the internal standard solution and shake to dissolve. (final conc 2 mg atrazine and 2 mg alachlor/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.05 gram atrazine into a small glass-stoppered flask or screw-cap tube. Add by pipette 25 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the atrazine. For coarse or granular materials, shake or tumble mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 2 mg atrazine and 2 mg alachlor/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is atrazine, then alachlor.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of atrazine and alachlor from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. alachlor})(\%\text{ purity alachlor})(\text{pk. ht. or area atrazine})}{(\text{wt. atrazine})(\%\text{ purity atrazine})(\text{pk. ht. or area alachlor})}$$

Determine the percent atrazine for each injection of the sample-internal standard solution as follows and calculate the average:

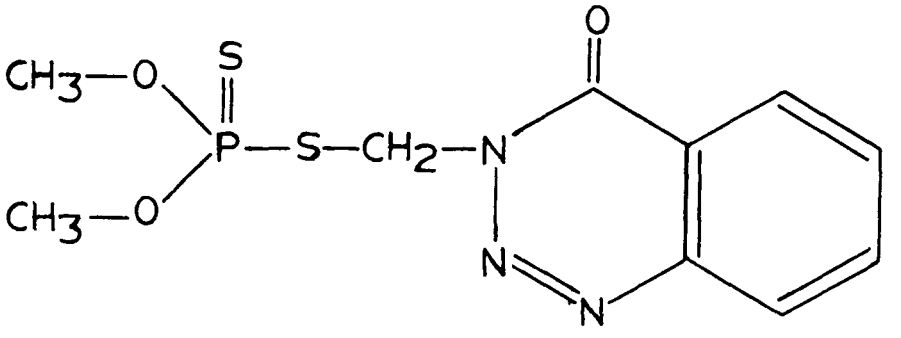
$$\% = \frac{(\text{wt. alachlor})(\%\text{ purity alachlor})(\text{pk. ht. or area atrazine})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area alachlor})(RF)} \quad (4\text{-}1)$$

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Note! This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Lab. Any comments, criticism, suggestion, data, etc. concerning this method will be appreciated.

Determination of Azinphos-methyl by Infrared Spectroscopy

Azinphos-methyl is the common name for O,O-dimethyl S-[4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] phosphorodithioate, a registered insecticide having the chemical structure:



Molecular formula: $C_{10}H_{12}N_3O_3PS_2$

Molecular weight: 317.34

Melting point: 73 to 74°C

Physical state and color: white, crystalline solid

Solubility: about 29 ppm in water at 25°C; soluble in most organic solvents

Stability: unstable at temperatures above 200°C; rapidly hydrolyzed by cold alkali and acid

Other names: Guthion (Bayer), Gusathion M (Bayer), Metiltriazotion (USSR), Carfene, Cotnion-Methyl, Bay 17147, R1582

Reagents:

1. Azinphos-methyl standard of known % purity
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.1 gram azinphos-methyl standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml carbon disulfide by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.5 gram azinphos-methyl into a glass-stoppered flask or screw-cap tube. Add 50 ml carbon disulfide by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precautions to prevent evaporation. (final conc 10 mg azinphos-methyl/ml)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings, scan both the standard and sample from 700 cm^{-1} to 600 cm^{-1} (14.2 μ to 16.2 μ).

Determine the absorbance of standard and sample using the peak at 653.6 cm^{-1} (15.3 μ) and basepoint 625 cm^{-1} (16.0 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent azinphos-methyl as follows:

$$\% = \frac{\text{(abs. sample)(conc. std in mg/ml)(\% purity std)}}{\text{(abs. std)(conc. sample in mg/ml)}}$$

(A concentration of 1 mg azinphos-methyl/ml carbon disulfide gives an absorbance of approx. 0.033 in a 0.2 mm cell.)

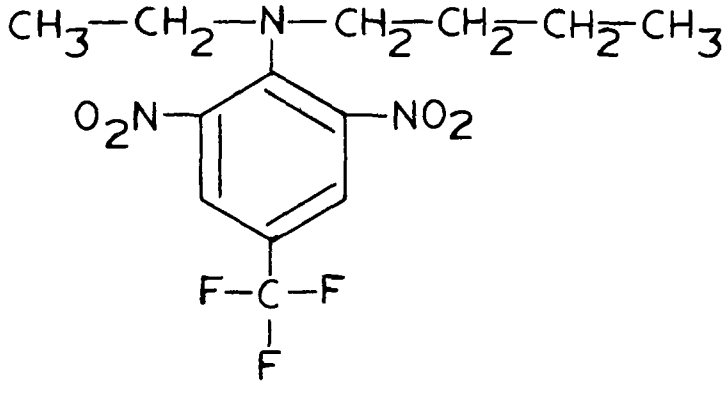
Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Everett Greer, EPA Region IX, San Francisco, California, submitted a similar method using:

scan range:	830 cm^{-1} to 700 cm^{-1} (12.0 μ to 14.0 μ)
analytical peak:	775.8 cm^{-1} (12.89 μ)
basepoint:	784.9 cm^{-1} (12.74 μ)
conc:	12 mg/ml

Determination of Benefin by Infrared Spectroscopy

Benefin is the common name for N-butyl-N-ethyl-α,α,α-trifluoro-2,6-dinitro-p-toluidine, a registered herbicide having the chemical structure:



Molecular formula: $C_{13}H_{16}F_3N_3O_4$

Molecular weight: 335.3

Melting point: 65 to 66.5°C

Physical state, color, and odor: Yellow-orange crystalline solid with no appreciable odor

Solubility: 70 ppm in water at 25°C; readily soluble in most organic solvents, though lower solubility in ethanol

Stability: stable, but susceptible to decomposition by ultraviolet radiation; compatible with most pesticides

Other names: Balan (Eli Lilly), benfluralin (BSI), Balfin, Banafin, Benalin, Binnell, Blulan, Bonalan, Carpidor, Quilan

Reagents:

1. Benefin standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.1 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.08 gram benefin standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 8 mg/ml)

Preparation of Sample:

For emulsifiable concentrates (approx. 20%), weigh 2.0 grams sample into a 50 ml volumetric flask, make to volume with chloroform and mix well. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc approx. 8 mg benefin/ml)

For 2.5% granules, weigh 6.4 grams into a glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary,

taking precaution to prevent evaporation. Evaporate a 25 ml aliquot to less than 10 ml, transfer to a 10 ml volumetric flask, and make to volume with chloroform. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 8 mg benefin/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1400 cm^{-1} to 1240 cm^{-1} (7.1 μ to 8.1 μ).

Determine the absorbance of standard and sample using the peak at 1310 cm^{-1} (7.63 μ) and a baseline from 1330 cm^{-1} to 1260 cm^{-1} (7.52 μ to 7.94 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent benefin as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

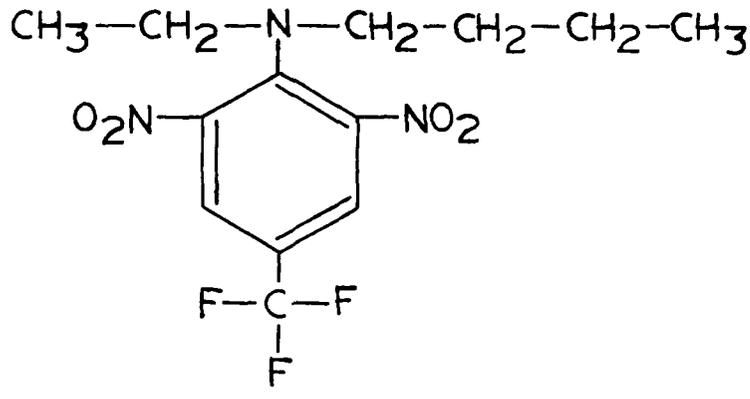
Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

October 1975

Benefin EPA-2
(Tentative)

Determination of Benefin by Gas-Liquid Chromatography (FID - Internal Standard)

Benefin is the common name for N-butyl-N-ethyl-a,a,a-trifluoro-2,6-dinitro-p-toluidine, a registered herbicide having the chemical structure:



Molecular formula: $C_{13}H_{16}F_3N_3O_4$

Molecular weight: 335.3

Melting point: 65 to 66.5°C

Physical state, color, and odor: Yellow-orange crystalline solid with no appreciable odor

Solubility: 70 ppm in water at 25°C; readily soluble in most organic solvents, though lower solubility in ethanol

Stability: stable, but susceptible to decomposition by ultraviolet radiation; compatible with most pesticides

Other names: Balan (Eli Lilly), benfluralin (BSI), Balfin, Banafin, Benalin, Binnell, Blulan, Bonalan, Carpidor, Quilan

Reagents:

1. Benefin standard of known % purity
2. Diazinon standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.200 gram diazinon into a 50 ml volumetric flask, dissolve in, and make to volume with acetone. (conc 4 mg diazinon/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm ID glass column packed with 5% SE-30 on 80/100 mesh Chromosorb W HP (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	160°
Injection temperature:	210°
Detector temperature:	210°
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi
Hydrogen pressure:	20 psi
Air pressure:	30 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram benefin standard into a small glass-stoppered flask or screw-cap tube. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 2.5 mg benefin and 4 mg diazinon/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.05 gram benefin into a small glass-stoppered flask or screw-cap tube. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the benefin. For coarse or granular materials, shake or tumble mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 2.5 mg benefin and 4 mg diazinon/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is benefin, then diazinon.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of benefin and diazinon from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. diazinon})(\%\text{ purity diazinon})(\text{pk. ht. or area benefin})}{(\text{wt. benefin})(\%\text{ purity benefin})(\text{pk. ht. or area diazinon})}$$

Determine the percent benefin for each injection of the sample-internal standard solution as follows and calculate the average:

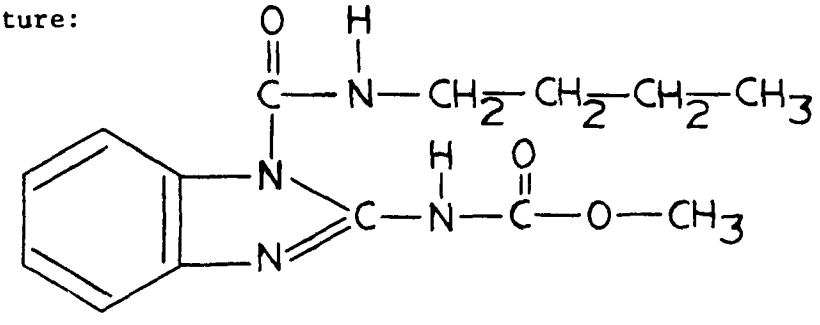
$$\% = \frac{(\text{wt. diazinon})(\%\text{ purity diazinon})(\text{pk. ht. or area benefin})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area diazinon})(RF)} \qquad (1)$$

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Note! This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Lab. Any comments, criticism, suggestion, data, etc. concerning this method will be appreciated.

Determination of Benomyl by Infrared Spectroscopy

Benomyl is the common name for methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate, a registered fungicide having the chemical structure:



Molecular formula: $C_{14}H_{18}N_4O_3$

Molecular weight: 290.3

Melting point: decomposes without melting

Physical state, color, and odor: white crystalline solid with a faint acrid odor

Solubility: practically insoluble in water or oils, but soluble in acetone, chloroform, or xylene

Stability: subject to decomposition in the presence of moisture; non-corrosive to metals

Other names: Benlate (DuPont), Tersan 1991

Reagents:

1. Benomyl standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps. These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.05 gram benomyl standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 5 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.25 gram benomyl into a glass-stoppered flask or screw-cap tube. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (If solution is not clear, add a little celite, shake, and re-centrifuge or re-filter.) (final conc 5 mg benomyl/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1850 cm^{-1} to 1640 cm^{-1} (5.4 μ to 6.1 μ).

Determine the absorbance of standard and sample using the peak at 1720 cm^{-1} (5.81 μ) and basepoint at 1810 cm^{-1} (5.52 μ).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent benomyl as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg benomyl/ml chloroform gives an absorbance of approx. 0.06 in a 0.2 mm cell.)

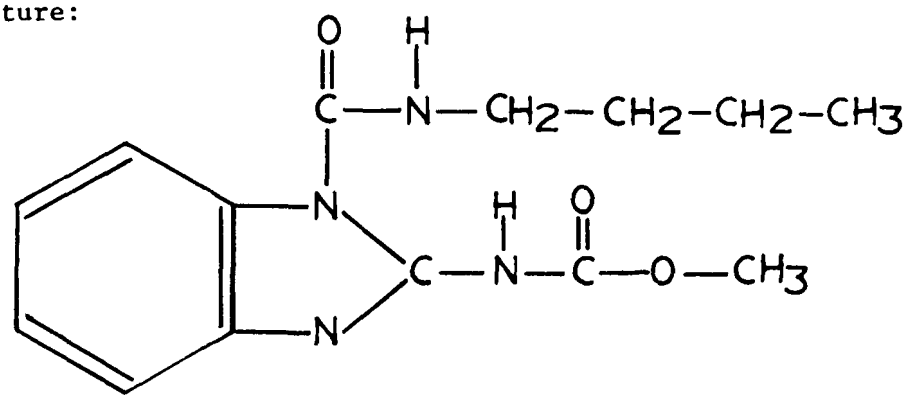
Method contributed by the Commonwealth of Virginia, Division of Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

February 1976

Benomyl EPA-2
(Tentative)

Determination of Benomyl in Powder Formulations by Ultraviolet Spectroscopy

Benomyl is the common name for methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate, a registered fungicide having the chemical structure:



Molecular formula: $C_{14}H_{18}N_4O_3$

Molecular weight: 290.3

Melting point: decomposes without melting

Physical state, color, and odor: white crystalline solid with a faint acrid odor

Solubility: practically insoluble in water or oils, but soluble in acetone, chloroform, or xylene

Stability: subject to decomposition in the presence of moisture; non-corrosive to metals

Other names: Benlate (DuPont), Tersan 1991

Reagents:

1. Benomyl standard of known % purity
2. Dioxane, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.04 gram benomyl standard into a 50 ml volumetric flask, dissolve, make to volume with dioxane, and mix thoroughly. Pipette a 5 ml aliquot into a second 50 ml volumetric flask, make to volume with dioxane, and mix thoroughly. Pipette a 5 ml aliquot into a third 50 ml volumetric flask, make to volume with dioxane, and again mix thoroughly. (final conc 8 µg/ml) Allow the last solution to stand for three hours with occasional shaking. (See note under procedure.)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.04 gram of benomyl into a 125 ml Erlenmeyer glass-stoppered flask. Add 50 ml dioxane by pipette and shake on a mechanical shaker for 30 minutes. Allow to stand until a clear solution is obtained, or, if necessary, centrifuge or filter a portion. Pipette 5 ml of the clear solution into a 50 ml volumetric flask, make to volume with dioxane, and mix thoroughly. Pipette 5 ml of this solution into another 50 ml volumetric flask, make to volume with dioxane and mix thoroughly. (final conc 8 µg benomyl/ml) Allow to stand for three hours with occasional shaking.

Note:

Benomyl absorbs strongly in the range of 260-310 nm. There are three pronounced peaks when the dioxane solution is examined immediately after the final dilution (282 nm, 287 nm, and 294 nm). It was observed, however, that the peak at 294 nm was diminishing gradually until it practically disappeared. Since this affects the peak at 287 nm, it is necessary to allow the solution to stand until complete equilibrium is reached. After 3 hours of standing the absorbance at 287 nm shows no further change. At this stage there is also a straight relationship between concentration and absorbance.

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 287 nm with dioxane in each cell. Scan both the standard and sample from 330 nm to 240 nm with distilled water in the reference cell. Measure the absorbance of both standard and sample at 287 nm.

Calculation:

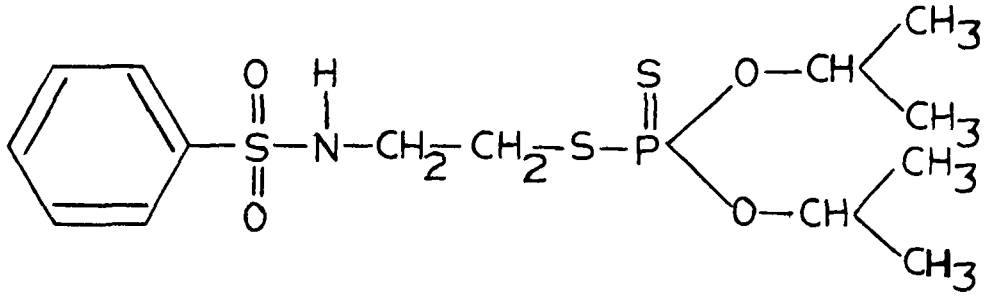
From the above absorbances and using the standard and sample concentrations, calculate the percent benomyl as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

Method submitted by Stelios Gerazounis, EPA Region II, New York, N. Y.

Determination of Bensulide by Infrared Spectroscopy

Bensulide is the common name for S-(O,O-diisopropyl phosphorodithioate) ester of N-(2-mercaptoethyl) benzenesulfonamide, a registered herbicide having the chemical structure:



Molecular formula: $C_{14}H_{24}NO_4PS_3$

Molecular weight: 397.5

Melting point: 34.4°C (supercools readily)

Physical state and color: colorless liquid or white crystalline solid

Solubility: 25 ppm in water at 20°C; slightly soluble in kerosene, moderately soluble in xylene, and readily soluble in acetone and methanol

Stability: relatively stable and non-corrosive; decomposes at elevated temperature over long periods of time (at 80°C in 50 hr and at 200°C in 18-40 hr)

Other names: Betasan - for turf use and Prefar - for crop use (Stauffer); N-2-(O,O-diisopropyl-phosphorothiolothionyl) ethyl benzenesulfonamide; diisopropyl S-(2-phenylsulfonylaminoethyl) phosphorothiolothionate

Reagents:

1. Bensulide standard of known % purity
2. Acetone, pesticide or spectro grade
3. Carbon disulfide, pesticide or spectro grade
4. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.1 gram bensulide standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg/ml)

Preparation of Sample:

For emulsifiable concentrates, weigh a portion of sample equivalent to 0.25 gram bensulide into a 25 ml volumetric flask. Make to volume with chloroform and mix well. Add a few grams anhydrous sodium sulfate to insure dryness. (final conc 10 mg bensulide/ml)

For fertilizers, dusts, or granules, weigh a portion of sample equivalent to 0.2 gram bensulide into a glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (Virginia laboratories report that a Soxhlet extracts too much filler from fertilizers.) Evaporate a 25 ml aliquot of the clear solution to less than 10 ml and transfer to a 10 ml volumetric flask. Make to volume with chloroform, mix well, and add a little anhydrous sodium sulfate to insure dryness. (final conc 10 mg bensulide/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and the sample from 714 cm^{-1} to 600 cm^{-1} (14 μ to 16.5 μ).

Determine the absorbance of standard and sample using the peak at 645.2 cm^{-1} (15.5 μ) and a basepoint at 613.5 cm^{-1} (16.3 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent bensulide as follows:

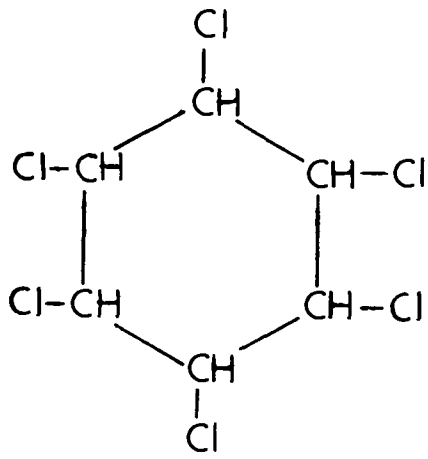
$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg bensulide/ml chloroform gives an absorbance of approx. 0.02 in a 0.2 mm cell.)

Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services.

Determination of BHC, gamma isomer in Lindane Dusts by Infrared Spectroscopy

BHC is the common name for 1,2,3,4,5,6-hexachlorocyclohexane, a registered insecticide having the chemical structure:



The technical product is a mixture of five or more isomers (65-70% alpha, 5-6% beta, 13% gamma, 6% delta -- Ramsey and Patterson (JAOAC 1946). The insecticidal activity is due mainly to the gamma isomer.

Lindane is the official name for a product containing not less than 99% gamma isomer and having a melting point of not less than 112°C.

BHC, gamma isomer

Molecular formula: $C_6H_6Cl_6$

Molecular weight: 290.8

Melting point: 112.9°C

Physical state, color, and odor: colorless, odorless, crystals

Solubility: 10 ppm in water at RT; slightly soluble in petroleum oils; soluble in acetone, aromatic and chlorinated hydrocarbons

Stability: stable to air, light, heat, and carbon dioxide; unattacked by strong acids; dehydrochlorinated by alkali

Other names: Gammexane (ICI Ltd), benzenehexachloride, HCH (Europe), 666 (Denmark), hexachlor (Sweden), hexachloran (USSR), Benzahex, Benzex, Dolmix, FBHC, HCCH, Hexafor, Hexyclan, Soprocide

Reagents:

1. BHC, gamma isomer of known % purity
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm cells
2. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.25 gram BHC, gamma isomer into a 50 ml glass-stoppered flask or screw-capped bottle. Add 25 ml carbon disulfide by pipette, shake to dissolve, and add a small amount of anhydrous sodium sulfate to insure dryness. (conc 10 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.25 gram of BHC gamma isomer into a 50 ml glass-stoppered flask or screw-capped bottle. Add 25 ml carbon disulfide by pipette and a small amount of anhydrous sodium sulfate; let stand for at least 30 minutes with occasional shaking. (conc 10 mg BHC/ml)

IR Determination:

With carbon disulfide in the reference cell and the spectrophotometer at the optimum quantitative analytical settings, scan both the standard and sample from 770 cm^{-1} to 650 cm^{-1} (13 μ to 15.4 μ). Measure the absorbance of the peak at 687 cm^{-1} (14.55 μ) using a baseline from 720 cm^{-1} to 673 cm^{-1} (13.9 μ to 14.85 μ).

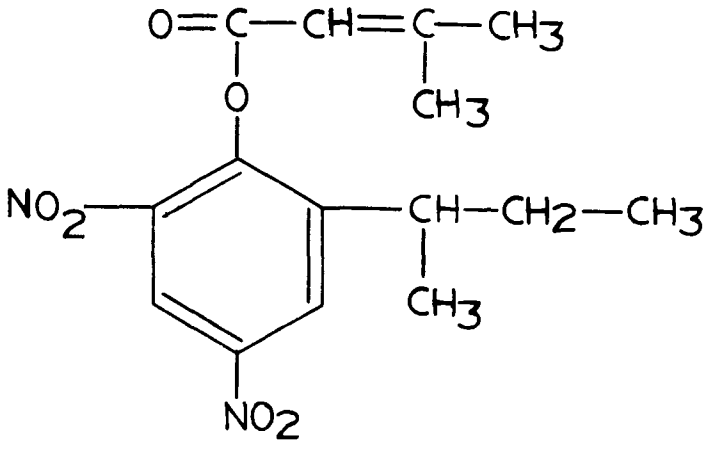
Calculation:

Calculate the percent of BHC, gamma isomer as follows:

$$\% = \frac{\text{(abs. sample)(conc. standard in mg/ml)(\% purity standard)}}{\text{(abs. standard)(conc. sample in mg/ml)}}$$

Determination of Binapacryl by Infrared Spectroscopy

Binapacryl is the accepted common name for 2-sec-butyl-4,6-dinitrophenyl 3-methyl-2-butenoate, a registered fungicide and miticide having the chemical structure:



Molecular formula: $C_{15}H_{18}N_2O_6$

Molecular weight: 322

Melting point: 68 to 69°C

Physical state, color, and odor: white crystalline solid with faint aromatic odor

Solubility: practically insoluble in water, but soluble in most organic solvents

Stability: unstable in concentrated alkalis and dilute acids; slight hydrolysis on long contact with water; slowly decomposed by ultraviolet light; non-corrosive; compatible with W.P. formulation of insecticides and non-alkaline fungicides

Other names: Acricid, Endosan, Morocide, HOE 2784 (Farbwerke Hoechst); NIA 9044 (Niagara); FMC 9044; Ambox, dinoseb methacrylate

Reagents:

1. Binapacryl standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm KBr or NaCl cells
2. Mechanical shaker
3. Soxhlet extraction apparatus
4. Centrifuge or filtration apparatus
5. Rotary evaporator
6. Cotton or glass wool
7. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.10 gram binapacryl standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg/ml)

Preparation of Sample:

For wettable powder or dust formulations, weigh a portion of sample equivalent to 0.5 gram binapacryl into a glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 10 mg binapacryl/ml)

If the results obtained by the above shake-out procedure on a 4% dust are low, another portion of sample should be checked using a Soxhlet extraction as follows: Weigh an amount of sample equivalent to 0.5 gram binapacryl into a Soxhlet thimble, plug with cotton or glass wool, and extract with chloroform for 2-3 hours. Evaporate to 30-40 ml, transfer quantitatively to a 50 ml volumetric flask, and make to volume with chloroform. Add a small amount anhydrous sodium sulfate to insure dryness. (final conc 10 mg binapacryl/ml)

For emulsifiable concentrates and aqueous dispersions, weigh a portion of sample equivalent to 0.5 gram binapacryl into a glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette, a few boiling chips to aid agitation, and sufficient anhydrous sodium sulfate to absorb all the water. Close tightly and shake vigorously on a shaking machine for one hour. Allow to settle. Filter or centrifuge if necessary to get a clear chloroform solution, taking precaution to prevent evaporation. (final conc 10 mg binapacryl/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1540 cm^{-1} to 1220 cm^{-1} (6.5 μ to 8.2 μ).

Determine the absorbance of standard and sample using the peak at 1346 cm^{-1} (7.43 μ) and baseline from 1408 cm^{-1} to 1273 cm^{-1} (7.10 μ to 7.85 μ).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent binapacryl as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Determination of Inorganic Boron Compounds in Formulations by Ignition and Titration

Borax is the trivial name for sodium tetraborate decahydrate, a registered herbicide and fungicide having the empirical formula:

$$Na_2B_4O_7 \cdot 10\ H_2O$$

Boric acid is a registered fungicide and insecticide having the empirical formula:

$$H_3BO_3$$

Borax:

Molecular formula: $Na_2B_4O_7$ (anhydrous)

Molecular weight: 201.3 (anhydrous)
381.4 (decahydrate)

Melting point: approx. 740°C (anhydrous)
approx. (enclosed space) 62°C (decahydrate)

Physical state, color, and odor: light gray odorless solid (anhydrous)
white crystalline odorless solid (decahydrate)

Solubility: in 100 ml water at 20°C, approx. 2.5 g anhydrous and approx. 5 g decahydrate; soluble in glycerol and ethylene glycol but insoluble in ethanol

Stability: the decahydrate loses 5 molecules of water of crystallization at 100°C, 4 more at 160°C, and becomes anhydrous at 320°C; its aqueous solution is alkaline, but it is hydrolyzed by mild alkali; not compatible with certain herbicides; also used as a flame retardant and a corrosive inhibitor for ferrous metals

Other names: sodium pyroborate, sodium biborate

Boric acid:

Molecular formula: H_3BO_3

Molecular weight: 61.84

Melting point: approx. 160°C

Physical state, color, and odor: odorless, colorless crystals or white granules or powder

Solubility: soluble in cold water, more soluble in boiling water; soluble in alcohol or glycerol

Stability: loses one molecule of water, forming metaboric acid HBO_2 when heated at 100-105°C; on long heating pyroboric acid $H_2B_4O_7$ is formed, and at higher temperatures the anhydride boric oxide B_2O_3 is formed; stable in air; incompatible with alkali carbonates and hydroxides

Other names: boracic acid, orthoboric acid

Principle of the Method:

The inorganic boron compound is extracted from the sample with warm water. Fluorine is removed by precipitation and filtration. Organic matter is destroyed by ignition. The boron (as boric acid) is titrated with sodium hydroxide using mannitol as a titration aid.

Reagents:

1. Acetic acid, ACS
2. Calcium acetate, 20% solution
3. Calcium hydroxide, saturated solution
4. Hydrochloric acid, dilute
5. Methyl red indicator solution
6. Sodium hydroxide, dilute
7. Sodium hydroxide, 0.02N standard solution
8. Mannitol (see note 1)

Equipment:

1. Platinum dish, 150 ml
2. Muffle furnace or Meker burner
3. Filtration apparatus
4. Titration apparatus
5. Usual laboratory glassware

Procedure:

Preparation of Sample:

Weigh and transfer to a 200 ml volumetric flask a portion of sample equivalent to 1 gram of boric acid, 1.5 grams of borax, or 0.5 gram of boric oxide. Digest with 150 ml warm water for 15-20 minutes, shaking frequently. Cool to room temperature, make to volume, and filter through a dry filter.

Removal of Fluorine Compounds:

Transfer a 100 ml aliquot of the filtrate to a 200 ml volumetric flask, acidify slightly with acetic acid, and precipitate the fluorine with an excess of calcium acetate solution. Check for complete precipitation by allowing a few milliliters of calcium acetate solution to run down the neck of the flask. Continue the addition of calcium acetate until there is no evidence of additional precipitation. Make to volume, mix thoroughly, and filter through a dry filter.

Ignition:

Pipette 100 ml of the clear filtrate into a platinum dish, add an excess of calcium hydroxide solution, evaporate to dryness, and ignite to destroy acetates and char other organic matter that may be present. Avoid an intense red heat. Cool, digest with about 50 ml hot water, and add HCl, drop by drop, until the reaction is distinctly acid to methyl red. Filter into a 500 ml Erlenmeyer flask, washing well with hot water.

Neutralization and Titration:

Exactly neutralize with sodium hydroxide; then make acid with hydrochloric acid using an excess equivalent to 1 ml 0.2N solution. Boil for about 5-10 minutes to expel carbon dioxide. Cool to room temperature and neutralize with 0.2N sodium hydroxide until the color of the solution changes from pink to yellow. If this neutral point has been passed or if there is any doubt, restore the pink color with acid and bring back to yellow with the very minimum amount of standard 0.02N sodium hydroxide.

Add 2-3 grams mannitol (note 1) and a few drops of phenolphthalein solution. Note the burette reading and titrate the solution with the 0.2N sodium hydroxide solution until a phenolphthalein pink color is obtained. The addition of the mannitol causes a red color to develop due to the presence of the methyl red indicator. During titration of the boric acid, this color will fade. As the titration continues, the red color due to phenolphthalein will develop. Add a little more mannitol and if the color disappears, continue the addition of the standard sodium hydroxide until it again appears. Repeat until the addition of mannitol has no further action on the end point. (note 2)

A blank should be run using the same reagents in the same quantities as used for the sample.

Calculation:

From the volume of 0.02N sodium hydroxide solution used after the addition of mannitol, corrected for the blank, calculate the percent of inorganic boron compound as follows:

$$\% = \frac{(\text{ml NaOH})(\text{N NaOH})(\text{milliequivalent weight compound})(100)}{(\text{grams sample})(100/200)(100/200)}$$

milliequivalent weights are:

0.03482 for boric oxide B_2O_3

0.06184 for boric acid H_3BO_3

0.05032 for sodium tetraborate, anhydrous $Na_2B_4O_7$

0.09536 for sodium tetraborate, decahydrate $Na_2B_4O_7 \cdot 10H_2O$

Notes:

(1) If mannitol is unavailable, neutral glycerol may be substituted, using a quantity equal to one-third the volume of the solution to be titrated, adding more if necessary.

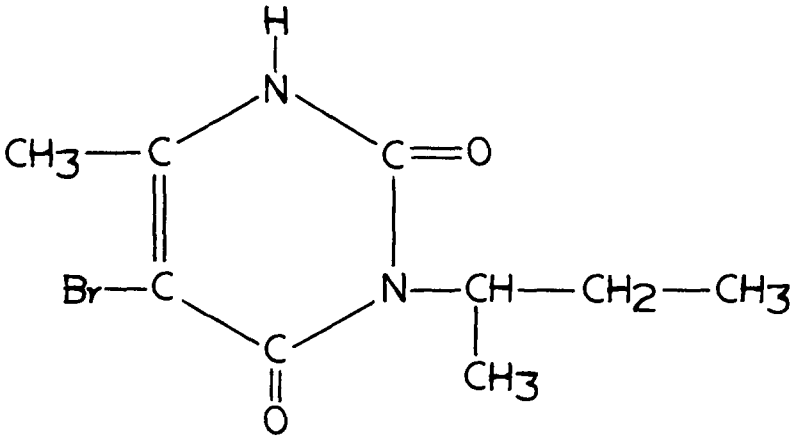
(2) Boric acid is a weak acid in aqueous solutions and cannot be neutralized by alkali in stoichiometric proportions. Polyvalent alcohols such as mannitol and glycerol form complex acids with boric acid which are much stronger than boric acid alone and are capable of reaction with alkali.

January 1976

Bromacil EPA-1
(Tentative)

Determination of Bromacil by Gas-Liquid Chromatography (FID - Internal Standard)

Bromacil is the accepted common name for 5-bromo-3-sec-butyl-6-methyluracil, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{13}BrN_2O_2$

Molecular weight: 261.1

Melting point: 158 to 159°C

Physical state, color, and odor: odorless, white crystalline solid

Solubility: 815 ppm in water at 25°C; moderately soluble in strong aqueous bases, acetone, acetonitrile, ethanol; sparingly soluble in hydrocarbons

Stability: temperature stable up to m.p. (gradually sublimes just below m.p.); stable in water, aqueous bases, and organic solvents; decomposes slowly in strong acids

Other names: Hyvar, Krovar (Du Pont); Borea, Ureabor, Borocil, Hibor

Reagents:

1. Bromacil standard of known % purity
2. Dieldrin standard of known HEOD content
3. Toluene, pesticide or spectro grade
4. Internal Standard solution - weigh 0.4 gram HEOD into a 100 ml volumetric flask; dissolve in and make to volume with toluene. (conc 4 mg HEOD/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 4 mm ID glass, packed with a 1+1 mixture of 10% DC-200 and 15% QF-1 on 60/80 Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Mechanical shaker
5. Centrifuge
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	200°C
Injection temperature:	220°C
Detector temperature:	300°C
Carrier gas:	Nitrogen
Carrier gas pressure:	20 psi (adjusted for specific GC)
Hydrogen flow rate:	adjust for specific GC
Air flow rate:	adjust for specific GC

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.135 gram bromacil standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 25 ml of the internal standard solution and shake to dissolve. (final conc 5.4 mg bromacil and 4 mg HEOD/ml)

Preparation of Sample:

For dry formulations and oil solutions, weigh a portion of sample equivalent to 0.135 gram bromacil into a small glass-stoppered or screw-capped flask. Add by pipette 25 ml internal standard solution and shake to dissolve the bromacil - at least 30 minutes for dry formulations. (final conc - see below)

For water-soluble salts and liquid formulations, weigh a portion of sample equivalent to 0.135 gram bromacil into a 50 ml centrifuge tube, add 0.75 ml 1+1 H_2SO_4, and mix by swirling. Add by pipette 25 ml internal standard solution and shake vigorously. Centrifuge until the organic layer is clear. (final conc 5.4 mg bromacil and 4 mg HEOD/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of bromacil and HEOD from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. HEOD})(\%\text{ purity HEOD})(\text{pk. ht. or area bromacil})}{(\text{wt. bromacil})(\%\text{ purity bromacil})(\text{pk. ht. or area HEOD})}$$

Determine the percent bromacil for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. HEOD})(\%\text{ purity HEOD})(\text{pk. ht. or area bromacil})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area HEOD})(RF)} \quad (41)$$

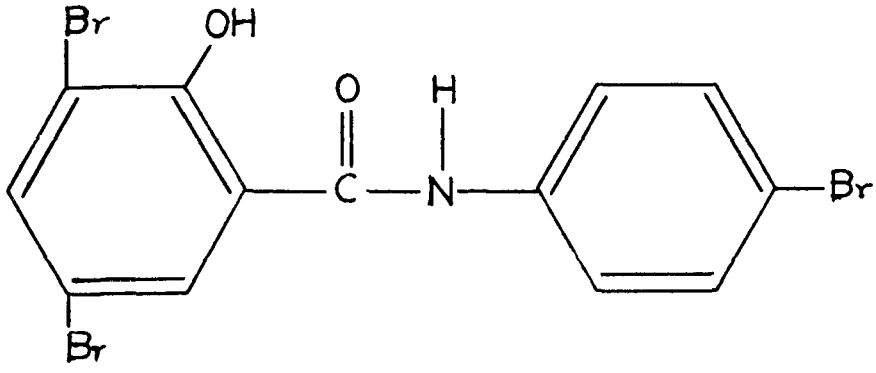
Note: The elution order was not given in the submitted method and will have to be determined the first time this method is used.

Method submitted by Mississippi State Chemical Laboratory, Box CR, Mississippi State, Mississippi 39762.

Determination of Polybrominated Salicylanilides by Ultraviolet Spectroscopy

Polybrominated salicylanilides are registered bacteriostats and fungistats. The commercial product commonly used in formulations contains 80% 3,4',5-tribromosalicylanilide and 20% 4',5-dibromosalicylanilide and is designated as polybrominated salicylanilide. The structure and chemical characteristics of these compounds are as follows:

3,4',5-tribromosalicylanilide



Molecular formula: $C_{13}H_8Br_3NO_2$

Molecular weight: 449.96

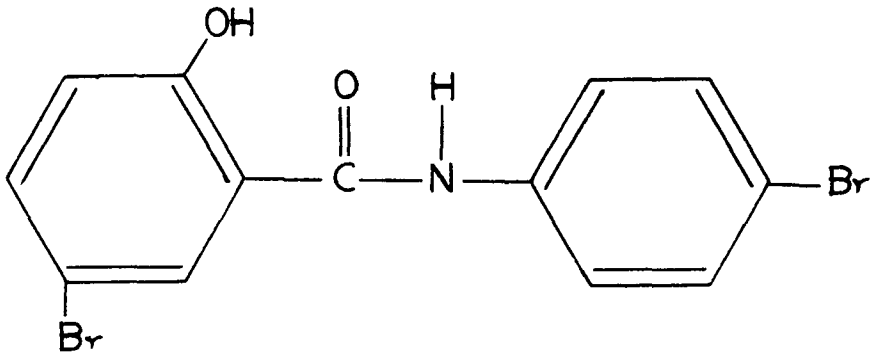
Melting point: 227-228°C

Physical state, color, odor, and taste: odorless, tasteless, white powder

Solubility: insoluble in water; soluble in acetone, benzene, ethyl acetate, ethanol, isopropanol; slightly soluble in carbon tetrachloride

Stability: under normal temperature conditions, stable when dry and in neutral solutions or in organic solvents; good light sensi-

4',5-dibromosalicylanilide



Molecular formula: $C_{13}H_9Br_2NO_2$

Molecular weight: 371.06

Melting point:

Physical state, color, and odor: odorless, tasteless, white powder

Solubility: (see 3,4',5-tribromosalicylanilide above)

Stability: (see 3,4',5-tribromosalicylanilide above)

Other names: Temasept

Reagents:

1. 3,4',5-tribromosalicylanilide of known % purity
2. 4',5-dibromosalicylanilide of known % purity
3. Ethanol, spectro grade
4. Sodium hydroxide, 0.1N solution

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Filtration apparatus or centrifuge
3. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh a portion of 3,4',5-tribromosalicylanilide and 4',5-dibromosalicylanilide in the ratio declared in the sample so that the total weight is 0.1 gram (e.g., 0.08 gram tribromo- and 0.02 gram dibromo-, total 0.1 gram for 80% tribromo- and 20% dibromo- as in the commercial polybrominated salicylanilide).

Place the weighed standard in a glass-stoppered or screw-capped flask, add 100 ml ethanol by pipette, and shake to dissolve. Mix thoroughly, pipette 10 ml to a 50 ml volumetric flask, and make to volume with ethanol. Again mix thoroughly and pipette 5 ml into another 50 ml volumetric flask. Add 5 ml 0.1N sodium hydroxide solution and 20 ml water; make to volume with ethanol and mix thoroughly. (final conc 20 µg polybrominated salicylanilide/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.02 gram polybrominated salicylanilide into a glass-stoppered or screw-capped flask, add 100 ml ethanol by pipette, and shake to dissolve. Allow any solid matter to settle and pipette 5 ml into a 50 ml volumetric flask. Add 5 ml 0.1N sodium hydroxide solution and 20 ml water; make to volume with ethanol and mix thoroughly. The solution must be clear; if not, centrifuge or filter, taking care to prevent loss by evaporation. (final conc 20 µg polybrominated salicylanilide/ml)

Prepare a blank solution using 5 ml 0.1N sodium hydroxide solution, 20 ml water, and 25 ml ethanol. Mix thoroughly.

Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 360 nm with the blank solution

in each cell. Scan both the standard and sample from 420 nm to 320 nm with the blank solution in the reference cell. Measure the absorbance of both standard and sample at 360 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent polybrominated salicylanilide as follows:

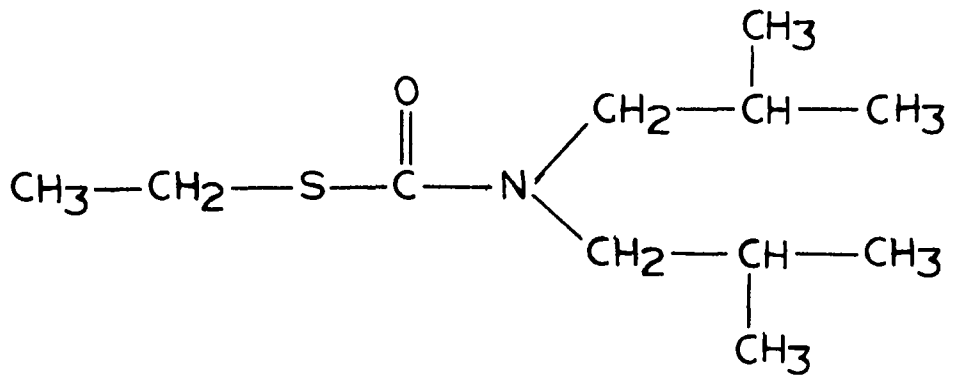
$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

September 1975

Butylate EPA-1
(Tentative)

Determination of Butylate by Gas-Liquid Chromatography (TCD)

Butylate is the common name for S-ethyl diisobutylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{11}H_{23}ONS$

Molecular weight: 217.4

Boiling point: 71°C at 10 mm

Physical state and color: Amber liquid

Solubility: 45 ppm in water at room temperature; miscible with kerosene, acetone, methyl isobutyl ketone, ethanol, xylene

Stability: stable under ordinary conditions; non-corrosive

Other names: Sutan (Stauffer), R1910

Reagents:

1. Butylate standard of known % purity
2. Chloroform, pesticide or spectro grade

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 5' x 1/4" glass column packed with 20% SE-30 on Chromosorb W, AW, DMCS (or equivalent column)
3. Precision liquid syringe: 50 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	180°C
Injection temperature:	240°C
Detector temperature:	270°C
Carrier gas:	Helium
Flow rate:	100 ml/min

Operating conditions for filament current, column temperature, or gas flow should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.20 gram butylate standard into a 10 ml volumetric flask; dissolve and make to volume with chloroform.(final conc 20 mg/ml)

Preparation of Sample:

For technical material and liquid formulations, weigh a portion of sample equivalent to 0.20 gram butylate into a 10 ml volumetric flask, make to volume with chloroform, and mix thoroughly. (final conc 20 mg butylate/ml)

For dry formulations, weigh a portion of sample equivalent to 1.0 gram butylate into a 125 ml screw-cap flask, add by pipette 50 ml chloroform, and shake for one hour. Allow to settle; filter or centrifuge if necessary, taking precautions to prevent evaporation. (final conc 20 mg butylate/ml)

Determination:

Using a precision liquid syringe, alternately inject three 20-40 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent butylate as follows:

$$\% = \frac{\text{(pk. ht. or area sample)(wt. std injected)(\% purity of std)}}{\text{(pk. ht. or area standard)(wt. sample injected)}}$$

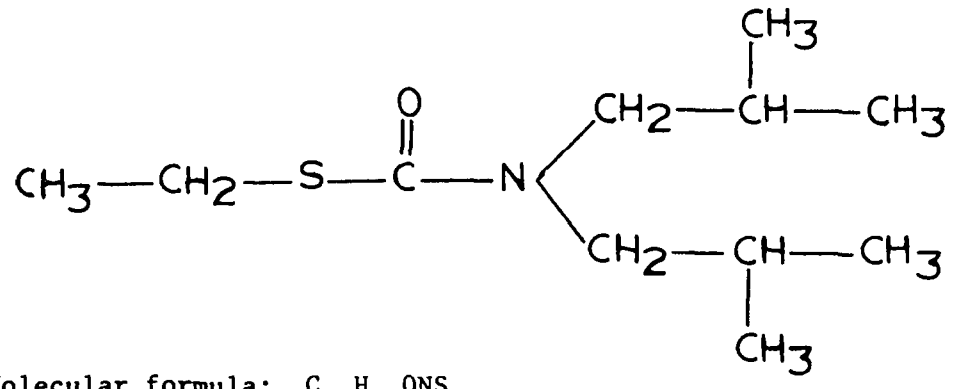
Method submitted by Eva Santos, EPA Region IX, San Francisco, California.

July 1975

Butylate EPA-2
(Tentative)

Determination of Butylate by High Pressure Liquid Chromatography

Butylate is the common name for S-ethyl diisobutylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{11}H_{23}ONS$

Molecular weight: 217.4

Boiling point: 71°C at 10 mm

Physical state and color: Amber liquid

Solubility: 45 ppm in water at room temperature; miscible with kerosene, acetone, methyl isobutyl ketone, ethanol, xylene

Stability: stable under ordinary conditions; non-corrosive

Other names: Sutan (Stauffer), R1910

Reagents:

1. Butylate standard of known % purity
2. Chloroform
3. Dichloromethane
4. Hexane
5. Methanol

All solvents should be pesticide or spectro grade.

Equipment:

1. High Pressure Liquid Chromatograph
2. High pressure liquid syringe or sample injection loop
3. Liquid chromatographic column, 4 mm I.D. x 25 cm packed with LiChrosorb Si 60 - 10 μ (or equivalent column)

Operating conditions for Hewlett-Packard Model 1010B LC:

Mobile phase: 80% Hexane + 19% Dichloromethane + 1% Methanol

Column temperature: ambient

Observed column pressure: 30 Kg/cm^2 (425 PSI)

Flow rate: 3 ml/min

Detector: UV at 240 nm

Chart speed: 0.5 in/min

Injection: 10 μl

Conditions may have to be varied by the analyst for other instruments, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.04 gram butylate standard into a 50 ml volumetric flask; dissolve and make to volume with chloroform (final conc 0.8 mg/ml).

Preparation of Sample:

Weigh an amount of sample equivalent to 0.08 gram butylate into a 100 ml volumetric flask; dissolve and make to volume with chloroform (final conc 0.8 mg butylate/ml).

Determination:

Using a high pressure liquid syringe, alternately inject three 10 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

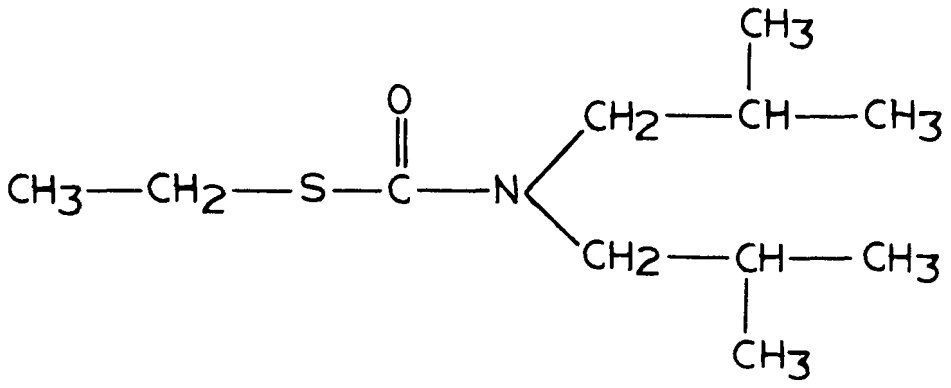
From the average peak height or peak area calculate the percent butylate as follows:

$$\% = \frac{\text{(pk. ht. or area sample)(wt. std injected)(\% purity of std)}}{\text{(pk. ht. or area standard)(wt. sample injected)}}$$

Method developed by Joseph B. Audino, Supervisor, Pesticide Formulation Laboratory, California Department of Food and Agriculture; and by Yoshihiko Kawano, Associate Chemist on sabbatical leave from the University of Hawaii.

Determination of Butylate by Gas-Liquid Chromatography (FID)

Butylate is the common name for S-ethyl diisobutylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{11}H_{23}ONS$

Molecular weight: 217.4

Boiling point: 71°C at 10 mm

Physical state and color: Amber liquid

Solubility: 45 ppm in water at room temperature; miscible with kerosene, acetone, methyl isobutyl ketone, ethanol, xylene

Stability: stable under ordinary conditions; non-corrosive

Other names: Sutan (Stauffer), R1910

Reagents:

1. Butylate standard of known % purity
2. Acetone, pesticide or spectro grade

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 1/4" glass column packed with 5% QF-1 on 60/80 Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	140°
Injection temperature:	215°
Detector temperature:	225°
Carrier gas:	Helium or Nitrogen
Flow rate:	55 ml/min

Operating conditions for column temperature, carrier gas flow, or hydrogen/air flow rates should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram butylate standard into a 25 ml volumetric flask; dissolve and make to volume with acetone. (final conc 2 mg butylate/ml)

Preparation of Sample:

For technical material and liquid formulations, weigh a portion of sample equivalent to 0.05 gram butylate into a 25 ml volumetric flask, make to volume with acetone, and mix thoroughly. (final conc 2 mg butylate/ml)

For dry formulations, weigh a portion of sample equivalent to 0.5 gram of butylate into a 125 ml screw-cap flask, add by pipette 50 ml acetone, and shake for one hour. Allow to settle; filter or centrifuge if necessary, taking precautions to prevent evaporation. Pipette 5 ml of the clear solution into a 25 ml volumetric flask and make to volume with acetone and mix thoroughly. (final conc 2 mg butylate/ml)

Determination:

Using a precision liquid syringe, alternately inject three 2-4 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

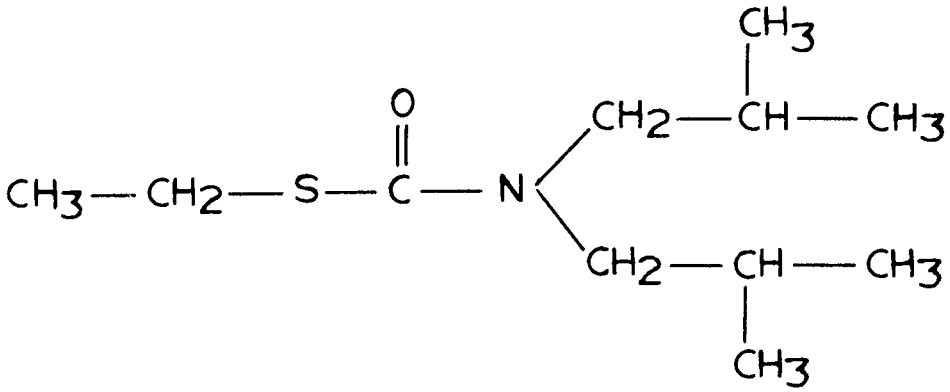
From the average peak height or peak area calculate the percent butylate as follows:

$$\% = \frac{\text{(pk. ht. or area sample)(wt. std injected)(\% purity of std)}}{\text{(pk. ht. or area standard)(wt. sample injected)}}$$

Method submitted by Eva Santos, EPA Region IX, San Francisco, California.

Determination of Butylate by Gas-Liquid Chromatography (FID - Internal Standard)

Butylate is the common name for S-ethyl diisobutylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{11}H_{23}ONS$

Molecular weight: 217.4

Boiling point: 71°C at 10 mm

Physical state and color: Amber liquid

Solubility: 45 ppm in water at room temperature; miscible with kerosene, acetone, methyl isobutyl ketone, ethanol, xylene

Stability: stable under ordinary conditions; non-corrosive

Other names: Sutan (Stauffer), R1910

Reagents:

1. Butylate standard of known % purity
2. S-Ethyl dipropylthiocarbamate (EPTC) standard of known % purity
3. Carbon disulfide, pesticide or spectro grade
4. Chloroform, pesticide or spectro grade

Reagents (Cont.):

5. Methanol, pesticide or spectro grade
6. Internal Standard solution - weigh 0.2 gram EPTC into a 50 ml volumetric flask; dissolve in and make to volume with a solvent mixture consisting of 80% carbon disulfide + 15% chloroform + 5% methanol. (conc 4 mg EPTC/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 4 mm glass column packed with 3% OV-1 on 60/80 Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	130°C
Injection temperature:	225°C
Detector temperature:	250°C
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi
Hydrogen pressure:	20 psi
Air pressure:	30 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.08 gram butylate standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 4 mg butylate and 4 mg EPTC/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.08 gram butylate into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the butylate. For coarse or granular materials, shake mechanically for 10-15 minutes or shake by hand intermittently for 25-30 minutes. (final conc 4 mg butylate and 4 mg EPTC/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is EPTC, then butylate.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of butylate and EPTC from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. EPTC})(\%\text{ purity EPTC})(\text{pk. ht. or area butylate})}{(\text{wt. butylate})(\%\text{ purity butylate})(\text{pk. ht. or area EPTC})}$$

Determine the percent butylate for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. EPTC})(\%\text{ purity EPTC})(\text{pk. ht. or area butylate})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area EPTC})(RF)} \quad (4-1)$$

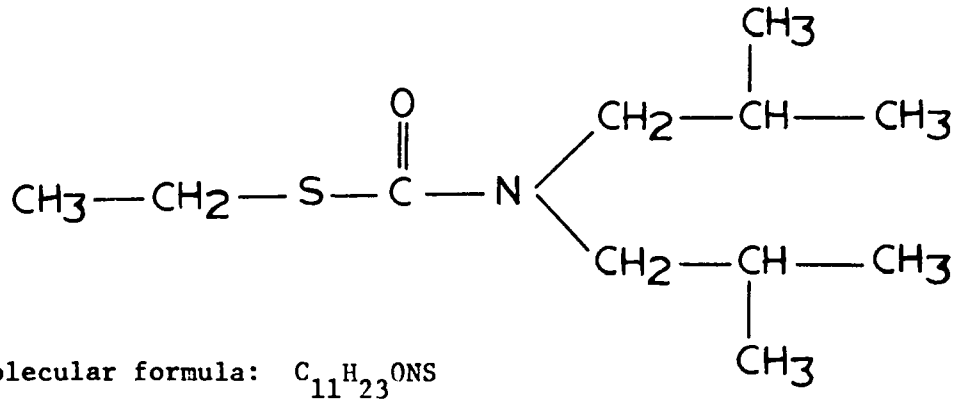
Method submitted by Division of Regulatory Services, Kentucky Agricultural Experiment Station, University of Kentucky, Lexington, Kentucky 40506.

October 1975

Butylate EPA-5
(Tentative)

Determination of Butylate by Gas-Liquid Chromatography (TCD - Internal Standard)

Butylate is the common name for S-ethyl diisobutylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{11}H_{23}ONS$

Molecular weight: 217.4

Boiling point: 71°C at 10 mm

Physical state and color: Amber liquid

Solubility: 45 ppm in water at room temperature; miscible with kerosene, acetone, methyl isobutyl ketone, ethanol, xylene

Stability: stable under ordinary conditions; non-corrosive

Other names: Sutan (Stauffer), R1910

Reagents:

1. Butylate standard of known % purity
2. Vernolate standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.25 gram vernolate into a 25 ml volumetric flask, dissolve in, and make to volume with acetone. (conc 10 mg vernolate/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 5' x 1/4" glass column packed with 5% PEG-1540 on 60/80 Chromosorb W AW DMCS
3. Precision liquid syringe: 25 or 50 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	150°C
Injection temperature:	200°C
Detector temperature:	200°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas flow rate:	30 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram butylate standard into a small glass-stoppered flask or screw-cap tube. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 10 mg butylate and 10 mg vernolate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram butylate into a small glass-stoppered flask or screw-cap tube. Add by pipette 10 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the butylate. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 10 mg butylate and 10 mg vernolate/ml)

Determination:

Inject 10-20 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is butylate, then vernolate.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of butylate and vernolate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. vernolate})(\%\text{ purity vernolate})(\text{pk. ht. or area butylate})}{(\text{wt. butylate})(\%\text{ purity butylate})(\text{pk. ht. or area vernolate})}$$

Determine the percent butylate for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. vernolate})(\%\text{ purity vernolate})(\text{pk. ht. or area butylate})(100)}{(\text{wt. sample})(\text{pk. ht. or area vernolate})(RF)}$$

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Note! This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Chemistry Lab. Any comments, criticism, suggestion, data, etc. concerning this method will be appreciated.

Determination of Cadmium in Fungicide Formulations by Atomic Absorption Spectroscopy

Cadmium compounds such as the carbonate, chloride, oxide, sebacate, succinate, and sulfate are registered turf fungicides.

Cadmium is a silver-white, blue-tinged, lustrous metal: atomic symbol, Cd; atomic weight, 112.40; m.p. 321°C, b.p. 767°C, and d. 8.65. It is insoluble in water; readily soluble in dilute HNO_3; slowly soluble in hot HCl; almost unattacked by cold, but converted into the sulfate by hot H_2SO_4. It is present to the extent of 49 to 87% in the above compounds.

Principle and Applicability of the Method:

This method is applicable for the analysis of cadmium in the presence of organic materials and in combination with dithiocarbamates, potassium chromate, coloring materials, and diluents. Using only a simple acid digestion and filtration with no need for any special extraction or clean-up procedures, most samples require less than 1 hour from weighing to analysis.

The secondary absorption at 326.1 nm is used for macro amounts of cadmium in formulations rather than the most sensitive absorption at 228.0 nm which is normally used for micro amounts.

Reagents:

1. Cadmium carbonate of known % cadmium
2. Concentrated nitric acid, ACS
3. Distilled or de-ionized water, free from metals

Equipment:

1. Atomic absorption spectrophotometer
2. Hot plate
3. Filtration apparatus
4. Whatman No. 42 (or equivalent) filter paper
5. Usual laboratory glassware

Procedure:

Preparation of Standard Solutions:

Standard solutions in the range of 100-500 ppm cadmium can be made from separate weighings of cadmium carbonate (0.1534 gram for each 100 ppm cadmium when made to 1 liter volume); however, it is more convenient to prepare a 1000 ppm stock solution and make appropriate dilutions.

A stock solution of 1000 ppm cadmium is made as follows: weigh 1.534 grams of cadmium carbonate into a 150 ml beaker, add 15 ml concentrated nitric acid, and cover with a watch glass. Boil gently to expel excess acid, cool, transfer to a 1000 ml volumetric flask and make to volume with water. Prepare solutions of 100, 200, 300, 400, and 500 ppm by diluting 10, 20, 30, 40, and 50 ml aliquots to 100 ml.

Preparation of Sample:

Weigh a portion of sample equivalent to 0.02-0.03 gram cadmium into a 150 ml beaker, add 15 ml concentrated nitric acid, and cover with a watch glass. After the initial reaction subsides and the vapor above the solution is pale yellow, carefully add 15 ml water and heat on a hot plate until the volume is reduced to approximately 15-20 ml. While the solution is still hot, filter through a Whatman No. 42 filter paper and wash with 50-60 ml water (equivalent

filter papers may be used if they retain the fine materials normally associated with clay carriers). Cool the filtrate; transfer to a 100 ml volumetric flask and make to volume with water.

Determination:

Following the manufacturer's manual for cadmium determination for the particular instrument being used, proceed as follows:

Allow atomic absorption spectrophotometer to warm up one-half hour and adjust Boling burner head so that the top of the oxidizing flame lies approximately 1" below the center of the hollow cathode tube. Regulate flame (acetylene and air are approximately 9 psig); determine the precise maximum for secondary absorption, using the most dilute standard, while holding lamp current at 6 ma. The 6 ma value is chosen to minimize any auto-absorption which has been reported in cadmium analysis. Aspirate standards and plot their absorbances against concentration in ppm.

Determine concentrations of samples from plotted values of standards. On some instruments where ppm may be read directly from a digital readout, the plotting of an absorbance-concentration curve is not necessary.

Using the above procedure, Beer's law is obeved in the 100-500 ppm range.

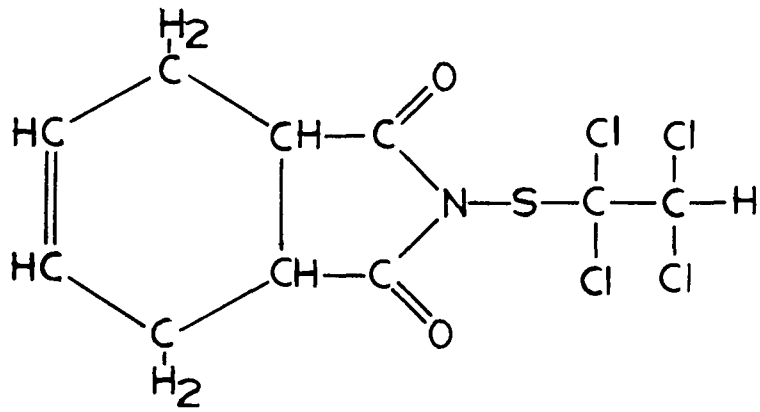
Calculation:

$$\% \text{ Cadmium} = \frac{(\text{ppm Cd})(10^{-6})(100)}{(\text{grams sample})(1/100)}$$

Method developed by Paul D. Jung and David Clarke, Division of Inspection and Regulation, Maryland Department of Agriculture, College Park, Md. 20742 (method published JAOAC Vol. 57, No. 2, 1974, pg. 379-381).

Determination of Captafol by Infrared Spectroscopy

Captafol is the common name for cis-N-((1,1,2,2-tetrachloroethyl-thio)-4-cyclohexene-1,2-dicarboximide, a registered fungicide having the chemical structure:



Molecular formula: $C_{10}H_9Cl_4NO_2S$

Molecular weight: 349.1

Melting point: 160 to 161°C

Physical state and color: white crystalline solid; technical material is a light tan powder with a characteristic odor.

Solubility: practically insoluble in water, slightly soluble in most organic solvents

Stability: stable except under strongly alkaline conditions, slowly decomposes at its melting point

Other names: Difolatan (Chevron Chem. Co.), Folcid

Reagents:

1. Captafol standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm KBr or NaCl cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.08 gram captafol standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 8 mg/ml)

Preparation of Sample:

For granular or dust formulations, weigh a portion of sample equivalent to 0.4 gram captafol into a glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 8 mg captafol/ml)

For flowable liquid (water) formulations, weigh a portion of sample equivalent to 0.4 gram captafol into a glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette, a few boiling chips to aid agitation, and sufficient anhydrous sodium sulfate to absorb all the water. Close tightly and shake vigorously on a shaking machine for one hour. Allow to settle. Filter or centrifuge if necessary to get a clear chloroform solution, taking precaution to prevent evaporation. (final conc 8 mg captafol/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 2000 cm^{-1} to 1540 cm^{-1} (5.0 μ-6.5 μ).

Determine the absorbance of standard and sample using the peak at 17.27 cm^{-1} (5.79 μ) and baseline from 18.18 cm^{-1} to 1639 cm^{-1} (5.5 μ to 6.1 μ).

Calculation:

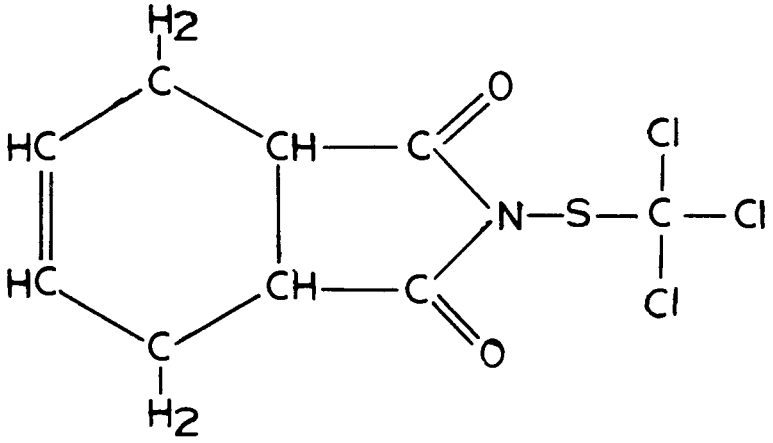
From the above absorbances and using the standard and sample concentrations, calculate the percent captafol as follows:

$$\% = \frac{\text{(abs. sample)(conc. std in mg/ml)(\% purity std)}}{\text{(abs. std)(conc. sample in mg/ml)}}$$

Method submitted by Eva Santos, EPA Product Analysis Laboratory, Region IX, San Francisco, California.

Determination of Captan by the Hydrolyzable Chlorine Method

Captan is the common name for N-trichloromethylthio-4-cyclohexene-1,2-dicarboximide, a registered fungicide having the chemical structure:



Molecular formula: $C_9H_8Cl_3NO_2S$

Molecular weight: 300.6

Melting point: 178°C (decomposes)

Physical state and color: white crystalline solid; technical material is a yellow amorphous solid (with a pungent odor) of 93-95% purity and m.p. 160-170°C

Solubility: less than 0.5 ppm in water at RT; insoluble in petroleum oils; at 25°C the solubility w/w is 7% in xylene, 5% in chloroform, 3% in acetone, 1% in isopropanol

Stability: stable except under alkaline conditions; decomposes at its melting point; non-corrosive but decomposition products are corrosive

Other names: Orthocide (Chevron Chem. Co.), Merpan, Vondcaptan

This method is based on measuring the hydrolyzable chlorine in captan and is designed for 100% captan. It has been used successfully for high concentration captan formulations when there are no interfering substances present. Any material containing hydrolyzable chlorine would interfere. The chloride is measured on the sample before and after hydrolysis and the difference calculated to equivalent captan.

Reagents:

1. Absolute methanol
2. Acetone
3. Hydrogen peroxide, 30%
4. Nitric acid, 1 + 1
5. Sodium hydroxide, 0.25N

Equipment:

1. Potentiometric titrimeter
2. Reflux apparatus
3. Usual laboratory glassware

Procedure:

Preparation of Sample:

Weigh a portion of sample equivalent to 0.25 gram captan into a 250 ml Erlenmeyer flask. Add 125 ml absolute methanol and swirl. (Do not allow to stand more than 45 minutes before proceeding since captan may slowly react with methanol.) Add acetone to the 250 ml mark and mix thoroughly to dissolve the captan. Adjust the volume as necessary because of solvent shrinkage, temperature change, etc. (With technical captan and formulations a flocculent precipitate or undissolved residue may be present.)

Transfer one 100 ml aliquot to a 500 ml standard taper Erlenmeyer (or other suitable) flask to be refluxed for the hydrolyzed chlorine content and another 100 ml aliquot to a 400 ml beaker for immediate titration of the non-hydrolyzed chlorine content.

Hydrolysis and Determination of Hydrolyzed Chlorine:

Add 50 ml of approx. 0.25N sodium hydroxide solution and a few boiling chips to the Erlenmeyer flask, connect to an upright condenser, and reflux for one hour.

(Titrate the non-hydrolyzed aliquot at this time.)

Turn off or remove the heat and cautiously add 5 ml 30% hydrogen peroxide thru the condenser. Cool somewhat and remove the flask from the condenser. Boil for 10 minutes to decompose the excess hydrogen peroxide and evaporate to about 60 ml. (If the solution is not practically colorless, add 5 ml more hydrogen peroxide and water if necessary to maintain the volume and boil another 10 minutes.)

Cool, add 10 ml 1 + 1 nitric acid, and titrate the chlorine potentiometrically.

Determination of Chlorine before Hydrolysis:

Add 10 ml 1 + 1 nitric acid to the 100 ml aliquot in the 400 ml beaker and titrate the chlorine potentiometrically.

Calculation:

The percent captan is obtained by subtracting the milliequivalents of chlorine found before hydrolysis (meq. Cl_B) from the milliequivalents of total chlorine found after hydrolysis (meq. Cl_T), multiplying by the milliequivalent weight of captan X 100, and dividing by the weight of sample X the aliquoting factor.

$$\% \text{ captan} = \frac{(\text{meq. } Cl_T - \text{meq. } Cl_B)(0.1002)(100)}{(\text{weight sample})(0.4)}$$

where: meq. Cl_T = N $AgNO_3$ X ml used for titration of hydrolyzed aliquot

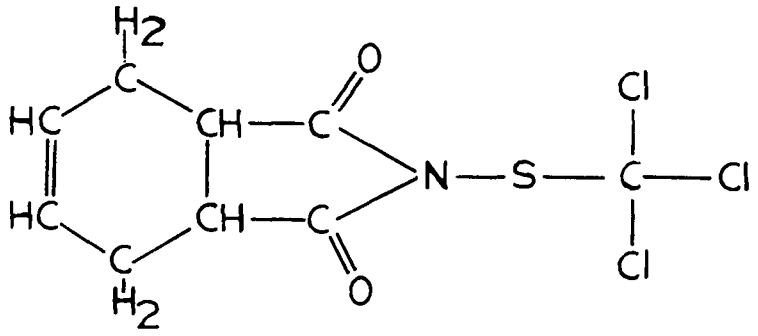
meq. Cl_B = N $AgNO_3$ X ml used for titration of non-hydrolyzed aliquot

$$\text{meq. wt. captan} = \frac{(300.6)}{(3)(1000)} = 0.1002$$

$$\text{aliquoting factor} = \frac{100}{250} = 0.4$$

Determination of Captan by Infrared Spectroscopy

Captan is the common name for N-trichloromethylthio-4-cyclohexene-1,2-dicarboximide, a registered fungicide having the chemical structure:



Molecular formula: $C_9H_8Cl_3NO_2S$

Molecular weight: 300.6

Melting point: 178°C (decomposes)

Physical state and color: white crystalline solid; technical material is a yellow amorphous solid (with a pungent odor) of 93-95% purity and m.p. 160-170°C

Solubility: less than 0.5 ppm in water at RT; insoluble in petroleum oils; at 25°C the solubility w/w is 7% in xylene, 5% in chloroform, 3% in acetone, 10% in isopropanol

Stability: stable except under alkaline conditions; decomposes at its melting point; non-corrosive but decomposition products are corrosive

Samples containing malathion and methoxychlor should be run by GLC.

Reagents:

1. Captan standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.1 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.1 gram captan standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.5 gram captan into a glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 10 mg captan/ml) For very low percent formulations requiring larger samples, use more solvent and evaporate an aliquot to a smaller volume to give a final concentration close to 10 mg captan/ml.

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1885 cm^{-1} to 1665 cm^{-1} (5.3 μ to 6.0 μ).

Determine the absorbance of standard and sample using the peak at 1735 cm^{-1} (5.76 μ) and basepoint at 1855 cm^{-1} (5.39 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent captan as follows:

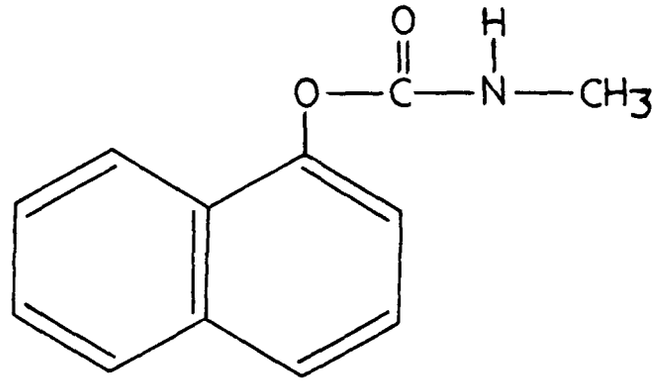
$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg captan/ml chloroform gives an absorbance of approx. 0.04 in a 0.1 mm cell.)

Method contributed by the Commonwealth of Virginia, Division of Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Determination of Carbaryl by Ultraviolet Spectroscopy

Carbaryl is the accepted common name for 1-naphthyl methylcarbamate, a registered insecticide having the chemical structure:



Molecular formula: $C_{12}H_{11}NO_2$

Molecular weight: 201.2

Melting point: 142°C

Physical state and color: white, crystalline solid

Solubility: 40 ppm in water at 30°C; soluble in most polar organic solvents such as acetone, dimethylformamide

Stability: stable to light, heat, and hydrolysis under normal storage conditions; non-corrosive to metals, packaging materials, or application equipment; compatible with most pesticides except those strongly alkaline which hydrolyze it to 1-naphthol

Other names: Sevin (Union Carbide), sevin (USSR), UC 7744, Hexavin Karbaspray, Ranyon, Septene, Tricarnam

This method is recommended only when the preferred infrared method (AOAC 12th Ed., 2nd Supplement, 6.B01-6.B04) cannot be used.

Reagents:

1. Carbaryl standard of known % purity
2. Ethanol, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.05 gram carbaryl standard into a 100 ml volumetric flask. Dissolve, make to volume with ethanol, and mix thoroughly. Pipette a 10 ml aliquot into a 50 ml volumetric flask and make to volume with ethanol. Mix thoroughly and pipette a 10 ml aliquot into a 50 ml volumetric flask. Make to volume and again mix thoroughly. (final conc 20 µg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.05 gram of carbaryl into a 250 ml Erlenmeyer glass-stoppered flask. Add 100 ml ethanol by pipette and shake on a mechanical shaker for one hour. Filter if necessary and pipette 10 ml of the clear filtrate into a 50 ml volumetric flask. Make to volume with ethanol, mix thoroughly, and pipette 10 ml into a 50 ml volumetric flask. Make to volume with ethanol and mix thoroughly. (final conc 20 µg carbaryl/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 280 nm with ethanol in each cell. Scan both the standard and sample from 350 nm to 250 nm with ethanol in the reference cell. Measure the absorbance of both standard and sample at 280 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent carbaryl as follows:

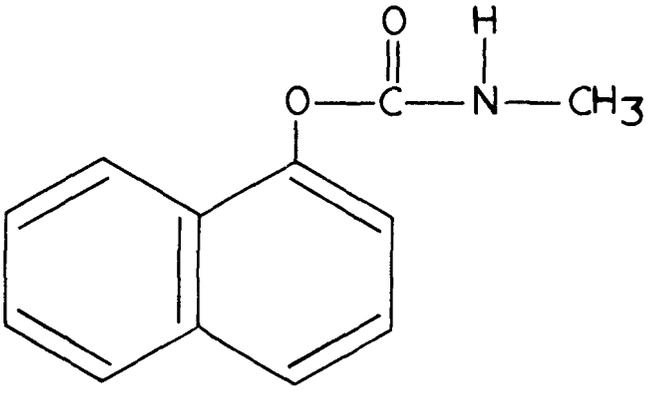
$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

October 1975

Carbaryl EPA-2
(Tentative)

Determination of Carbaryl by High Pressure Liquid Chromatography

Carbaryl is the accepted common name for 1-naphthyl methylcarbamate, a registered insecticide having the chemical structure:



Molecular formula: $C_{12}H_{11}NO_2$

Molecular weight: 201.2

Melting point: 142°C

Physical state and color: white, crystalline solid

Solubility: 40 ppm in water at 30°C; soluble in most polar organic solvents such as acetone, dimethylformamide

Stability: stable to light, heat, and hydrolysis under normal storage conditions; non-corrosive to metals, packaging materials, or application equipment; compatible with most pesticides except those strongly alkaline which hydrolyze it to 1-naphthol

Other names: Sevin (Union Carbide), sevin (USSR), UC 7744, Hexavin Karbaspray, Ranyon, Septene, Tricarnam

Reagents:

1. Carbaryl standard of known % purity
2. Methanol, pesticide or spectro grade

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm. If a variable wavelength UV detector is available, other wavelengths may be useful to increase sensitivity or eliminate interference.
2. Suitable column such as:
   a. DuPont ODS Permaphase, 1 meter x 2.1 mm ID
   b. Perkin Elmer Sil-X 11 RP, 1/2 meter x 2.6 mm ID
3. High pressure liquid syringe or sample injection loop
4. Usual laboratory glassware

Operating Conditions:

Mobile phase:	20% methanol + 80% water
Column temperature:	50-55°C
Chart speed:	5 min/inch or equivalent
Flow rate:	0.5 to 1.5 ml/min (Perkin Elmer instrument with 1/2 meter column)
Pressure:	400 psi (DuPont instrument with 1 meter column)
Attenuation:	adjusted

Conditions may have to be varied by the analyst for other instruments, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.3 gram carbaryl standard into a glass-stoppered flask or screw-cap bottle, add 100 ml methanol by pipette, dissolve, and mix well (final conc 3 mg/ml).

Preparation of Sample:

Weigh an amount of sample equivalent to 0.3 gram carbaryl into a glass-stoppered flask or screw-cap bottle, add 100 ml methanol by pipette, and shake thoroughly to dissolve the carbaryl. Allow any solid matter to settle; filter or centrifuge if necessary (final conc 3 mg carbaryl/ml).

Determination:

Alternately inject three 5 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

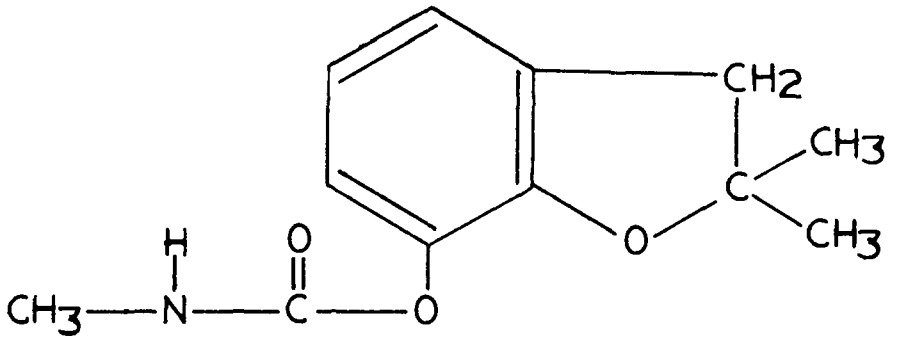
From the average peak height or peak area calculate the percent carbaryl as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Elmer H. Hayes, EPA, Beltsville, Md.

Determination of Carbofuran by Infrared Spectroscopy

Carbofuran is the accepted common name for 2,3-dihydro-2,2-dimethyl-7-benzofuranyl methyl carbamate, a registered insecticide, acaricide, and nematocide having the chemical structure:



Molecular formula: $C_{12}H_{15}NO_3$

Molecular weight: 221.3

Melting point: 150-152°C

Physical state, color, and odor: Odorless, white, crystalline solid

Solubility: solubility at 25°C is 700 ppm in water, 15% in acetone, 14% in acetonitrile, 4% in benzene, 9% in cyclohexanone, 27% in dimethylformamide

Stability: stable under neutral or acid conditions, unstable in alkaline media

Other names: Furadan (Niagara), NIA 10242, Bay 70142, FMC 10242, Curaterr

Reagents:

1. Carbofuran standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.15 gram carbofuran standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 15 mg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.75 gram carbofuran into a glass-stoppered flask or screw-cap tube. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precautions to prevent evaporation. (final conc 15 mg carbofuran/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings, scan both the standard and sample from 1000 cm^{-1} to 800 cm^{-1} (10 μ to 12.5 μ).

Determine the absorbance of standard and sample using the peak at 875 cm^{-1} (11.93 μ) and baseline from 900 cm^{-1} to 845 cm^{-1} (11.11 μ to 11.83 μ).

(The N-H band at 3460 cm^{-1} (2.89 μ) is also very good.)

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent carbofuran as follows:

$$\% = \frac{\text{(abs. sample)(conc. std in mg/ml)(\% purity std)}}{\text{(abs. std)(conc. sample in mg/ml)}}$$

(A concentration of 1 mg carbofuran/ml chloroform gives an absorbance of approx. 0.02 in a 0.2 mm cell.)

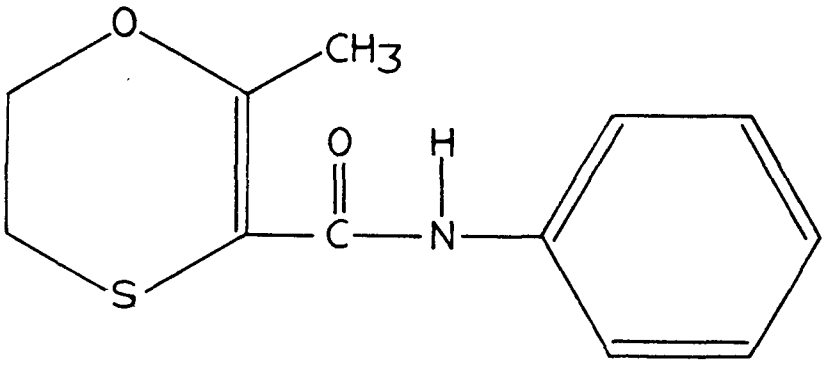
Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

November 1975

Carboxin EPA-1
(Tentative)

Determination of Carboxin in Dusts and Powders by Infrared Spectroscopy

Carboxin is the common name for 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide, a registered fungicide having the chemical structure:



Molecular formula: $C_{12}H_{13}NO_2S$

Molecular weight: 235

Melting point: 91.5 to 92.5°C; a dimorphic form has a m.p. of 98 to 100°C

Physical state, color, and odor: odorless, white, crystalline solid
(The technical product is at least 97% pure.)

Solubility: 170 ppm in water at 25°C; soluble in acetone, benzene, dimethyl sulfoxide, ethanol, methanol

Stability: compatible with all except highly alkaline or acidic pesticides

Other names: Vitavax, D735 (Uniroyal); DCMO

Reagents:

1. Carboxin standard of known % purity
2. Benzene, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording, with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker
3. Soxhlet extraction apparatus
4. Rotary evaporator or steam bath with short reflux column
5. Filtration apparatus or centrifuge
6. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.08 gram carboxin standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml benzene by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 8 mg/ml)

Preparation of Sample:

For Shake-out extraction, weigh a portion of sample equivalent to 0.8 gram carboxin into a 250 ml glass-stoppered or screw-cap Erlenmeyer flask. Add by pipette 100 ml benzene, stopper tightly, and shake on a mechanical shaker for 2 hours. Allow to settle; filter or centrifuge if necessary, taking precaution to prevent evaporation. (final conc 8 mg carboxin/ml)

For Soxhlet extraction, weigh a portion of sample equivalent to 0.8 gram carboxin into a Soxhlet thimble, plug with cotton or glass wool, and extract with benzene for 3 hours. Evaporate to a suitable volume under vacuum on a rotary evaporator or on a steam bath using a short reflux column. Quantitatively transfer to a 100 ml volumetric flask and make to volume with benzene. Add a small amount of granular anhydrous sodium sulfate to insure dryness. (final conc 8 mg carboxin/ml)

Determination:

With benzene in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1820 cm^{-1} to 1110 cm^{-1} (5.5 μ to 9.0 μ).

Determine the absorbance of standard and sample at either of the following three bands:

Peak	Basepoint
1675 cm^{-1} (5.97 μ)	1630 cm^{-1} (6.13 μ)
1585 cm^{-1} (6.30 μ)	1630 cm^{-1} (6.13 μ)
1290 cm^{-1} (7.75 μ)	1265 cm^{-1} (7.90 μ)

Either of these bands may be used with comparable results.

Calculation:

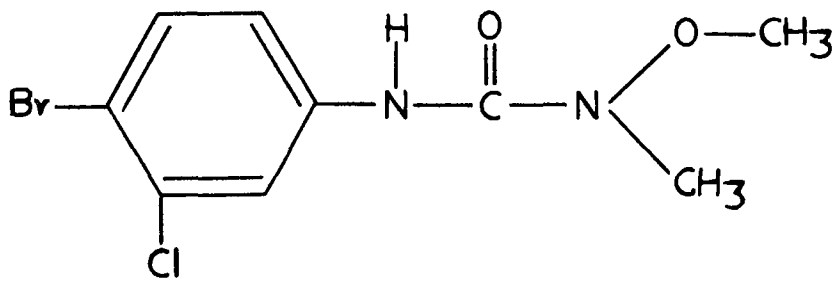
From the above absorbances and using the standard and sample concentrations, calculate the percent carboxin as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

This method is based on an EPA experimental method using data from Uniroyal. Any suggestions, data, criticisms, and information on its use will be appreciated.

Determination of Chlorbromuron by Gas-Liquid Chromatography (FID)

Chlorbromuron is the accepted common name for 3-(4-bromo-3-chlorophenyl)-1-methoxy-1-methylurea, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{10}BrClN_2O_2$

Molecular weight: 293.6

Melting point: 97°C (The technical grade has a purity of 95% and melts at 90-95°C)

Physical state, color, and odor: off-white crystalline solid with a mild odor

Solubility: 50 ppm in water at RT; soluble in acetone, chloroform, methyl ethyl ketone, dimethylformamide; slightly soluble in xylene

Stability: stable at RT; non-corrosive; compatible with other WP formulations

Other names: Bromex (Nor-Am), Maloran (CIBA-GEIGY), chlorobromuron (France)

Reagents:

1. Chlorbromuron standard of known % purity
2. Acetone, pesticide or spectro grade

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 2' x 1/4" glass column packed with 2% SE-52 on 70/80 Anakrom ABS (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	180°C
Injection temperature:	225°C
Detector temperature:	225°C
Carrier gas:	Helium or Nitrogen
Flow rate:	55 ml/min

Operating parameters (above) as well as hydrogen/air flow rates, attenuation, and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram chlorbromuron standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml acetone by pipette, close tightly and shake to dissolve. (final conc 10 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.5 gram chlorbromuron into a glass-stoppered flask or screw-cap bottle, add 50 ml acetone by pipette, close tightly, and shake for one hour. Allow to settle; filter or centrifuge if necessary, taking precautions to prevent evaporation. (final conc 10 mg chlorbromuron/ml)

Determination:

Using a precision liquid syringe, alternately inject three 2-3 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent chlorbromuron as follows:

$$\% = \frac{\text{(pk. ht. or area sample)(wt. std injected)(\% purity std)}}{\text{(pk. ht. or area std)(wt. sample injected)}}$$

This method is based on one of EPA's Experimental Methods (No. 10) which was adapted from another method from Ciba.

Comments, suggestions, data, results, etc. on this method are most welcome.

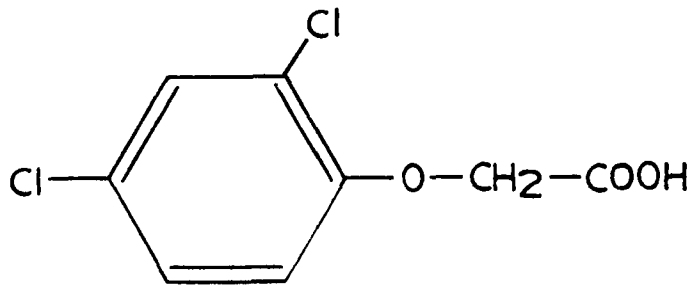
Definition, Structure, and Technical Data

The chlorophenoxy herbicides are a group of chemical compounds consisting mainly of mono-, di-, or tri- chlorinated phenoxy acetic, propionic, or butyric acids. These compounds are registered herbicides; however, some uses are restricted.

Formulations of these compounds may contain alkali metal salts which are marketed in the solid state or as concentrated aqueous solutions containing 10 to 40% active ingredient calculated as the acid. Salts with amines are almost exclusively aqueous solutions containing 40 to 70% active ingredient. The esters are marketed in the form of emulsifiable concentrates and as oil solutions for aerial spraying. Formulations may contain various substances such as wetting agents, emulsifiers, anti-precipitation agents, etc.

Structure and technical data for 11 of these compounds is given below. For each compound the common name is followed by the chemical name, structure, physical and chemical data, and other names.

2,4-D (ISO, BSI, WSSA), 2,4-dichlorophenoxyacetic acid



Molecular formula: $C_8H_6Cl_2O_3$

Molecular weight: 221.0

Physical state, color and odor: white crystalline solid, odorless when pure, otherwise slight phenolic odor

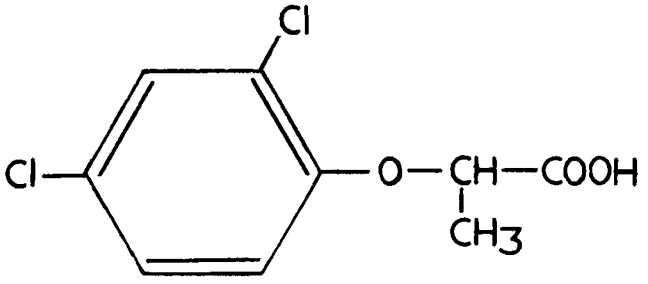
Melting point: 140 to 141°C (pure), 135 to 138°C (technical)

Solubility: about 600 ppm in water at 25°C; soluble in aqueous alkali and in alcohols, ether, acetone; insoluble in petroleum oils

Stability: non-hygroscopic but corrosive; forms salts and esters of varying properties and stabilities

Other names: Agrotect, Amoxone, Aqua-Kleen, Chipco Turf Herbicide D, Chloroxone, Crop Rider, Decamine, Ded-Weed, Dormone, Esteron, Estone, Fernesta, Fernimine, Fernoxone, Ferxone, Hedonal, Pennamine D, Salvo, Tributon, Vergemaster, Vertron 2D, Visko-Rhop, Weedar, Weedone

Dichlorprop (ISO, BSI, WSSA), 2-(2,4-dichlorophenoxy) propionic acid



Molecular formula: $C_9H_8Cl_2O_3$

Molecular weight: 235.1

Physical state, color, and odor: white crystalline solid, odorless when pure; technical, slight phenolic odor and tan color

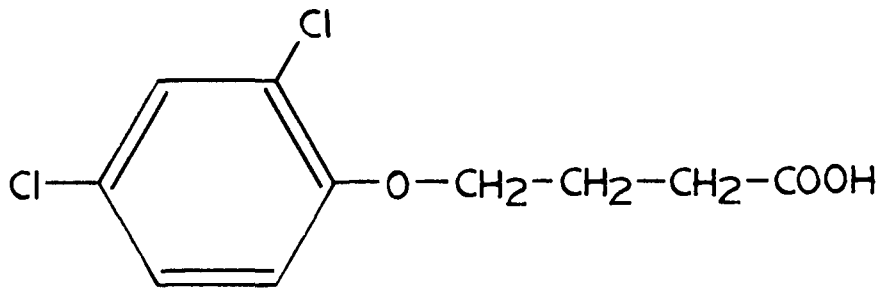
Melting point: 117.5 to 118.1°C (pure), 114 to 117°C (technical)

Solubility: about 350 ppm in water at 20°C; soluble in most organic solvents

Stability: acid is stable to heat and resistant to reduction, hydrolysis, and atmospheric oxidation

Other names: Cornox RK (Boots Co. Ltd), RD 406, 2,4-DP (USSR), Weedone 2,4-DP, Weedone 170, Envert 171

2,4-DB (BSI, WSSA), 4-(2,4-dichlorophenoxy) butyric acid



Molecular formula: $C_{10}H_{10}Cl_2O_3$

Molecular weight: 249.1

Physical state, color, and odor: white crystalline solid, odorless when pure

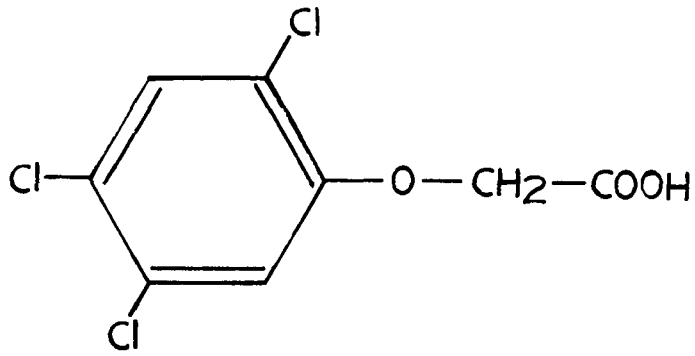
Melting point: 117 to 121°C depending on purity

Solubility: practically insoluble in water; slightly soluble in benzene, toluene, and kerosene; very soluble in acetone, alcohol, and ether

Stability: acids, salts, and esters are stable

Other names: Embutox (May & Baker Ltd), Butoxone (Chipman), Butyrac (Amchem), MB 2878

2,4,5-T (ISO, BSI, WSSA), 2,4,5-trichlorophenoxy acetic acid



Molecular formula: $C_8H_5Cl_3O_3$

Molecular weight: 255.5

Physical state and color: white crystals

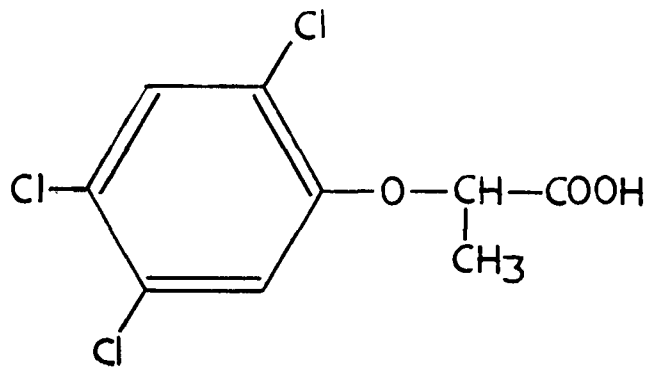
Melting point: 156.6°C (pure), 150-151°C (technical)

Solubility: about 278 ppm in water at 25°C; soluble in acetone, ethanol, and ether; salts with alkali metals and amines are water-soluble but oil-insoluble; esters are oil-soluble but water-insoluble

Stability: stable and non-corrosive

Other names: Weedone 2,4,5-T (Amchem), Brush-Rhop (Transvaal Inc.), Estron 245 (Dow), Decamine, Ded-Weed Brush Killer, Fence Rider, Forron, Fruitone A, Inverton 245, Line Rider, Reddon, Tormona, Tributon, Trioxone, Weedar

Silvex (WSSA, ANSI), 2-(2,4,5-trichlorophenoxy) propionic acid



Molecular formula: $C_9H_7Cl_3O_3$

Molecular weight: 269.5

Physical state, color, and odor: white powder, low odor

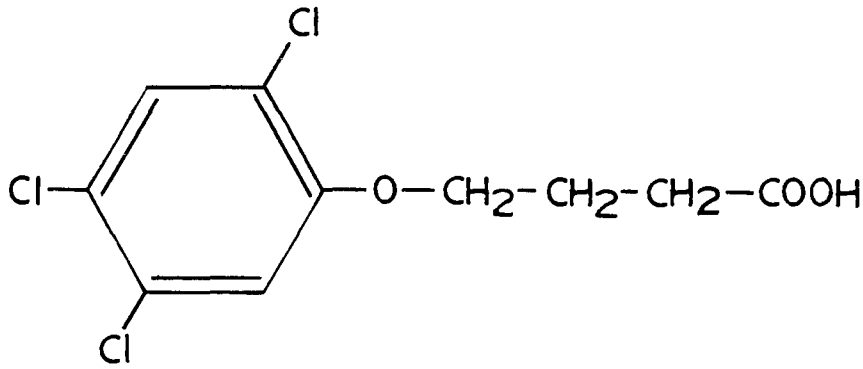
Melting point: 179 to 181°C

Solubility: about 140 ppm in water at 25°C; soluble in acetone and methanol

Stability: non-corrosive to spray equipment

Other names: ferroprop (common name ISO and BSI), Kuron (Dow), Weedone 2,4,5-TP (Amchem), Aqua-Vex, Ded-Weed, Fruitone T, Garlon, Kurosal, 2,4,5-TP

2,4,5-TB (ISO), 4-(2,4,5-trichlorophenoxy) butyric acid



Molecular formula: $C_{10}H_9Cl_3O_3$

Molecular weight: 283.5

Physical state and color: white crystals

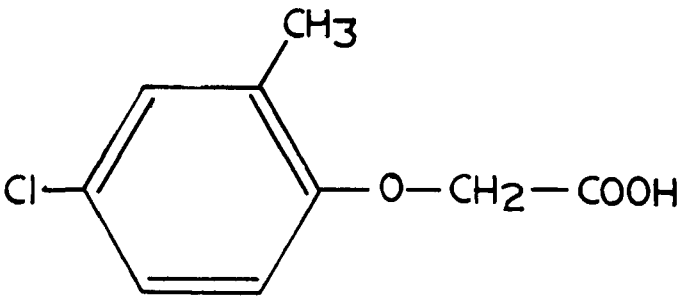
Melting point: 114 to 115°C

Solubility: similar to other compounds of this group

Stability: similar to other compounds of this group

Other names: 4-2,4,5-TB

MCPA (BSI, WSSA), (2-methyl-4-chlorophenoxy) acetic acid



Molecular formula: $C_9H_9ClO_3$

Molecular weight: 200.6

Physical state and color: white crystalline solid (pure), light brown solid (technical)

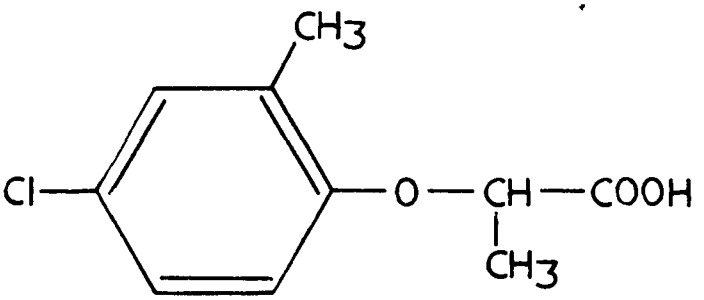
Melting point: 118 to 119°C (pure), 100 to 115°C (technical)

Solubility: about 825 ppm in water at RT; soluble in ethanol and ether; forms water-soluble salts with alkali metals and organic bases; oil-soluble esters may be prepared

Stability: solutions of alkali metals are alkaline and will corrode aluminum and zinc; water-soluble salts may be precipitated by hard water

Other names: Agroxone (Plant Protection Ltd); Agritox (May & Baker Ltd); Cornox M (The Boots Co. Ltd); Chiptox, Rhomene, Rhonox (Chipman Div. Rhodia Inc.); metaxon (USSR); Bordermaster; Hormotuho; Kilsem; MCP; Mephanac; Zelan

Mecoprop (ISO, BSI, WSSA), 2-(2-methyl-4-chlorophenoxy) propionic acid



Molecular formula: $C_{10}H_{11}ClO_3$

Molecular weight: 214.6

Physical state, color, and odor: colorless, odorless, crystalline solid; technical product may have a slight phenolic odor

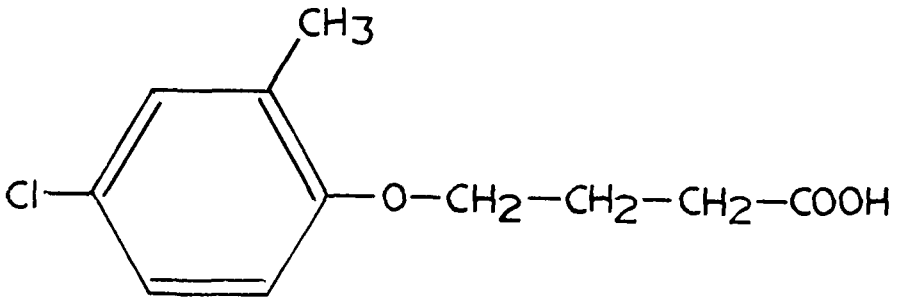
Melting point: 94 to 95°C (technical 90°C or above)

Solubility: about 620 ppm in water at 20°C; readily soluble in most organic solvents; forms water-soluble salts

Stability: stable to heat; resistant to reduction, hydrolysis, and atmospheric oxidation; corrosive to some metals

Other names: MCPP, CMPP, Iso-Comox (The Boots Co. Ltd), RD 4593, Chipco Turf Herbicide MCPP, Hedonal MCPP, Kilprop, Mepro, Methoxone

MCPB (WSSA), 4-(2-methyl-4-chlorophenoxy) butyric acid



Molecular formula: $C_{11}H_{13}ClO_3$

Molecular weight: 228.5

Physical state and color: white solid

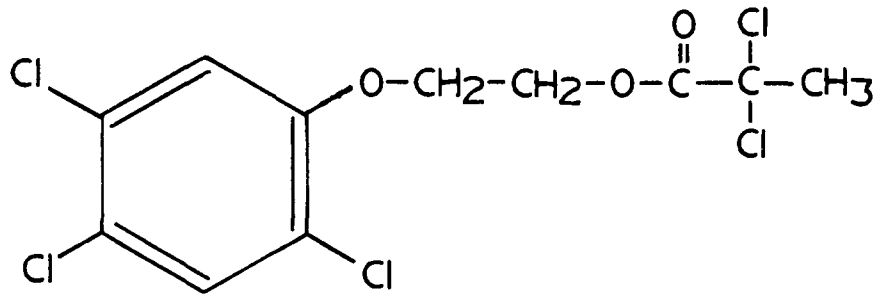
Melting point: 100 to 101°C (pure), 99 to 100°C (technical, about 90% purity)

Solubility: about 44 ppm in water at RT; slightly soluble in carbon tetrachloride or benzene; soluble in acetone, alcohol, and ether; forms water-soluble salts with alkali metals

Stability: somewhat incompatible with hard water

Other names: Tropotox (May & Baker Ltd), MB 3046, Can-Trol (Chipman Div. of Rhodia Inc.), Thistrol (Amchem), PDQ, 2,4-MCPB (France), 2M-4Kh-M (USSR)

Erbon (ANSI, WSSA), 2-(2,4,5-trichlorophenoxy) ethyl-2,2-dichloropropionate



Molecular formula: $C_{11}H_9Cl_5O_3$

Molecular weight: 366.5

Physical state and color: white solid (pure), dark brown solid (technical)

Melting point: 49 to 50°C; bp 161 to 164°C at 0.5 mm Hg

Solubility: practically insoluble in water; soluble in acetone, ethanol, kerosene, xylene, and most oils

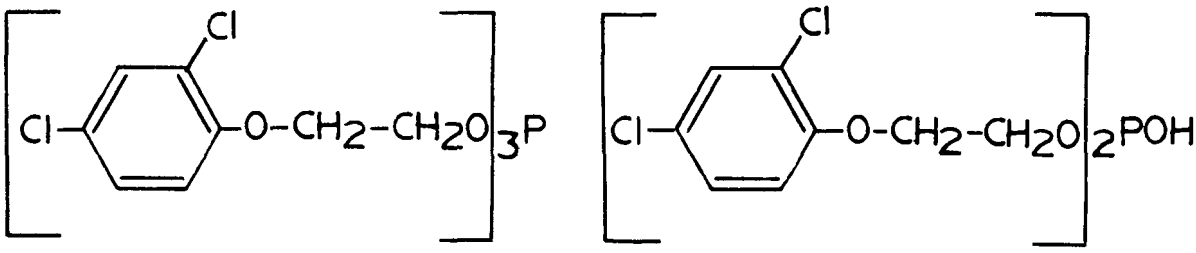
Stability: stable to UV light; non-flammable and non-corrosive

Other names: Baron, Erbon (Dow Chem. Co.)

2,4-DEP (WSSA), a mixture of

tris [2-(2,4-dichlorophenoxy) ethyl] phosphite and

bis [2-(2,4-dichlorophenoxy) ethyl] phosphite



tris form bis form

Molecular formula: $C_{24}H_{21}Cl_6O_6P$ (tris), $C_{16}H_{15}Cl_4O_5P$ (bis)

Molecular weight: 649.4 (tris), 460 (bis)

Physical state, color, and odor: dark amber viscous liquid with a phenolic odor

Boiling point: above 200°C at 0.1 mm Hg

Solubility: practically insoluble in water; miscible with xylene and aromatic hydrocarbons

Stability: stable when anhydrous; in presence of water or soil, slowly hydrolyzed to 2,4-dichlorophenoxyethanol and phosphoric acid; corrosive to iron and mild steel

Other names: Falone (Uniroyal), 3Y9

Determination of 2,4-D and 2,4,5-T in Formulations by Ultraviolet Spectroscopy

For definition, structure, and technical data on these compounds, see Chlorophenoxy Herbicides EPA-1. See note at end of method.

Principle of the Method:

A portion of sample is refluxed with sodium hydroxide whereby the esters are saponified and the herbicide acids are converted into sodium salts. The alkaline solution is extracted with ether to remove oils and other organic solvent-soluble substances. The solution is then acidified and the free herbicide acids are extracted with carbon tetrachloride which is evaporated. The herbicide acids are then dissolved in sodium hydroxide solution and read in an ultraviolet spectrophotometer.

Reagents:

1. 2,4-D and/or 2,4,5-T standards of known % purity
2. Sodium hydroxide, 25% solution (freshly prepared)
3. Ethyl ether, ACS
4. Sulfuric acid, 1+1 solution
5. Carbon tetrachloride, ACS
6. Sodium hydroxide, 1N solution
7. Sodium hydroxide, 0.1N solution (dilute above solution 1:10)

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Refluxing apparatus

3. Filtration apparatus

4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.08 gram 2,4-D acid or 2,4,5-T acid (0.08 gram of each, if both are present) into a 100 ml volumetric flask, dissolve in, and make to volume with 0.1N sodium hydroxide solution. Mix thoroughly and pipette 5 ml into a second 100 ml volumetric flask. Make to volume with 0.1N sodium hydroxide solution and mix thoroughly. (final conc 40 µg 2,4-D and/or 2,4,5-T/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.04 gram 2,4-D acid or 2,4,5-T acid (0.04 gram each, if both are present) into a 125 ml standard taper Erlenmeyer flask. Add 10 ml 25% sodium hydroxide solution and several small glass beads. Attach to a reflux condenser and reflux for at least one hour. Turn off the heat, wash down the condenser with 10-15 ml water, remove from apparatus, and cool to room temperature. Transfer the solution quantitatively to a 125 ml separatory funnel, washing the Erlenmeyer flask with 4-5 small portions of water.

Extract this solution with two 50 ml portions of ethyl ether. Wash the ether extracts with two 10 ml portions of 1N sodium hydroxide solution and add the wash solutions to the alkaline sample solution; discard the ether extracts. Neutralize the alkaline sample solution carefully with 1+1 sulfuric acid and add 1 ml in excess. The neutral point is indicated by precipitation of the free organic acids.

Extract the acidified sample solution successively with 25, 15, 10, and 10 ml portions of carbon tetrachloride, shaking for 2-3 minutes each time. If the extracts are cloudy, combine in a 125 ml

separatory funnel and clarify by washing with 10 ml water. Filter the carbon tetrachloride extracts through a piece of cotton (wet with carbon tetrachloride) into a 100 ml volumetric flask, make to volume, and mix thoroughly.

Pipette 10 ml of the above solution into a 125 ml standard taper Erlenmeyer flask and evaporate to dryness under vacuum, warming in a water bath at about 40°C. Dissolve the residue in 10 ml of 1N sodium hydroxide solution, transfer quantitatively to a 100 ml volumetric flask, and make to volume with water. (final conc 40 µg 2,4-D and/or 2,4,5-T/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 284 nm for 2,4-D or ~~289~~ 296 nm for 2,4,5-T (296 nm when both are present) with 0.1N sodium hydroxide solution in each cell. Scan both the standard and sample from 350 nm to 250 nm with 0.1N sodium hydroxide solution in the reference cell.

Measure the absorbance of standard and sample solutions at 284 nm for 2,4-D (secondary maximum 290 nm) and at 289 nm for 2,4,5-T (secondary maximum 296 nm).

Calculation:

Calculate the percent 2,4-D alone using the absorbance at 284 nm or the percent 2,4,5-T alone using the absorbance at 289 nm; or, when both are present use the absorbance at 296 nm for 2,4,5-T.

$$\% = \frac{(\text{abs. sample})(\text{conc. standard in } \mu g/ml)(\% \text{ purity standard})}{(\text{abs. standard})(\text{conc. sample in } \mu g/ml)}$$

Note! Although this method is for 2,4-D and 2,4,5-T, it may be usable for other chlorophenoxy herbicides. Data and comments on the use of this method for other compounds, including linearity, accuracy, and precision are most welcome by the Methods Editorial Committee.

Determination of Chlorophenoxy Herbicide Acids and Esters by High Pressure Liquid Chromatography

For definition, structure, and technical data on chlorophenoxy herbicide free acids, see Chlorophenoxy Herbicides EPA-1. (Data and conversion factors for salts and esters of these compounds will appear in supplements to this manual or in a later revised edition.)

Principle of the Method:

Formulations of chlorophenoxy herbicides as esters or free acids are dissolved in methanol and subjected to HPLC analysis using the same column but different mobile phases. Esters are determined using a 40% methanol-60% water mobile phase and the free acids are determined using a 10% methanol-90% 0.0025M aqueous phosphoric acid mobile phase. (Alkylamine salts have not been studied enough to include in this method; however, a conversion into the free acid should allow HPLC determination. Data and comments on analysis of these compounds would be appreciated by the editorial committee.)

Reagents:

1. Chlorophenoxy herbicide acid or ester standards of known % purity
2. Methanol - ACS
3. Phosphoric acid, 0.0025M aqueous solution
4. Ethyl ether - ACS

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm. If a variable wavelength UV detector is available, other wavelengths may be useful to increase sensitivity or eliminate interference. 235 nm has been found good for chlorophenoxy herbicides.
2. Column: 1 meter x 2.1 mm ID stainless steel packed with DuPont ODS Permaphase (or equivalent column such as Perkin Elmer ODS Sil-X 11 RP)
3. High pressure liquid syringe or sample injection loop
4. Mechanical shaking apparatus
5. Usual laboratory glassware

Operating Conditions:

1. Mobile phase: esters - 40% methanol + 60% water
   free acids - 10% methanol + 90% 0.0025M aqueous phosphoric acid solution
2. Column temperature: 55°C
3. Pressure: 700-1000 psi (DuPont - constant pressure)
4. Flow rate: 0.5 to 1.5 ml/min (Perkin-Elmer - constant flow)
5. Chart speed: 5 minutes/inch or equivalent
6. Attenuation: adjust for 60-80% pen response for 5 µl injection

Conditions may have to be varied by the analyst for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.25 gram of chlorophenoxy herbicide acid or ester standard into a 125 ml glass-stoppered flask or screw-cap bottle, add 50 ml methanol by pipette, and shake to dissolve. (conc 5 mg/ml)

Preparation of Sample:

For liquid formulations, weigh a portion of sample equivalent to 0.25 gram chlorophenoxy herbicide acid or ester into a 50 ml volumetric flask; make to volume with methanol. (conc 5 mg/ml)

For solid formulations (powders or granules), weigh a portion of sample equivalent to 0.5 gram chlorophenoxy herbicide acid or ester into a 300 ml glass-stoppered flask or screw-cap bottle, add 200 ml ethyl ether, and shake on a mechanical shaker for one hour. Allow to settle, pipette 20 ml into a small glass-stoppered flask, and evaporate to a "moist" dryness. Add 10 ml methanol by pipette and shake to dissolve residue. (final conc 5 mg/ml)

Determination:

Alternately inject three 5 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent chlorophenoxy herbicide as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\%\ \text{purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Notes:

1. If a peak for a declared acid herbicide does not appear using the 10% methanol-90% 0.0025M phosphoric acid mobile solvent, either it is not present or it is in the ester form. This can be confirmed by changing the mobile phase to 40% methanol-60% water to determine ester herbicides. The reverse would be true if a declared ester herbicide did not appear using the "ester mobile phase." A switch to the "acid mobile phase" would then determine the acid herbicide.

2. Due to the mixture of the branched heptyl radical with methyl groups in the 3, 4, or 5 position, isooctyl esters give peaks of varying patterns and cannot be analyzed. The analysis will distinguish the isooctyl ester from the other ester.

Method submitted by Elmer H. Hayes, EPA, Beltsville, Md.

Determination of Butoxyethyl Esters of 2,4-D and 2,4,5-T in Liquid Formulations by Gas-Liquid Chromatography (FID-IS)

For definition, structure, and technical data on 2,4-D and 2,4,5-T acids, see Chlorophenoxy Herbicides EPA-1. (Data and conversion factors for esters will appear in supplements or in a later revision of this manual.)

Reagents:

1. 2,4-D butoxyethyl ester standard of known % purity
2. 2,4,5-T butoxyethyl ester standard of known % purity
3. Acetone, pesticide or spectro grade
4. Dibutyl phthalate, technical (or better)
5. Internal standard solution - weigh 0.2 gram dibutyl phthalate into a 100 ml volumetric flask; dissolve in and make to volume with acetone. (conc 2 mg dibutyl phthalate/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm ID glass, packed with 5% OV-210 on 80/100 mesh Chromosorb W HP
3. Precision liquid syringe: 1 or 5 µl
4. Mechanical shaker or a Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack to hold 25 mm x 200 mm screw-top culture tubes
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	175°C
Injection temperature:	225°C
Detector temperature:	225°C
Carrier gas:	Nitrogen
Carrier gas flow rate:	Adjusted for particular GC
Hydrogen flow rate:	Adjusted for particular GC
Air flow rate:	Adjusted for particular GC

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram butoxyethyl ester of 2,4-D and/or 2,4,5-T standard into a small glass-stoppered flask or screw-cap tube, add 20 ml internal standard solution by pipette, and shake to dissolve. (conc 5 mg 2,4-D and/or 2,4,5-T butoxyethyl esters and 2 mg dibutyl phthalate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram chlorophenoxy herbicide (as above) into a glass-stoppered bottle or screw-cap tube, add 20 ml internal standard solution by pipette, and shake or tumble for one hour. Allow to settle; filter or centrifuge if necessary. (conc 5 mg chlorophenoxy herbicide and 2 mg dibutyl phthalate/ml)

Determination:

Inject 0.2-0.4 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is dibutyl phthalate, 2,4-D ester, and 2,4,5-T ester.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of the dibutyl phthalate and the chlorophenoxy herbicides from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

IS = Internal standard = dibutyl phthalate

CPH = Chlorophenoxy herbicide

$$RF = \frac{(\text{wt. IS})(\%\text{ purity IS})(\text{pk. ht. or area CPH})}{(\text{wt. CPH})(\%\text{ purity CPH})(\text{pk. ht. or area IS})}$$

Determine the percent CPH for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. IS})(\%\text{ purity IS})(\text{pk. ht. or area CPH})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area IS})(RF)}$$

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Note! This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Chemistry Lab. Any comments, criticisms, suggestions, data, etc. concerning this method and its use for other chlorophenoxy herbicides will be appreciated by the editorial committee.

Determination of 2,4-D acid (1%) and Silvex acid (0.5%) in Fertilizer Formulations by Gas-Liquid Chromatography (FID-IS using on-column derivatization)

For definition, structure, and technical data on 2,4-D and silvex, see Chlorophenoxy Herbicides EPA-1.

Principle of the Method:

The standard chlorophenoxy herbicide and the extracted chlorophenoxy herbicide from the sample are made to a definite volume with the internal standard solution, dibutyl phthalate in acetone. A portion of either is injected along with a portion of the derivatizing compound N-methyl-N-trimethylsilyl-2,2,2-trifluoroacetamide. The formed derivative is detected and measured in a flame ionization detector.

Reagents:

1. 2,4-D acid standard of known % purity
2. Silvex acid standard of known % purity
3. Acetone, pesticide or spectro grade
4. Ethyl ether, pesticide or spectro grade
5. Dibutyl phthalate, technical (or better)
6. Anhydrous sodium sulfate, ACS granular
7. N-methyl-N-trimethylsilyl-2,2,2-trifluoroacetamide (Eastman 11732): referred to in this method as MSTFA
8. Internal standard solution - weigh 0.625 gram dibutyl phthalate into a 500 ml volumetric flask; dissolve in and make to volume with acetone. (conc 1.25 mg dibutyl phthalate/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 4 mm ID glass column packed with 10% OV-1 on 60/80 Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Soxhlet or Goldfisch extraction apparatus
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	Program from 210° to 245°C at 4°/minute, hold 4 minutes at final temp. of 245°C
Injection temperature:	250°C
Detector temperature:	250°C
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi, adjust for particular GC
Hydrogen pressure:	20 psi, adjust for particular GC
Air pressure:	30 psi, adjust for particular GC
Chart speed:	0.25 inches/minute

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.15 gram 2,4-D acid standard and 0.075 gram silvex acid standard into a 125 ml glass-stoppered flask or screw-cap

bottle, add 100 ml internal standard solution, and shake to dissolve. (conc 1.5 mg 2,4-D acid, 0.75 mg silvex acid, and 1.25 mg dibutyl phthalate/ml)

Preparation of Sample:

Extract 3.75 grams of sample for 1% 2,4-D and 0.5% silvex (or the equivalent for other % formulations) in a Soxhlet or Goldfisch apparatus for 4-5 hours with ethyl ether. Evaporate the ether on a steam bath aided by a gentle stream of dry air. Dissolve the residue in 25 ml internal standard solution and dry with a little anhydrous sodium sulfate. (conc 1.5 mg 2,4-D acid, 0.75 mg silvex acid, and 1.25 mg dibutyl phthalate/ml)

Determination:

Injections are made with the syringe filled as follows: 0.5 µl acetone, 0.5 µl air, 1.0 µl MSTFA, 0.5 µl air, 2 µl of either standard or sample. Inject 2 µl of standard as above and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is 2,4-D, silvex, dibutyl phthalate.

Proceed with the determination, making at least three injections each of standard and sample solutions using the above mixture for the injections.

Calculation:

Measure the peak heights or areas of 2,4-D, silvex, and dibutyl phthalate for both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

IS = internal standard = dibutyl phthalate

CPH = chlorophenoxy herbicide

$$RF = \frac{(\text{wt. IS})(\%\text{ purity IS})(\text{pk. ht. or area CPH})}{(\text{wt. CPH})(\%\text{ purity CPH})(\text{pk. ht. or area IS})}$$

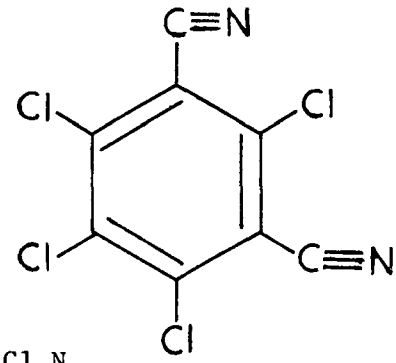
Determine the percent CPH for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. IS})(\%\text{ purity IS})(\text{pk. ht. or area CPH})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area IS})(\text{RF})}$$ U-1

Method submitted by Division of Regulatory Services, Kentucky Agricultural Experiment Station, University of Kentucky, Lexington, Kentucky 40506. Data and information on this method and other chlorophenoxy herbicides will be appreciated by the editorial committee.

Determination of Chlorothalonil by Infrared Spectroscopy

Chlorothalonil is the common name for tetrachloroisophthalonitrile, a registered fungicide having the chemical structure:



Molecular formula: $C_8Cl_4N_2$

Molecular weight: 266

Melting point: 250 to 251°C

Physical state, color, and odor: white crystalline solid, odorless in pure form; the technical product (about 98% pure) has a slightly pungent odor.

Solubility: Insoluble in water (0.6 ppm); slightly soluble in acetone (2% w/w), cyclohexanone (3% w/w), methyl ethyl ketone (2% w/w), xylene (8% w/w), and kerosene less than 1%

Stability: stable to ultraviolet radiation and to moderately alkaline and acid aqueous media; thermally stable under normal storage conditions; non-corrosive

Other names: Daconil 2787 (Diamond Shamrock Chem. Co.); Bravo; Termil; 2,4,5,6-tetrachloro-1,3-dicyanobenzene; 2,4,5,6-tetrachloro-3-cyanobenzonitrile

Reagents:

1. Chlorothalonil standard of known % purity
2. Methylene chloride, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps. These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.1 gram chlorothalonil standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml methylene chloride by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg/ml)

Preparation of Sample:

For emulsifiable concentrates, weigh a portion of sample equivalent to 0.5 gram chlorothalonil into a glass-stoppered flask or screw-cap bottle. Add 50 ml methylene chloride by

pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 10 mg chlorothalonil/ml) For low percent formulations requiring large samples, use more solvent and evaporate an aliquot to a smaller volume to give a concentration close to 10 mg chlorothalonil/ml.

For flowable formulations, weigh a portion of sample equivalent to 0.5 gram chlorothalonil into a glass-stoppered flask or screw-cap bottle. Add 50 ml methylene chloride by pipette and sufficient anhydrous sodium sulfate to dry and clarify the methylene chloride solution. (final conc 10 mg chlorothalonil/ml)

Determination:

With methylene chloride in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1050 cm^{-1} to 900 cm^{-1} (9.5 μ to 11.1 μ).

Determine the absorbance of standard and sample using the peak near 980 cm^{-1} (10.2 μ) and a baseline from 1000 cm^{-1} to 940 cm^{-1} (10 μ to 10.64 μ).

Calculation:

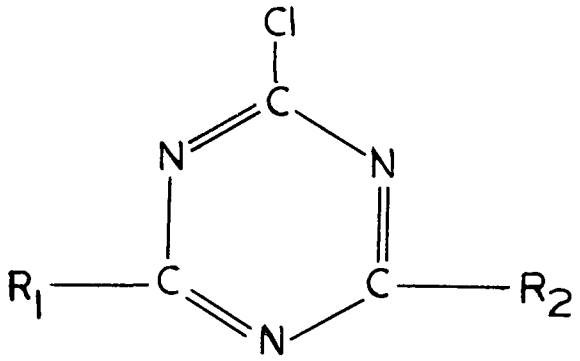
From the above absorbances and using the standard and sample solution concentrations, calculate the percent chlorothalonil as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

This method is based on an IR E.C. method submitted by the Commonwealth of Virginia, Division of Laboratory Services. It should be considered a tentative method. Any criticism, modification, or verification will be appreciated.

Determination of Chloro-Triazine Herbicides by Chlorine Potentiometric Titration

Several chlorine-containing triazine derivative compounds are registered as herbicides. They are of the general chemical structure:



The R_1 and R_2 groups are ethylamino, diethylamino, or isopropylamino. As a group, these compounds generally are: white, crystalline solids; practically insoluble in water, soluble in organic solvents; stable in neutral or slightly acidic or basic media, but hydrolyzed by alkali or mineral acid at higher temperatures; stable to light and heat; and compatible with most other pesticides.

Principle of the Method:

A potentiometric titration with silver nitrate is used to determine the total ionic chloride. This includes the chloride liberated from the triazine by treatment with morpholine and any inorganic chloride present in the sample. The inorganic chlorine is subtracted from the total chlorine and the resulting organic chlorine is calculated as the chloro-triazine herbicide using the appropriate factor for the particular herbicide claimed.

Reagents:

1. Morpholine
2. Sulfuric acid, 1+4 solution
3. Methyl red indicator
4. Silver nitrate, 0.1N standard solution
5. Ethanol, 95%
6. Sodium or potassium chloride, 0.1N standard solution (exact normality need not be known if the same volume is titrated as is added to sample)

Equipment:

1. Potentiometric titrimeter with a silver electrode and a silver-silver chloride electrode
2. Steam bath
3. Usual laboratory glassware

Procedure:

Determination of Total Chlorine:

Weigh a portion of sample equivalent to 0.4-0.5 gram of the chloro-triazine derivative into a 125 ml Erlenmeyer flask. Add 20 ml morpholine and heat on the steam bath at full heat for at least 30 minutes with frequent shaking. Transfer to a 250 ml beaker with water, acidify with 1+4 sulfuric acid solution using methyl red as indicator, and cool to room temperature. Titrate potentiometrically with 0.1N silver nitrate standard solution.

Calculate the total chloride as follows:

$$\% \text{ Total chloride} = \frac{(\text{ml } AgNO_3)(\text{N } AgNO_3)(.03545)(100)}{(\text{grams sample})}$$

Determination of Inorganic Chloride:

Weigh a portion of sample equivalent to 0.4-0.5 gram of the chloro-triazine derivative into a 250 ml beaker. Add 20 ml ethanol, 150 ml water, and exactly 10 ml of the standard chloride solution. Acidify with 1+4 sulfuric acid solution using methyl red as indicator. Titrate potentiometrically with the 0.1N silver nitrate solution.

Titrate exactly 10 ml of the standard chloride solution as above except for the sample. Subtract the volume of silver nitrate used for the standard chloride solution alone from the volume of silver nitrate used for the sample plus the added standard chloride solution.

Calculate the inorganic chloride as follows:

$$\% \text{ Inorganic chloride} = \frac{(\text{net ml } AgNO_3)(N\ AgNO_3)(.03545)(100)}{(\text{grams sample})}$$

Determination of Organic Chloride:

The percent organic chloride is found by subtracting the percent inorganic chloride from the percent total chloride.

% Organic chloride = % Total chloride - % Inorganic chloride

Calculation of the Chloro-Triazine Herbicide:

The percent chloro-triazine derivative herbicide in the sample is determined by multiplying the % inorganic chloride by the appropriate factor for converting chloride to compound.

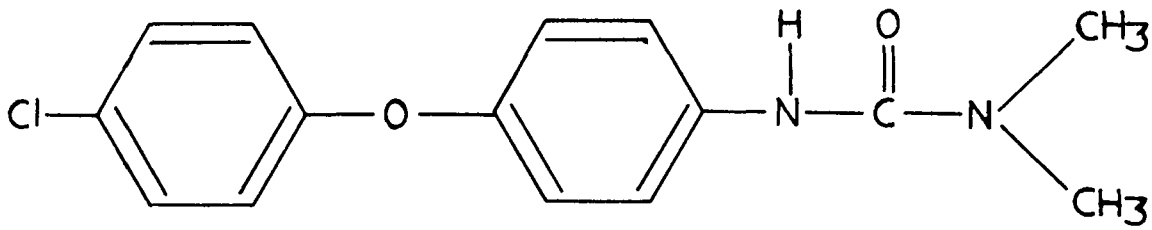
% Triazine herbicide = % Organic chloride X factor (Cl to cmpd.)

The factors for several chloro-triazine herbicides are as follows:

Anilazine	6.784
Atrazine	6.085
Cyanazine (2 Cl)	3.886
Propazine	6.480
Simazine	5.690

Determination of Chloroxuron in Dust by Infrared Spectroscopy

Chloroxuron is the accepted common name for 3-(p-(p-chlorophenoxy) phenyl)-1,1-dimethylurea, a registered herbicide having the chemical structure:



Molecular formula: $C_{15}H_{15}ClN_2O_2$

Molecular weight: 290.7

Melting point: 149 to 150°C

Physical state, color, and odor: crystalline, white, odorless solid

Solubility: about 3 ppm in water; slightly soluble in ethanol or benzene; very soluble in acetone or chloroform

Stability: stable; non-corrosive; subject to decomposition by UV

Other names: Tenoran (Ciba-Geigy), Norex, Nor-Am, C-1983, Chloroxifenidim

Reagents:

1. Chloroxuron standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm KBr or NaCl cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.12 gram chloroxuron standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 12 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 1.2 grams chloroxuron into a glass-stoppered flask or screw-cap bottle. Add 100 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 12 mg chloroxuron/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR being used, scan both the standard and sample from 1430 cm^{-1} to 1250 cm^{-1} (7.0 μ to 8.0 μ).

Determine the absorbance of standard and sample using the peak at 1351 cm^{-1} (7.40 μ) and basepoint at 1316 cm^{-1} (7.60 μ).

Calculation:

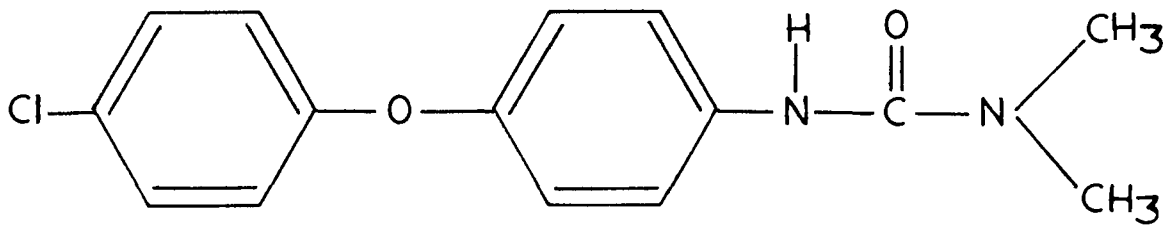
From the above absorbances and using the standard and sample solution concentrations, calculate the percent chloroxuron as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Method submitted by Eva Santos, EPA Product Analysis Laboratory, San Francisco, California.

Determination of Chloroxuron by Gas-Liquid Chromatography (TCD - Internal Standard)

Chloroxuron is the accepted common name for 3-(p-(p-chlorophenoxy) phenyl)-1,1-dimethylurea, a registered herbicide having the chemical structure:



Molecular formula: $C_{15}H_{15}ClN_2O_2$

Molecular weight: 290.7

Melting point: 149 to 150°C

Physical state, color, and odor: crystalline, white, odorless solid

Solubility: about 3 ppm in water; slightly soluble in ethanol or benzene; very soluble in acetone or chloroform

Stability: stable; non-corrosive; subject to decomposition by UV

Other names: Tenoran (Ciba-Geigy), Norex, Nor-Am, C-1983, Chloroxifenidim

Reagents:

1. Chloroxuron standard of known % purity
2. Dieldrin standard of known HEOD content
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.5 gram dieldrin into a 50 ml volumetric flask; dissolve in and make to volume with acetone. (conc 10 mg dieldrin/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 4' x 1/8" stainless steel packed with 10% SE-30 on Chromosorb W AW DMCS (or equivalent column)
3. Precision liquid syringe: 25 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	170°C
Injection temperature:	200°C
Detector temperature:	200°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas pressure:	40 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.08 gram chloroxuron standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 4 mg chloroxuron and 10 mg dieldrin/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.08 gram chloroxuron into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the chloroxuron. For coarse or granular materials, shake mechanically for 10-15 minutes or shake by hand intermittently for 25-30 minutes. (final conc 4 mg chloroxuron and 10 mg dieldrin/ml)

Determination:

Inject 10-20 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within approx. 15 minutes and peak heights of from 1/2 to 3/4 full scale. The elution time of chloroxuron is approx. 3.5 minutes and that of dieldrin approx. 9 minutes.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of chloroxuron and dieldrin from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. dieldrin})(\%\text{ purity dieldrin})(\text{pk. ht. or area chloroxuron})}{(\text{wt. chloroxuron})(\%\text{ purity chloroxuron})(\text{pk. ht. or area dieldrin})}$$

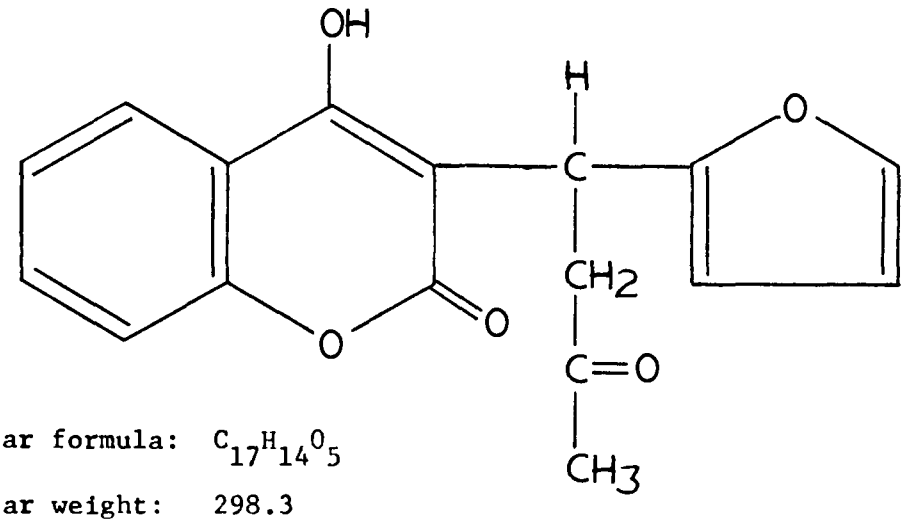
Determine the percent chloroxuron for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. dieldrin})(\%\text{ purity dieldrin})(\text{pk. ht. or area chloroxuron})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area dieldrin})(RF)}$$

This method is based on EPA, Office of Pesticide Programs, Technical Services Division, Experimental Method No. 15A. The original source is unknown and some changes have been made in this write-up; therefore, any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated.

Determination of Coumafuryl in Baits by Ultraviolet Spectroscopy

Coumafuryl is a common name for 3-(alpha-acetonylfurfuryl)-4-hydroxycoumarin, a registered rodenticide having the chemical structure:



Molecular formula: $C_{17}H_{14}O_5$

Molecular weight: 298.3

Melting point: pure 122-124°C; technical 119-120°C

Physical state and color: white to tan crystalline solid

Solubility: slightly soluble in cold water; soluble in benzene, chloroform, methanol, ethanol, isopropanol, ethylene dichloride, toluene; soluble in most inorganic and organic bases to form salts

Stability: stable under normal conditions

Other names: Fumarin (Amchem), fumarin (Great Britain, New Zealand), tomarin (Turkey)

This method is for determining coumafuryl in most bait materials and is especially useful for glaze-like coated baits and pellets containing about 0.025% coumafuryl.

Reagents:

1. Coumafuryl standard of known % purity
2. Sodium pyrophosphate, 1% solution - dissolve 5 grams $Na_4P_2O_7.10\ H_2O$ in water and make to 500 ml.
3. Ethyl ether-petroleum ether (20-80) - extract 200 ml petroleum ether three times with 20 ml portions of pyrophosphate solution and add 50 ml ethyl ether.
4. Hydrochloric acid, 2.5N solution

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Centrifuge with 100 ml glass-stoppered centrifuge tubes
4. Aspirator or suction device with fine tip glass tube
5. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram coumafuryl standard into a 100 ml volumetric flask; dissolve and make to volume with 1% sodium pyrophosphate solution. Mix thoroughly and pipette 5 ml into a 50 ml volumetric flask. Make to volume with pyrophosphate solution, mix well, pipette 5 ml into a second 50 ml volumetric flask, and make to volume with pyrophosphate solution. (final conc 10 µg/ml)

Preparation of Sample:

Weigh an amount of finely ground sample equivalent to 0.0005 gram coumafuryl (2 grams of 0.025% product) into a 125 ml glass-stoppered flask, add by pipette 50 ml 1% sodium pyrophosphate

solution, and shake on a mechanical shaker for one hour. Transfer 30-40 ml to a glass-stoppered centrifuge tube and centrifuge for at least 5 minutes. Pipette 25 ml of this solution into a clean dry 100 ml centrifuge tube. Add 5 ml 2.5N hydrochloric acid and by pipette 50 ml of the mixed ether solution. Shake for five minutes. If an emulsion forms, centrifuge to break the emulsion. Pipette 20 ml of the ether layer to a clean centrifuge tube and add 10 ml pyrophosphate solution by pipette. Shake for 2 minutes and remove the ether layer using an aspirator with a glass tube drawn to a fine tip. If the aqueous layer is not clear, centrifuge for a few minutes with the stopper off to remove any residual ether. (final conc 10 µg coumafuryl/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen for 0 and 100% at 305 nm with 1% pyrophosphate solution in each cell. Scan both standard and sample from 350 nm to 250 nm with the pyrophosphate solution in the reference cell.

Calculation:

Measure the absorbance of standard and sample at 305 nm and calculate the percent coumafuryl as follows:

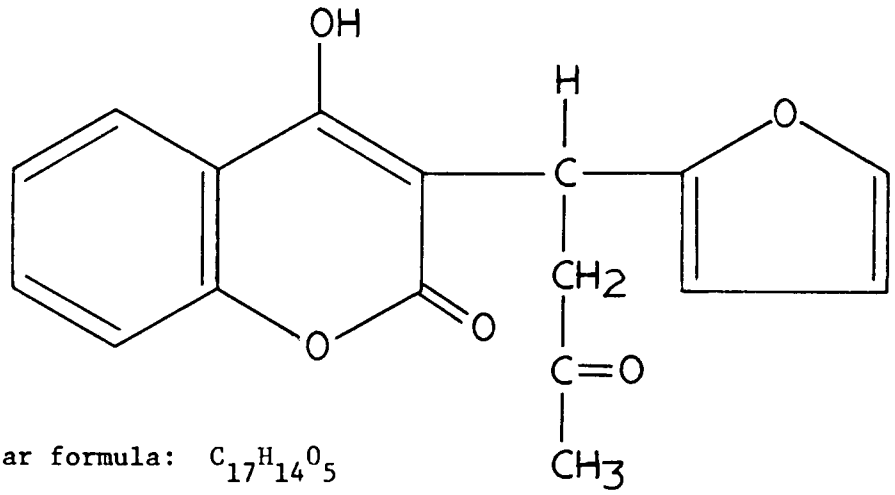
$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

or using dilution factors, as follows:

$$\% = \frac{(\text{abs. sample})(\text{wt. std})(\text{purity std})(1/100)(5/50)(5/50)(100)}{(\text{abs. std})(\text{wt. sample})(1/50)(5/50)(10/10)}$$

Determination of Coumafuryl in Concentrates by Ultraviolet Spectroscopy

Coumafuryl is a common name for 3-(alpha-acetonylfurfuryl)-4-hydroxycoumarin, a registered rodenticide having the chemical structure:



Molecular formula: $C_{17}H_{14}O_5$

Molecular weight: 298.3

Melting point: pure 122-124°C; technical 119-120°C

Physical state and color: white to tan crystalline solid

Solubility: slightly soluble in cold water; soluble in benzene, chloroform, methanol, ethanol, isopropanol, ethylene dichloride, toluene; soluble in most inorganic and organic bases to form salts

Stability: stable under normal conditions

Other names: Fumarin (Amchem), fumarin (Great Britain, New Zealand), tomarin (Turkey)

This method is for determining coumafuryl in powders containing about 0.5% coumafuryl.

Reagents:

1. Coumafuryl standard of known % purity
2. Sodium pyrophosphate, 1% solution - dissolve 5 grams $Na_4P_2O_7.10\ H_2O$ in water and make to 500 ml.
3. Ethyl ether, ACS
4. Petroleum ether - extract 200 ml petroleum ether three times with 20 ml of 1% sodium pyrophosphate solution.

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Centrifuge with 16 x 150 mm glass-stoppered tubes
4. Aspirator or suction device with fine tip glass tube
5. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram coumafuryl standard into a 100 ml volumetric flask; dissolve and make to volume with 1% sodium pyrophosphate solution. Mix thoroughly and pipette 5 ml into a 50 ml volumetric flask. Make to volume with pyrophosphate solution, mix well, pipette 5 ml into a second 50 ml volumetric flask, and make to volume with pyrophosphate solution. (final conc 10 µg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.0025 gram coumafuryl (0.5 gram of 0.5% product) into a 125 ml glass-stoppered flask, add 50 ml ethyl ether by pipette, and shake on a mechanical shaker

for at least 30 minutes. If necessary, centrifuge a portion to clarify. Pipette 2 ml of the clear ether solution into a 16 x 150 mm glass-stoppered centrifuge tube. Add 10 ml of 1% sodium pyrophosphate solution by pipette, shake vigorously for two minutes, and centrifuge at high speed until the aqueous layer is clear. Draw off the ether layer and any remaining emulsion using an aspirator with a glass tube drawn into a fine tip. Add 2 ml ethyl ether, shake, centrifuge, and draw off the ether. Repeat twice more with 2 ml portions of petroleum ether. If the aqueous layer is not clear, centrifuge for a few minutes with the stopper off to remove any residual ether. (final conc 10 µg coumafuryl/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen for 0 and 100% at 305 nm with 1% pyrophosphate solution in each cell. Scan both standard and sample from 350 nm to 250 nm with the pyrophosphate solution in the reference cell.

Calculation:

Measure the absorbance of standard and sample at 305 nm and calculate the percent coumafuryl as follows:

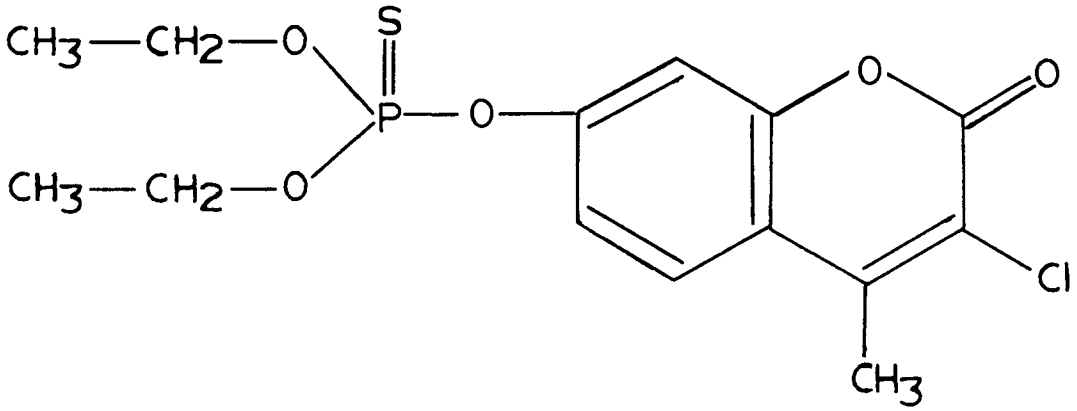
$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

or using dilution factors, as follows:

$$\% = \frac{(\text{abs. sample})(\text{wt. std})(\text{purity std})(1/100)(5/50)(5/50)(100)}{(\text{abs. std})(\text{wt. sample})(1/50)(2/10)}$$

Determination of Coumaphos by Infrared Spectroscopy

Coumaphos is the common name for O,O-diethyl O-(3-chloro-4-methyl-2-oxo-2H-1-benzopyran-7-yl) phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_{14}H_{16}ClO_5PS$

Molecular weight: 362.8

Melting point: pure - 95°C; technical - 91 to 92°C

Physical state and color: pure - colorless crystalline solid; technical - tan or brownish crystalline solid

Solubility: insoluble in water (1.5 ppm at RT); soluble in aromatic solvents, less so in alcohols and ketones

Stability: hydrolyzes slowly under alkaline conditions; incompatible with piperonyl butoxide

Other names: Co-Ral (Chemagro), Resitox (Bayer), Asuntol, Baymix, Meldane, Muscatox, Bay 21/199

Reagents:

1. Coumaphos standard of known % purity
2. Acetone, pesticide or spectro grade
3. Carbon disulfide, pesticide or spectro grade
4. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm KBr or NaCl cells
2. Mechanical shaker
3. Soxhlet extraction apparatus
4. Centrifuge or filtration apparatus
5. Rotary evaporator
6. Cotton or glass wool
7. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.10 gram coumaphos standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml carbon disulfide by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg/ml)

Preparation of Sample:

For high percent formulations (more than 10%), weigh a portion of sample equivalent to 0.5 gram coumaphos into a glass-stoppered flask or screw-cap bottle. Add 50 ml carbon disulfide by pipette

and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 10 mg coumaphos/ml)

For low percent (less than 10%) formulations, weigh a portion of sample equivalent to 0.5 gram coumaphos into a Soxhlet extraction thimble, plug with cotton or glass wool, and extract with acetone for three hours. Evaporate the acetone completely on a rotary evaporator. Dissolve the residue, transfer to a 50 ml volumetric flask, and make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate to clarify and dry the solution. (final conc 10 mg coumaphos/ml)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1430 cm^{-1} to 1110 cm^{-1} (7 μ-9 μ).

Determine the absorbance of standard and sample using the peak at 1277 cm^{-1} (7.83 μ) and baseline from 1307 cm^{-1} to 1227 cm^{-1} (7.65 μ to 8.15 μ).

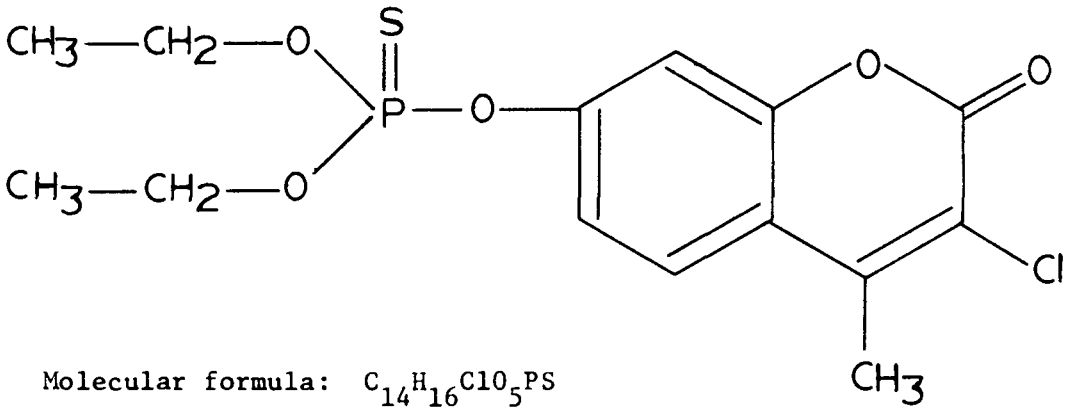
Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent coumaphos as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Determination of Coumaphos by High Pressure Liquid Chromatography

Coumaphos is the common name for O,O-diethyl O-(3-chloro-4-methyl-2-oxo-2H-1-benzopyran-7-yl) phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_{14}H_{16}ClO_5PS$

Molecular weight: 362.8

Melting point: pure - 95°C; technical - 91 to 92°C

Physical state and color: Pure - colorless crystalline solid; technical - tan or brownish crystalline solid

Solubility: insoluble in water (1.5 ppm at RT); soluble in aromatic solvents, less so in alcohols and ketones

Stability: hydrolyzes slowly under alkaline conditions; incompatible with piperonyl butoxide

Other names: Co-Ral (Chemagro), Resitox (Bayer), Asuntol, Baymix, Meldane, Muscatox, Bay 21/199

Reagents:

1. Coumaphos standard of known % purity
2. Methanol, ACS

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm. If a variable wavelength UV detector is available, other wavelengths may be useful to increase sensitivity or eliminate interference.
2. Suitable column such as:
   a. DuPont ODS Permaphase, 1 meter x 2.1 mm ID
   b. Perkin Elmer ODS Sil-X 11 RP, 1/2 meter x 2.6 mm ID
3. High pressure liquid syringe or sample injection loop
4. Usual laboratory glassware

Operating Conditions:

Mobile phase:	40% methanol + 60% water
Column temperature:	50-55°C
Chart speed:	5 min/inch or equivalent
Flow rate:	0.5 to 1.5 ml/min (Perkin-Elmer 1/2 meter column)
Pressure:	700 psi (DuPont 1 meter column)
Attenuation:	Adjusted

Conditions may have to be varied by the analyst for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram coumaphos standard into a small glass-stoppered flask or vial, add 10 ml methanol by pipette, dissolve and mix well. (final conc 5 mg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.5 gram coumaphos into a glass-stoppered flask or vial, add 100 ml methanol by pipette and shake thoroughly to dissolve the coumaphos. Allow any solid matter to settle; filter or centrifuge if necessary. (final conc 5 mg coumaphos/ml)

Determination:

Alternately inject three 10 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

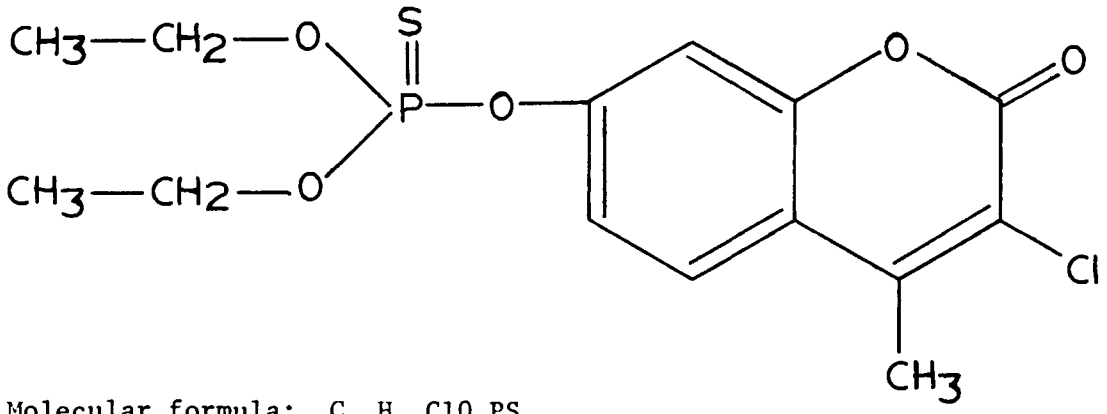
From the average peak height or peak area calculate the percent coumaphos as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Elmer H. Hayes, EPA, Beltsville, Md.

Determination of Coumaphos by Gas-Liquid Chromatography (FID - Internal Standard)

Coumaphos is the common name for O,O-diethyl O-(3-chloro-4-methyl-2-oxo-2H-1-benzopyran-7-yl) phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_{14}H_{16}ClO_5PS$

Molecular weight: 362.8

Melting point: pure - 95°C; technical - 91 to 92°C

Physical state and color: pure - colorless crystalline solid; technical - tan or brownish crystalline solid

Solubility: insoluble in water (1.5 ppm at RT); soluble in aromatic solvents, less so in alcohols and ketones

Stability: hydrolyzes slowly under alkaline conditions, incompatible with piperonyl butoxide

Other names: Co-Ral (Chemagro), Resitox (Bayer), Asuntol, Baymix, Meldane, Muscatox, Bay 21/199

Reagents:

1. Coumaphos standard of known % purity
2. Tetradifon standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.09 gram tetradifon into a 200 ml volumetric flask, dissolve in, and make to volume with acetone. (conc 0.45 mg tetradifon/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 5' x 1/8" stainless steel packed with 3% SE-30 on 100/120 mesh Varaport 30 (or equivalent column such as: 6' x 2 mm ID glass column packed with 3% OV-1 on 60/80 mesh Gas Chrom Q)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	210-220°C
Injection temperature:	250°C
Detector temperature:	250°C
Carrier gas:	Nitrogen
Carrier gas flow rate:	60 ml/min
Hydrogen flow rate:	30 ml/min
Air flow rate:	300 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram coumaphos standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 50 ml of the internal standard solution and shake to dissolve. (final conc 1 mg coumaphos and 0.45 mg tetradifon/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.05 gram coumaphos into a small glass-stoppered flask or screw-cap bottle. Add by pipette 50 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the coumaphos. For coarse or granular materials, shake mechanically for 10-15 minutes or shake by hand intermittently for 25-30 minutes. (final conc 1 mg coumaphos and 0.45 mg tetradifon/ml)

Determination:

Inject 1-3 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and to give peak heights of 1/2 to 3/4 full scale. The elution order is tetradifon, then coumaphos.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of coumaphos and tetradifon from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. tetradifon})(\%\text{ purity tetradifon})(\text{pk. ht. or area coumaphos})}{(\text{wt. coumaphos})(\%\text{ purity coumaphos})(\text{pk. ht. or area tetradifon})}$$

Determine the percent coumaphos for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. tetradifon})(\%\text{ purity tetradifon})(\text{pk. ht. or area coumaphos})\cancel{(100)}}{(\text{wt. sample})(\text{pk. ht. or area tetradifon})(RF)} \quad (4-1)$$

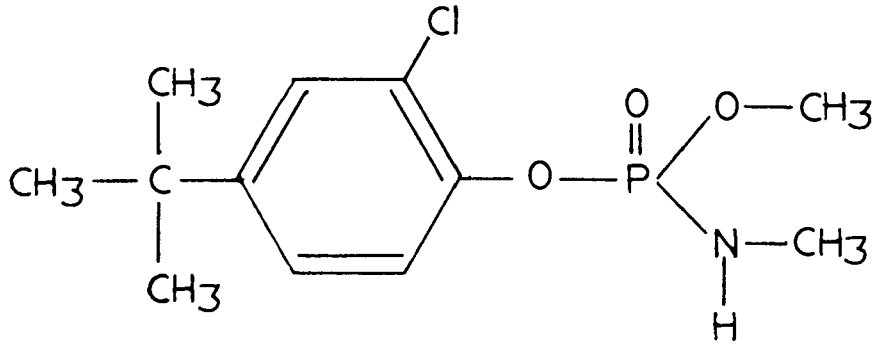
Method submitted by Division of Regulatory Services, Kentucky Agricultural Experiment Station, University of Kentucky, Lexington, Kentucky 40506.

November 1975

Crufomate EPA-1
(Tentative)

Determination of Crufomate by Infrared Spectroscopy

Crufomate is the accepted common name for 4-tert-butyl-2-chlorophenyl methyl methylphosphoramidate, a registered insecticide and helminthicide having the chemical structure:



Molecular formula: $C_{12}H_{19}ClNO_3P$

Molecular weight: 292.1

Melting point: 60°C; technical product b.p. 117 to 118°C at 0.01 mm Hg

Physical state and color: white crystalline solid; technical product is a yellow oil

Solubility: practically insoluble in water and light petroleum but is readily soluble in acetone, acetonitrile, benzene, carbon tetrachloride

Stability: stable at pH 7 or below; incompatible with alkaline pesticides

Other names: Ruelene, Dowco 132 (Dow Chemical Co.); O-methyl O-2-chloro-4-tert-butylphenol N-methylamidophosphate

Reagents:

1. Crufomate standard of known % purity
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording, with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker
3. Rotary evaporator with a 60°C water bath
4. Filtration apparatus or centrifuge
5. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram crufomate standard into a small flask or vial, add by pipette 10 ml carbon disulfide, and shake to dissolve. Add a small amount of granular anhydrous sodium sulfate to insure dryness. (conc 10 mg crufomate/ml)

Preparation of Sample:

For dust, granules, and wettable powder, weigh a portion of sample equivalent to 1 gram crufomate into a 250 ml glass-stoppered Erlenmeyer flask, add by pipette 100 ml carbon disulfide, stopper, and shake on a mechanical shaker for 1 hour. Allow to settle; filter or centrifuge if necessary. Add a small amount of granular anhydrous sodium sulfate to insure dryness. (conc 10 mg crufomate/ml)

For liquid formulations and emulsifiable concentrates, weigh a portion of sample equivalent to 1 gram crufomate into a 100 ml volumetric flask, make to volume with carbon disulfide, and mix thoroughly. (Interference from solvents in the sample can sometimes be removed by evaporation on a rotary evaporator under vacuum at about 60°C before making to volume.) Add a small amount of granular anhydrous sodium sulfate to insure dryness and clarify the solution. (conc 10 mg crufomate/ml)

An alternative extraction procedure for liquid formulations and E.C.'s is to shake a 1 gram sample with 100 ml carbon disulfide and 25-50 ml water in a sealed bottle or flask for 2 hours on a shaker. Allow to stand for 15 minutes or longer to permit the carbon disulfide and water layers to separate. With a syringe, draw off 20-25 ml of carbon disulfide from the bottom of the bottle and transfer to small vial. Add anhydrous sodium sulfate to insure dryness and clarify the solution. (conc 10 mg crufomate/ml)

IR Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1430 cm^{-1} to 900 cm^{-1} (7.0 μ to 11.0 μ).

Determine the absorbance of standard and sample using the peak at 1042 cm^{-1} (9.60 μ) and a baseline from 1333 cm^{-1} to 1000 cm^{-1} (7.50 μ to 10 μ).

Calculation:

From the above absorbances, calculate the percent crufomate as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

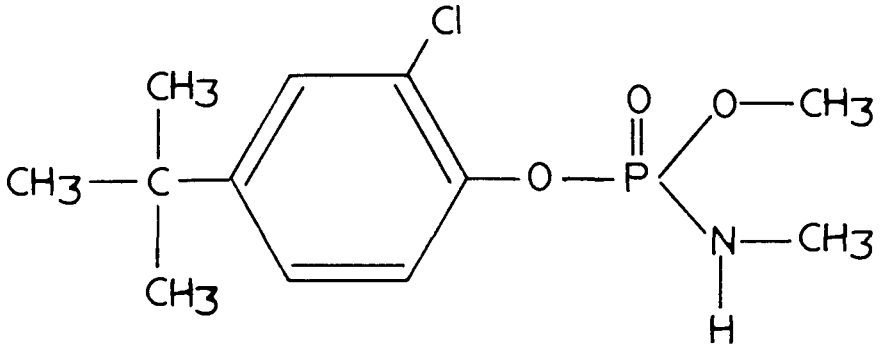
This method is adapted from Dow Chemical Company method no. 72733, September 20, 1965.

November 1975

Crufomate EPA-2
(Tentative)

Determination of Crufomate by Gas-Liquid Chromatography (TCD - Internal Standard)

Crufomate is the accepted common name for 4-tert-butyl-2-chlorophenyl methyl methylphosphoramidate, a registered insecticide and helminthicide having the chemical structure:



Molecular formula: $C_{12}H_{19}ClNO_3P$

Molecular weight: 292.1

Melting point: 60°C; technical product b.p. 117 to 118°C at 0.01 mm Hg

Physical state and color: white crystalline solid; technical product is a yellow oil

Solubility: practically insoluble in water and light petroleum but is readily soluble in acetone, acetonitrile, benzene, carbon tetrachloride

Stability: stable at pH 7 or below; incompatible with alkaline pesticides

Other names: Ruelene, Dowco 132 (Dow Chemical Co.); O-methyl O-2-chloro-4-tert-butylphenol N-methylamidophosphate

Reagents:

1. Crufomate standard of known % purity
2. Dieldrin standard of known HEOD content
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.5 gram HEOD into a 25 ml volumetric flask; dissolve in and make to volume with acetone. (conc 20 mg HEOD/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 6' x 1/8" stainless steel, packed with 10% SE-30 on Chromosorb W AW DMCS (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	170°C
Injection temperature:	200°C
Detector temperature:	200°C
Filament current:	225°C
Carrier gas:	Helium
Carrier gas pressure:	40 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram crufomate standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 10 mg crufomate and 20 mg HEOD/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram crufomate into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the crufomate. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 10 mg crufomate and 20 mg HEOD/ml)

Determination:

Inject 5 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is crufomate, then HEOD.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of crufomate and HEOD from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. HEOD})(\%\text{ purity HEOD})(\text{pk. ht. or area crufomate})}{(\text{wt. crufomate})(\%\text{ purity crufomate})(\text{pk. ht. or area HEOD})}$$

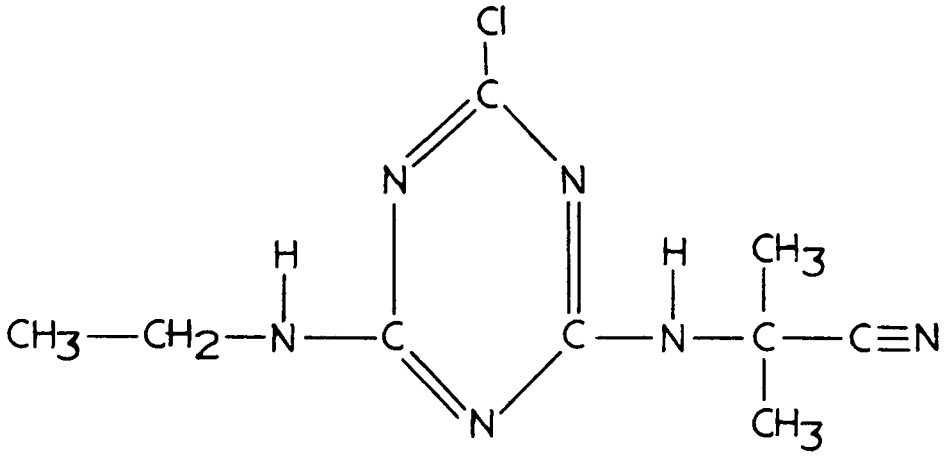
Determine the percent crufomate for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. HEOD})(\%\text{ purity HEOD})(\text{pk. ht. or area crufomate})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area HEOD})(RF)}$$ (4-1)

Method submitted by David Persch and George Radan, EPA Region II, New York, N. Y.

Determination of Cyanazine by Infrared Spectroscopy

Cyanazine is the common name for 2-(4-chloro-6-ethylamino-s-triazin-2-ylamino)-2-methylpropionitrile, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{13}ClN_6$

Molecular weight: 240.7

Melting point: 166.5 to 167°C

Physical state and color: white crystalline solid

Solubility: at 25°C its solubility is 171 ppm in water, 19.5% in acetone, 1.5% in benzene, 21% in chloroform, 4.5% in ethanol, 1.5% in hexane, 21% in methylcyclohexanone

Stability: stable to heat and light, and to hydrolysis in neutral or slightly acidic or basic media

Other names: Bladex (Shell), Fortrol, SD 15418, WL 19805

Reagents:

1. Cyanazine standard of known % purity
2. Methylene chloride, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps. These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.25 gram cyanazine standard into a small glass-stoppered flask or screw-cap tube, add 10 ml methylene chloride by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 25 mg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 1.25 gram cyanazine into a glass-stoppered flask or screw-cap bottle. Add 50 ml methylene chloride by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precautions to prevent evaporation. (final conc 25 mg cyanazine/ml)

Determination:

With methylene chloride in the reference cell, and using the optimum quantitative analytical settings, scan both the standard and sample from 1090 cm^{-1} to 930 cm^{-1} (9.1 μ to 10.8 μ).

Determine the absorbance of standard and sample using the peak at 1060 cm^{-1} (9.43 μ) and basepoint 955 cm^{-1} (10.47 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent cyanazine as follows:

$$\% = \frac{\text{(abs. sample)(conc. std in mg/ml)(\% purity std)}}{\text{(abs. std)(conc. sample in mg/ml)}}$$

(A concentration of 1 mg cyanazine/ml methylene chloride gives an absorbance of approx. 0.016 in a .5 mm cell.)

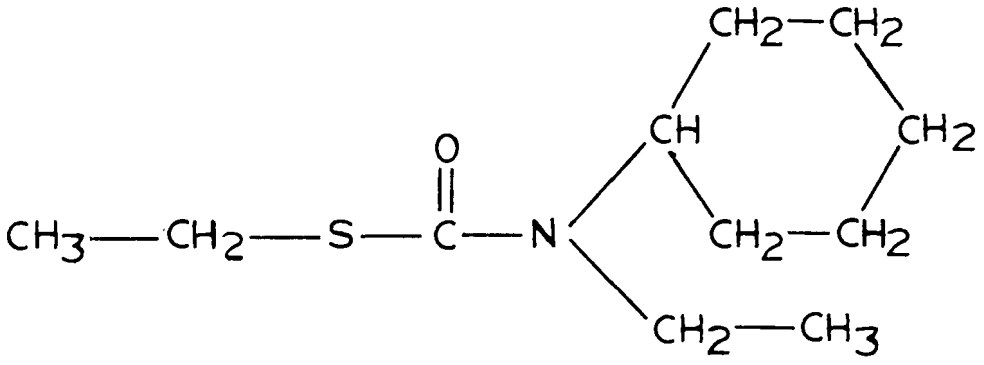
Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

September 1975

Cycloate EPA-1
(Tentative)

Determination of Cycloate by Gas-Liquid Chromatography (TCD)

Cycloate is the common name for S-ethyl cyclohexylethylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{11}H_{21}NOS$

Molecular weight: 215.4

Boiling point: 145°C at 10 mm Hg

Physical state, color, and odor: colorless liquid with an aromatic odor

Solubility: about 100 ppm in water at RT; miscible with most organic solvents

Stability: stable; non-corrosive

Other names: Ro-Neet (Stauffer Chem. Co.), Eurex, R-2063

Reagents:

1. Cycloate standard of known % purity
2. Chloroform, pesticide or spectro grade

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 5' x 1/4" glass column packed with 20% SE-30 on 60/80 Chromosorb W, AW, DMCS (or equivalent column)
3. Precision liquid syringe: 50 µl
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	210°C
Injection temperature:	240°C
Detector temperature:	270°C
Carrier gas:	Helium
Flow rate:	100 ml/min

Operating conditions for filament current, column temperature, or gas flow should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.20 gram of cycloate standard into a 10 ml volumetric flask; dissolve and make to volume with chloroform. (final conc 20 mg/ml)

Preparation of Sample:

For technical material and liquid formulations, weigh a portion of sample equivalent to 0.20 gram cycloate into a 10 ml volumetric flask, make to volume with chloroform, and mix thoroughly. (final conc 20 mg cycloate/ml)

For dry formulations, weigh a portion of sample equivalent to 1.0 gram cycloate into a 125 ml screw-cap flask, add by pipette 50 ml chloroform, and shake for one hour. Allow to settle; filter or centrifuge if necessary, taking precautions to prevent evaporation. (final conc 20 mg cycloate/ml)

Determination:

Using a precision liquid syringe, alternately inject three 20-40 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent cycloate as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

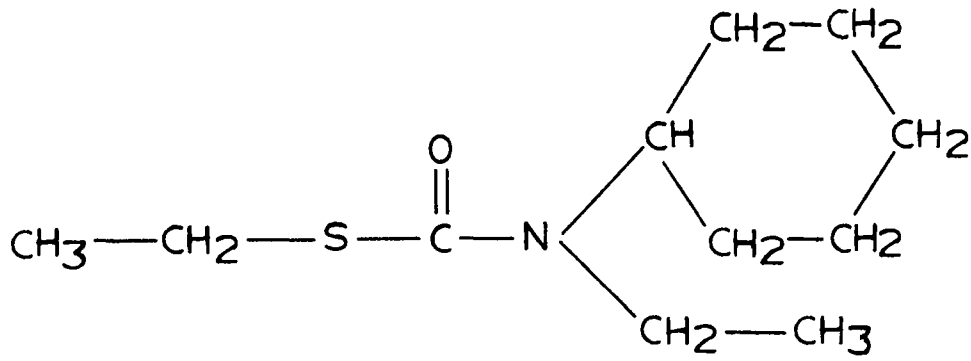
Method submitted by Evangelina Santos, EPA Region IX, San Francisco, California.

September 1975

Cycloate EPA-2
(Tentative)

Determination of Cycloate by Gas-Liquid Chromatography (FID)

Cycloate is the common name for S-ethyl cyclohexylethylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{11}H_{21}NOS$

Molecular weight: 215.4

Boiling point: 145°C at 10 mm Hg

Physical state, color, and odor: colorless liquid with an aromatic odor

Solubility: about 100 ppm in water at RT; miscible with most organic solvents

Stability: stable; non-corrosive

Other names: Ro-Neet (Stauffer Chem. Co.), Eurex, R-2063

Reagents:

1. Cycloate standard of known % purity
2. Acetone, pesticide or spectro grade

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 1/4" glass column packed with 3% OV-1 on 80/100 Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	175°C
Injection temperature:	225°C
Detector temperature:	220°C
Carrier gas:	Helium or Nitrogen
Flow rate:	50 ml/min

Operating conditions for column temperature, carrier gas flow, or hydrogen/air flow rates should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.10 gram cycloate standard into a 50 ml volumetric flask; dissolve and make to volume with acetone. (final conc 2 mg/ml)

Preparation of Sample:

For technical material and liquid formulations, weigh a portion of sample equivalent to 0.10 gram cycloate into a 50 ml volumetric flask, make to volume with acetone, and mix thoroughly. (final conc 2 mg cycloate/ml)

For dry formulations, weigh a portion of sample equivalent to 0.2 gram of butylate into a 125 ml screw-cap flask, add by pipette 50 ml acetone, and shake for one hour. Allow to settle; filter or centrifuge if necessary, taking precautions to prevent evaporation. Pipette 25 ml of the clear solution into a 50 ml volumetric flask and make to volume with acetone and mix thoroughly. (final conc 2 mg cycloate/ml)

Determination:

Using a precision liquid syringe, alternately inject three 2-4 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

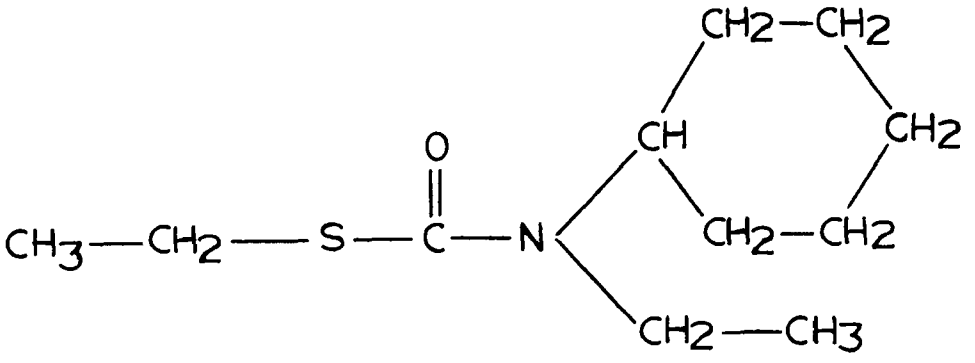
From the average peak height or peak area calculate the percent cycloate as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method developed by Evangelina Santos, EPA Region IX, San Francisco, California.

Determination of Cycloate by Gas-Liquid Chromatography (FID - Internal Standard)

Cycloate is the common name for S-ethyl cyclohexylethylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{11}H_{21}NOS$

Molecular weight: 215.4

Boiling point: 145°C at 10 mm Hg

Physical state, color, and odor: colorless liquid with an aromatic odor

Solubility: about 100 ppm in water at RT; miscible with most organic solvents

Stability: stable; non-corrosive

Other names: Ro-Neet (Stauffer Chem. Co.), Eurex, R-2063

Reagents:

1. Cycloate standard of known % purity
2. Pebulate standard of known % purity
3. Carbon disulfide, pesticide or spectro grade
4. Chloroform, pesticide or spectro grade

Reagents (Cont.):

5. Methanol, pesticide or spectro grade
6. Internal Standard solution - weigh 0.2 gram pebulate into a 50 ml volumetric flask, dissolve in, and make to volume with a solvent mixture consisting of 80% carbon disulfide + 15% chloroform + 5% methanol. (conc 4 mg pebulate/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 4 mm ID glass column packed with 3% OV-1 on 60/80 mesh Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	140°C
Injection temperature:	225°C
Detector temperature:	250°C
Carrier gas:	Nitrogen
Carrier gas flow rate:	(not stated in the method)
Hydrogen flow rate:	(not stated in the method)
Air flow rate:	(not stated in the method)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.08 gram cycloate standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 4 mg cycloate and 4 mg pebulate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.08 gram cycloate into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the cycloate. For coarse or granular materials, shake mechanically for 10-15 minutes or shake by hand intermittently for 25-30 minutes. (final conc 4 mg cycloate and 4 mg pebulate/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is pebulate, then cycloate.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of cycloate and pebulate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. pebulate})(\%\text{ purity pebulate})(\text{pk. ht. or area cycloate})}{(\text{wt. cycloate})(\%\text{ purity cycloate})(\text{pk. ht. or area pebulate})}$$

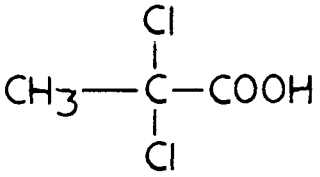
Determine the percent cycloate for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. pebulate})(\%\text{ purity pebulate})(\text{pk. ht. or area cycloate})(100)}{(\text{wt. sample})(\text{pk. ht. or area pebulate})(RF)}$$ (a-1)

Method submitted by Division of Regulatory Services, Kentucky Agricultural Experiment Station, University of Kentucky, Lexington, Kentucky 40506.

Determination of Dalapon by Infrared Spectroscopy

Dalapon is the accepted common name for 2,2-dichloropropionic acid, a registered herbicide having the chemical structure:



Molecular formula: $C_3H_4Cl_2O_2$

Molecular weight: 143

Boiling point: 185 to 190°C

Physical state, color, and odor: colorless, odorless liquid

Solubility: very soluble in water, ethanol, alkali solvents; soluble in ether, carbon disulfide

Stability: nonflammable; compatible with hard water and liquid fertilizers; mildly corrosive; stable in dry form; sodium and magnesium salts are hygroscopic

Other names: Dowpon, Radapon (Dow Chem. Co.); Basfapon, Ded-Weed, Gramevin, Unipon

Reagents:

1. 2,2-Dichloropropionic acid (or sodium salt) of known % purity
2. Carbon disulfide, ACS (spectroscopic grade preferred)
3. Sulfuric acid, 1+3
4. Anhydrous sodium sulfate, ACS granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 1.0 mm NaCl or KBr cells
2. Mechanical shaker, wrist action
3. 4 oz. screw-cap bottles
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.6-0.7 gram 2,2-dichloropropionic acid, or 0.7-0.8 gram 2,2-dichloropropionic acid sodium salt into a 4 oz. screw-cap bottle. Proceed as under Preparation of Sample, second paragraph, "Add 2 ml - - -."

Preparation of Sample:

Weigh a portion of sample equivalent to 0.6-0.7 gram 2,2-dichloropropionic acid or 0.7-0.8 gram 2,2-dichloropropionic acid sodium salt into a 4 oz. screw-cap bottle.

Add 2 ml sulfuric acid solution and mix well. By pipette add 100 ml carbon disulfide and shake on a mechanical shaker for 20 minutes. Add sufficient granular anhydrous sodium sulfate to absorb all the water and clarify the solution. Shake an additional 10 minutes and allow to settle.

Determination:

Using the optimum quantitative analytical settings for the particular IR spectrophotometer being used, scan the standard and sample solutions from 1333 cm^{-1} to 910 cm^{-1} (7.5 μ to 11.0 μ) using carbon disulfide in the reference cell. For qualitative comparison, run a full scan.

Determine the absorbance of both the standard and sample using the peak at 1130 cm^{-1} (8.85 μ) and a base line from 1155 cm^{-1} to 1015 cm^{-1} (8.65 μ to 9.85 μ).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent dalapon (or dalapon sodium salt) as follows:

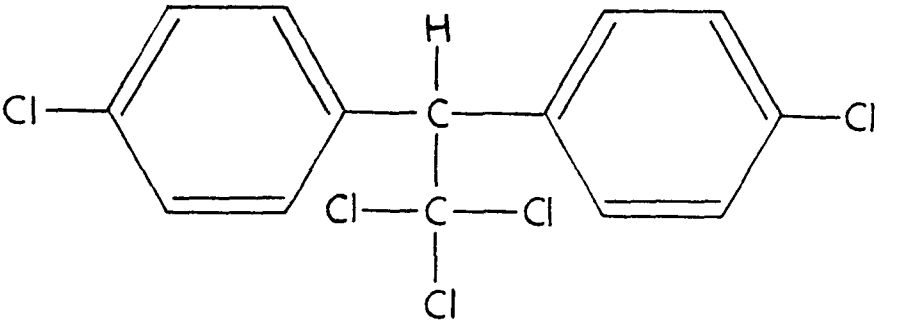
$$\% = \frac{(\text{abs. sample})(\text{wt. std})(\text{purity std})(1/100)(100)}{(\text{abs. std})(\text{grams sample})(1/100)}$$

% dalapon sodium salt = (1.1537)(% dalapon)

This method was adapted from The Dow Chemical Company method for Dowpon C.

Determination of DDT in Emulsifiable Concentrates Containing a Volatile Solvent by Infrared Spectroscopy

DDT is a common name for dichlorodiphenyltrichoroethane, an insecticide having the chemical structure:



p,p'-isomer data:

Molecular formula: $C_{14}H_9Cl_5$

Molecular weight: 354.5

Melting point: 108.5°C

Physical state and color: colorless crystals

Solubility: practically insoluble in water; moderately soluble in hydroxylic and polar solvents such as alcohol, and in petroleum oils; soluble in most aromatic and chlorinated solvents

Stability: dehydrochlorinated at temperatures above m.p., a reaction catalyzed by ferric and aluminum chloride and by UV light; readily dehydrochlorinated when in solution in organic solvents by alkali or organic bases; otherwise stable and inert, unattacked by acid and alkaline permanganate or by aqueous acids and alkalis

Technical: The technical product (up to 30% o,p'-isomer) is a waxy solid of indefinite m.p. and of similar solubility to the p,p'-isomer.

Other names: Gesarol, Guesarol, Neocid (Ciba-Geigy); Dicophane (British Pharmacopeia); chlorophenothane (U.S. Pharmacopoeia); Zerdane (France); anofex, Dedelo, Didimac, Genitox, Gesapon, Gesarex, Gyron, Ixodex, Kopsol, Pentachlorin, Rukseam, 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane

Reagents:

1. Technical DDT standard
2. Carbon disulfide, ACS

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm NaCl or KBr cells
2. Rotary evaporator with 60° water bath
3. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.4 gram technical DDT into a 25 ml volumetric flask, dissolve in, and make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate to insure dryness. (conc 16 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.4 gram technical DDT into a 125 ml standard tapered Erlenmeyer flask and evaporate the

solvent on a rotary evaporator using a water bath at 60°C. The solvent (e.g., xylene) can usually be evaporated in about 10 minutes, but the DDT may not crystallize; however, the last traces of solvent may be removed with a gentle stream of air.

Dissolve the residue, transfer quantitatively to a 25 ml volumetric flask, and make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate to insure dryness. (conc 16 mg tech. DDT/ml)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan the standard and sample from 1175 cm^{-1} to 950 cm^{-1} (8.5 μ to 10.5 μ).

Determine the absorbance of standard and sample using the peak at 1017 cm^{-1} (9.83 μ) and baseline from 1064 cm^{-1} to 970 cm^{-1} (9.4 μ to 10.3 μ).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent technical DDT as follows:

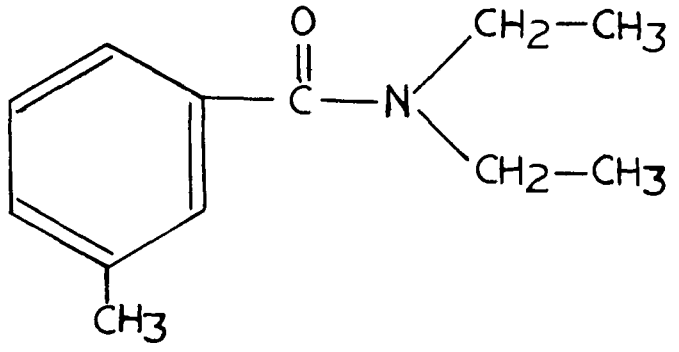
$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

December 1975

Deet EPA-1
(Tentative)

Determination of Deet by Infrared Spectroscopy

Deet is the common name for N,N-diethyl-m-toluamide, a registered insect repellent having the chemical formula:



Molecular formula: $C_{12}H_{17}NO$

Molecular weight: 191.3

Boiling point: 111°C at 1 mm Hg

Physical state and color: colorless to amber liquid, nearly odorless; the technical product contains 85-95% m isomer; the o and p isomers are highly repellent but less effective than the m isomer

Solubility: practically insoluble in water; miscible with ethanol, isopropanol, propylene glycol, cottonseed oil, ether, benzene

Stability: stable under normal conditions; non-corrosive to most metals

Other names: Metadelphene (Hercules), Delphene, Detamide, Off

This method is primarily for alcohol solutions.

Reagents:

1. Deet standard of known % purity
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm NaCl or KBr cells
2. Rotary evaporator
3. Water bath at 50°C
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.4 gram deet standard into a 10 ml volumetric flask and make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate to insure dryness. (conc 40 mg/ml)

Preparation of Sample:

Weigh a portion of sample (alcohol solution and aerosol non-volatile) equivalent to 0.4 gram deet into a 125 ml Erlenmeyer flask and evaporate the alcohol under vacuum on a rotary evaporator at 50°C. (The alcohol may be removed by heating on a steam bath for a few minutes with a slow current of air passing into the flask.) Do not heat any longer than necessary to remove the alcohol. Transfer the residue quantitatively to a 10 ml volumetric flask and make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate and shake thoroughly to remove water and clarify the solution. (final conc 40 mg deet/ml)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 770 cm^{-1} to 665 cm^{-1} (13 μ to 15 μ).

Determine the absorbance of standard and sample using the peak at 706.7 cm^{-1} (14.15 μ) and basepoint 692.5 cm^{-1} (14.44 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent deet as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

The above method is based on the old USDA, PRD Methods Clearing House Method No. 382.0 and on EPA's Exp. Method 26B and is for alcohol solutions of the meta isomer.

The para isomer may be determined in a similar manner using 877.2 cm^{-1} (11.4 μ) analytical peak and 862.1 cm^{-1} (11.6 μ) basepoint.

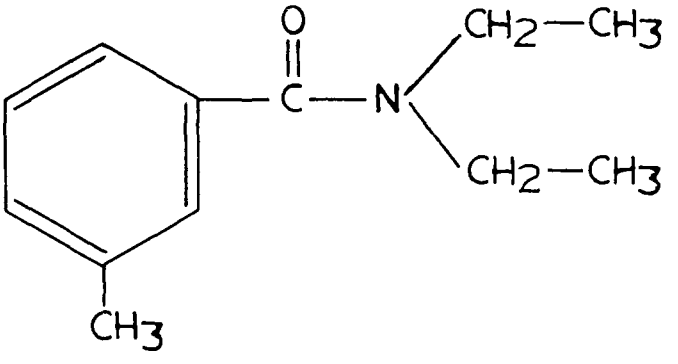
Some success has been obtained by the Beltsville Chemistry Laboratory on aerosols, creams, and sticks: sometimes by extraction from aqueous mixtures using carbon disulfide, filtering, and drying with anhydrous sodium sulfate; and sometimes by choosing another IR wavelength where interferences from sample components (IR scanned) are not present.

December 1975

Deet EPA-2
(Tentative)

Determination of Deet by Gas-Liquid Chromatography (TCD - Internal Standard)

Deet is the common name for N,N-diethyl-m-toluamide, a registered insect repellent having the chemical formula:



Molecular formula: $C_{12}H_{17}NO$

Molecular weight: 191.3

Boiling point: 111°C at 1 mm Hg

Physical state and color: colorless to amber liquid, nearly odorless; the technical product contains 85-95% m isomer; the o and p isomers are highly repellent but less effective than the m isomer

Solubility: practically insoluble in water; miscible with ethanol, isopropanol, propylene glycol, cottonseed oil, ether, benzene

Stability: stable under normal conditions; non-corrosive to most metals

Other names: Metadelphene (Hercules), Delphene, Detamide, Off

This method is for aerosols containing MGK 264, MGK 326, and MGK Repellent II.

Reagents:

1. Deet standard of known % purity
2. Heptachlor standard of known % purity
3. Benzene, pesticide or spectro grade
4. Internal Standard solution - weigh 1.2 grams heptachlor into a 100 ml volumetric flask; dissolve in and make to volume with benzene. (conc 12 mg heptachlor/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 6' x 1/8" O.D. stainless steel, packed with 10% SE-30 on 80/100 Diatoport S (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	190°C
Injection temperature:	215°C
Detector temperature:	215°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas flow rate:	adjust for specific GC

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.08 gram deet standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution and shake thoroughly. (final conc 4 mg deet and 12 mg heptachlor/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.08 gram deet into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly. (final conc 4 mg deet and 12 mg heptachlor/ml)

Determination:

Inject 2-3 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is deet, then heptachlor. Technical heptachlor gives a second small peak which should be eluted before another injection.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of deet and heptachlor from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. heptachlor})(\%\text{ purity heptachlor})(\text{pk. ht. or area deet})}{(\text{wt. deet})(\%\text{ purity deet})(\text{pk. ht. or area heptachlor})}$$

Determine the percent deet for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. heptachlor})(\%\ \text{purity heptachlor})(\text{pk. ht. or area deet})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area heptachlor})(\text{RF})}$$ 4-1

This method is based on EPA's Exp. Method No. 26 submitted by Stelios Gerazounis, EPA, Region II, New York, N. Y.

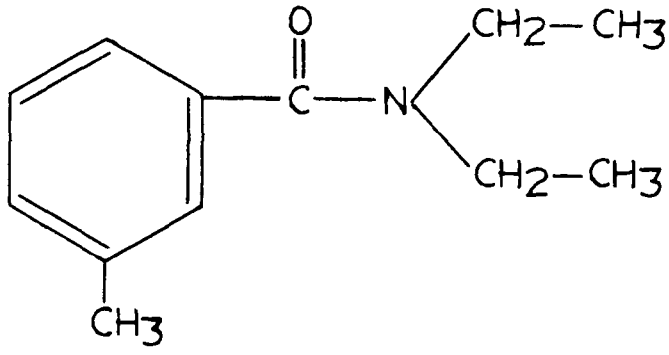
Although specifically for aerosol samples, this method with modification could be used for other deet formulations. Any suggestions, data, comments, etc. will be appreciated.

December 1975

Deet EPA-3
(Tentative)

Determination of Deet by Gas-Liquid Chromatography (FID - Internal Standard)

Deet is the common name for N,N-diethyl-m-toluamide, a registered insect repellent having the chemical formula:



Molecular formula: $C_{12}H_{17}NO$

Molecular weight: 191.3

Boiling point: 111°C at 1 mm Hg

Physical state and color: colorless to amber liquid, nearly odorless; the technical product contains 85-95% m isomer; the o and p isomers are highly repellent but less effective than the m isomer

Solubility: practically insoluble in water; miscible with ethanol, isopropanol, propylene glycol, cottonseed oil, ether, benzene

Stability: stable under normal conditions; non-corrosive to most metals

Other names: Metadelphene (Hercules), Delphene, Detamide, Off

Reagents:

1. Deet standard of known % purity
2. Vernolate standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.2 gram vernolate standard into a 100 ml volumetric flask, dissolve in, and make to volume with acetone. (conc 2 mg vernolate/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm ID glass column packed with 3% OV-17 on 80/100 Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	150°C
Injection temperature:	200°C
Detector temperature:	200°C
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi (adjusted for specific GC)
Hydrogen pressure:	20 psi (adjusted for specific GC)
Air pressure:	30 psi (adjusted for specific GC)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.075 gram deet standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 25 ml of the internal standard solution and shake thoroughly. (final conc 3 mg deet and 2 mg vernolate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.075 gram deet into a small glass-stoppered flask or screw-cap bottle. Add by pipette 25 ml of the internal standard solution. Close tightly and shake thoroughly. (final conc 3 mg deet and 2 mg vernolate/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is vernolate, then deet.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of deet and vernolate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. vernolate})(\%\text{ purity vernolate})(\text{pk. ht. or area deet})}{(\text{wt. deet})(\%\text{ purity deet})(\text{pk. ht. or area vernolate})}$$

Determine the percent deet for each injection of the sample-internal standard solution as follows and calculate the average:

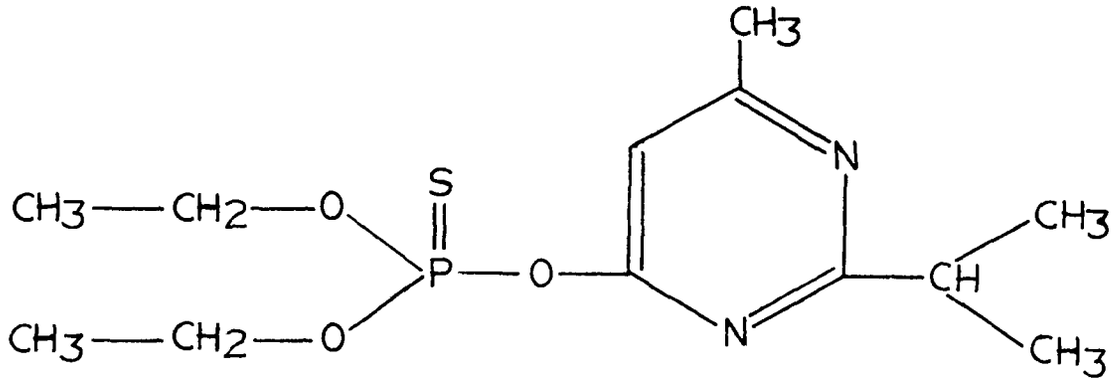
$$\% = \frac{(\text{wt. vernolate})(\%\text{ purity vernolate})(\text{pk. ht. or area deet})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area vernolate})(\text{RF})}$$ 4.1

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Note! This method has been designated as tentative since it is a Va. Exp. Tent. method and because some of the data has been suggested by EPA's Beltsville Chemistry Lab. Any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated, especially as related to analysis of different deet formulations.

Determination of Diazinon by Gas-Liquid Chromatography (TCD)

Diazinon is the common name (ISO and BSI, except U.S. where it is a registered trademark) for O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate; a registered insecticide, acaricide, and nematocide having the chemical structure:



Molecular formula: $C_{12}H_{21}N_2O_3PS$

Molecular weight: 304.3

Boiling point: 83 to 84°C under 0.002 mm Hg

Physical state and color: colorless liquid; the technical product (about 95% pure) is light amber to dark brown.

Solubility: 0.004% (40 ppm) in water at RT; miscible with aliphatic and aromatic solvents, alcohols, and ketones; soluble in petroleum oils

Stability: decomposes about 120°C; susceptible to oxidation; stable in alkaline media but slowly hydrolyzed in water and dilute acids; compatible with most pesticides but should not be combined with copper fungicides; the presence of traces of water promotes hydrolysis on storage to the highly poisonous tetraethyl monothiopyrophosphate

Other names: Spectracide, Diazinon, G-24480 (Ciba-Geigy); Basudin, Diazajet, Diazide, Diazol, Dazzel, Gardentox, Neocidol, Nucidol, Sarolex

Reagents:

1. Diazinon standard of known % purity
2. Acetone, pesticide or spectro grade

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 4' x 1/4" O.D. glass column packed with 5% SE-30 on 60/80 mesh Chromosorb W, AW, DMCS (or equivalent column)
3. Precision liquid syringe: 50 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	170°C
Injection temperature:	200°C
Detector temperature:	200°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas pressure:	30-40 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram diazinon standard into a 10 ml volumetric flask; dissolve in and make to volume with acetone. (final conc 10 mg diazinon/ml)

Preparation of Sample:

For emulsifiable concentrates and liquid formulations, weigh a portion of sample equivalent to 0.1 gram diazinon into a 10 ml volumetric flask, make to volume with acetone, and mix thoroughly. (final conc 10 mg diazinon/ml)

For dry formulations, weigh a portion of sample equivalent to 0.5 gram diazinon into a 125 ml screw-cap flask, add by pipette 50 ml acetone, and shake for one hour. Allow to settle; filter or centrifuge if necessary, taking precautions to prevent evaporation. (final conc 10 mg diazinon/ml)

Determination:

Using a precision liquid syringe, alternately inject three 15-25 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent diazinon as follows:

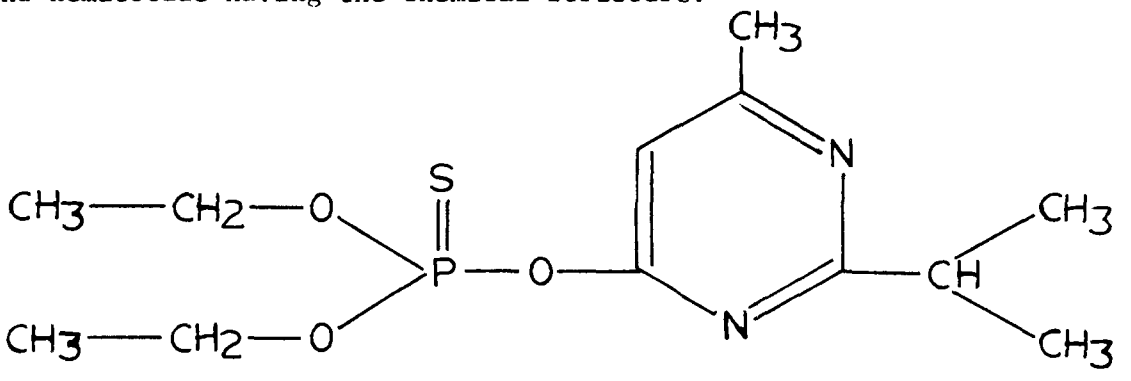
$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

November 1975

Diazinon EPA-2
(Tentative)

Determination of Diazinon by High Pressure Liquid Chromatography

Diazinon is the common name (ISO and BSI, except U.S. where it is a registered trademark) for O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate; a registered insecticide, acaricide, and nematocide having the chemical structure:



Molecular formula: $C_{12}H_{21}N_2O_3PS$

Molecular weight: 304.3

Boiling point: 83 to 84°C under 0.002 mm Hg

Physical state and color: colorless liquid; the technical product (about 95% pure) is light amber to dark brown.

Solubility: 0.004% (40 ppm) in water at RT; miscible with aliphatic and aromatic solvents, alcohols, and ketones; soluble in petroleum oils

Stability: decomposes about 120°C; susceptible to oxidation; stable in alkaline media but slowly hydrolyzed in water and dilute acids; compatible with most pesticides but should not be combined with copper fungicides; the presence of traces of water promotes hydrolysis on storage to the highly poisonous tetraethyl monothiopyrophosphate

Other names: Spectracide, Diazinon, G-24480 (Ciba-Geigy); Basudin, Diazajet, Diazide, Diazol, Dazzel, Gardentox, Neocidol, Nucidol, Sarolex

Reagents:

1. Diazinon standard of known % purity
2. Methanol, pesticide or spectro grade

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm. If a variable wavelength UV detector is available, other wavelengths may be useful to increase sensitivity or eliminate interference. 235 nm has been found useful for methyl parathion.
2. Suitable column such as:
   a. DuPont ODS Permaphase, 1 meter x 2.1 mm ID
   b. Perkin Elmer ODS Sil-X-II RP, 1/2 meter x 2.6 mm ID
3. High pressure liquid syringe or sample injection loop
4. Usual laboratory glassware

Operating Conditions:

Mobile phase:	20% methanol + 80% water
Column temperature:	50-55°C
Chart speed:	5 min/inch or equivalent
Flow rate:	0.5 to 1.5 ml/min (Perkin-Elmer 1/2 meter column)
Pressure:	900 psi (DuPont 1 meter column)
Attenuation:	Adjusted

Conditions may have to be varied by the analyst for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram diazinon standard into a 50 ml volumetric flask, add 50 ml methanol by pipette, and mix thoroughly. (final conc 2 mg diazinon/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.1 gram diazinon into a glass-stoppered flask or vial, add 50 ml methanol by pipette, and shake thoroughly to dissolve the diazinon. Allow any solid matter to settle; filter or centrifuge if necessary. (final conc 2 mg diazinon/ml)

Determination:

Alternately inject three 5 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

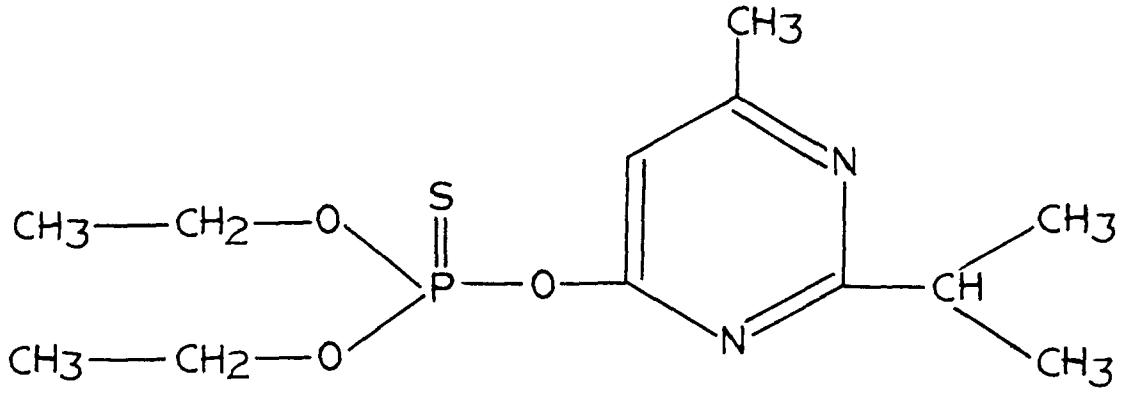
From the average peak height or peak area calculate the percent diazinon as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Elmer H. Hayes, EPA, Beltsville, Md.

Determination of Diazinon by Infrared Spectroscopy

Diazinon is the common name (ISO and BSI, except U.S. where it is a registered trademark) for O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate; a registered insecticide, acaricide, and nematocide having the chemical structure:



Molecular formula: $C_{12}H_{21}N_2O_3PS$

Molecular weight: 304.3

Boiling point: 83 to 84°C under 0.002 mm Hg

Physical state and color: colorless liquid; the technical product (about 95% pure) is light amber to dark brown.

Solubility: 0.004% (40 ppm) in water at RT; miscible with aliphatic and aromatic solvents, alcohols, and ketones; soluble in petroleum oils

Stability: decomposes about 120°C; susceptible to oxidation; stable in alkaline media but slowly hydrolyzed in water and dilute acids; compatible with most pesticides but should not be combined with copper fungicides; the presence of traces of water promotes hydrolysis on storage to the highly poisonous tetraethyl monothiopyrophosphate

Other names: Spectracide, Diazinon, G-24480 (Ciba-Geigy); Basudin, Diazajet, Diazide, Diazol, Dazzel, Gardentox, Neocidol, Nucidol, Sarolex

Reagents:

1. Diazinon standard of known % purity
2. Acetone, pesticide or spectro grade

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.1 gram diazinon standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml acetone by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg diazinon/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.5 gram diazinon into a glass-stoppered flask or screw-cap tube. Add 50 ml acetone by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle centrifuge or filter if necessary, taking precautions to prevent evaporation. (final conc 10 mg diazinon/ml)

Determination:

With acetone in the reference cell, and using the optimum quantitative analytical settings, scan both the standard and sample from 925 cm^{-1} to 715 cm^{-1} (10.8 μ to 14.0 μ).

Determine the absorbance of standard and sample using the peak at 833.3 cm^{-1} (12.0 μ) and a baseline from 719.4 cm^{-1} to 1123.6 cm^{-1} (13.9 μ to 8.9 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent diazinon as follows:

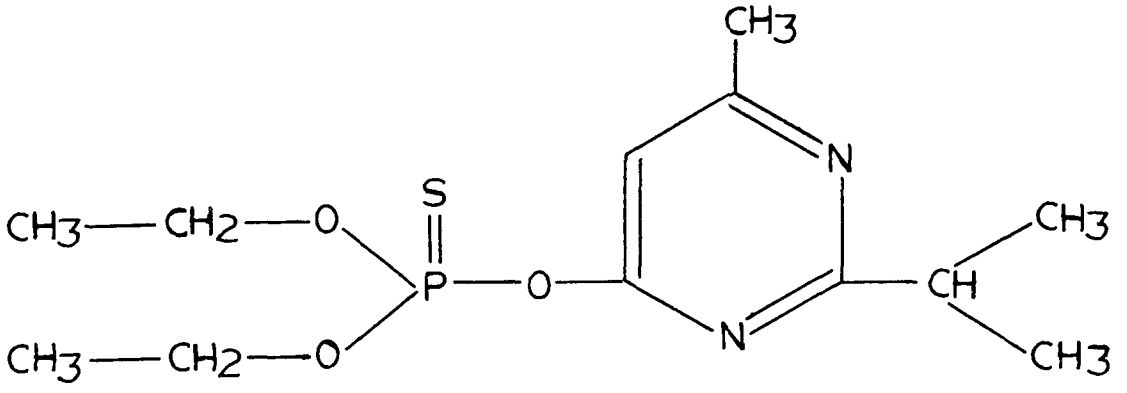
$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg diazinon/ml acetone gives an absorbance of approx. 0.033 in a 0.2 mm cell.)

Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Va. 23219.

Determination of Diazinon by Gas-Liquid Chromatography (FID - Internal Standard)

Diazinon is the common name (ISO and BSI, except U.S. where it is a registered trademark) for O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate; a registered insecticide, acaricide, and nematocide having the chemical structure:



Molecular formula: $C_{12}H_{21}N_2O_3PS$

Molecular weight: 304.3

Boiling point: 83 to 84°C under 0.002 mm Hg

Physical state and color: colorless liquid; the technical product (about 95% pure) is light amber to dark brown.

Solubility: 0.004% (40 ppm) in water at RT; miscible with aliphatic and aromatic solvents, alcohols, and ketones; soluble in petroleum oils

Stability: decomposes about 120°C; susceptible to oxidation; stable in alkaline media but slowly hydrolyzed in water and dilute acids; compatible with most pesticides but should not be combined with copper fungicides; the presence of traces of water promotes hydrolysis on storage to the highly poisonous tetraethyl monothiopyrophosphate

Other names: Spectracide, Diazinon, G-24480 (Ciba-Geigy); Basudin, Diazajet, Diazide, Diazol, Dazzel, Gardentox, Neocidol, Nucidol, Sarolex

Reagents:

1. Diazinon standard of known % purity
2. Aldrin of known HHDN content
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.150 gram HHDN into a 50 ml volumetric flask, dissolve in, and make to volume with acetone. (conc 3 mg HHDN/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 4 mm ID glass column packed with 3% OV-1 on 60/80 mesh Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	175°C
Injection temperature:	260°C
Detector temperature:	255°C
Carrier gas:	Nitrogen
Carrier gas pressure:	(not stated in method) (40-60 psi)
Hydrogen pressure:	20 psi
Air pressure:	30 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.04 gram diazinon standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 2 mg diazinon and 3 mg HHDN/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.04 gram diazinon into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the diazinon. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 2 mg diazinon and 3 mg HHDN/ml)

Determination:

Inject 2-3 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is diazinon, then HHDN.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of diazinon and HHDN from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. HHDN})(\%\text{ purity HHDN})(\text{pk. ht. or area diazinon})}{(\text{wt. diazinon})(\%\text{ purity diazinon})(\text{pk. ht. or area HHDN})}$$

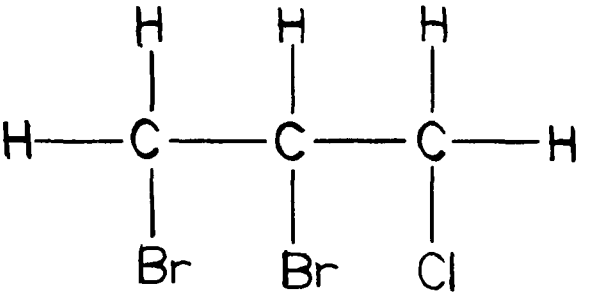
Determine the percent diazinon for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. HHDN})(\%\text{ purity HHDN})(\text{pk. ht. or area diazinon})(100)}{(\text{wt. sample})(\text{pk. ht. or area HHDN})(RF)} \qquad (4\text{-}1)$$

Method submitted by Division of Regulatory Services, Kentucky Agricultural Experiment Station, University of Kentucky, Lexington, Kentucky 40506.

Determination of Dibromochloropropane by Infrared Spectroscopy

Dibromochloropropane is the trivial name for 1,2-dibromo-3-chloropropane, a registered soil fumigant and nematocide having the chemical structure:



Molecular formula: $C_3H_5Br_2Cl$

Molecular weight: 236.3

Boiling point: 196°C

Physical state, color, and odor: amber to dark brown dense liquid with a mildly pungent odor

Solubility: 1000 ppm in water; miscible with aliphatic and aromatic solvents

Stability: stable to hydrolysis in neutral or acid media; hydrolyzed by alkali to 2-bromoallyl alcohol; corrodes aluminum, magnesium, and tin alloys

Other names: Fumazone (Dow Chemical Co.), Nemagon (Shell Development Co.), DBCP, Nemafume, BBC 12, OS 1897

Reagents:

1. Dibromochloropropane standard of known % purity
2. Acetone, pesticide or spectro grade
3. Carbon disulfide, pesticide or spectro grade
4. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm KBr cells
2. Mechanical shaker*
3. Rotary evaporator
4. Centrifuge or filtration apparatus
5. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.5 gram dibromochloropropane into a 10 ml volumetric flask, dissolve in, and make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 50 mg/ml)

Preparation of Sample:

For emulsifiable concentrates, weigh a portion of sample equivalent to 0.5 gram dibromochloropropane into a 10 ml volumetric flask, make to volume with carbon disulfide, and mix well. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 50 mg dibromochloropropane/ml)

For granular formulations, weigh a portion of sample equivalent to 1.0 gram dibromochloropropane into a glass-stoppered flask or screw-cap tube. Add 50 ml acetone by pipette and 1-2 grams anhydrous sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. Evaporate a 25 ml aliquot to dryness on a water bath using a gentle stream of dry air; evaporate the last one or two ml with air only. Dissolve in about 4-5 ml carbon disulfide, transfer to a 10 ml volumetric flask, and make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 50 mg dibromochloropropane/ml)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan the standard and sample from 800 cm^{-1} to 500 cm^{-1} (12.5 μ to 20 μ).

Determine the absorbance of standard and sample using the peak at 572 cm^{-1} (17.48 μ) and baseline from 610 cm^{-1} to 520 cm^{-1} (16.4 μ to 19.2 μ).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent dibromochloropropane as follows:

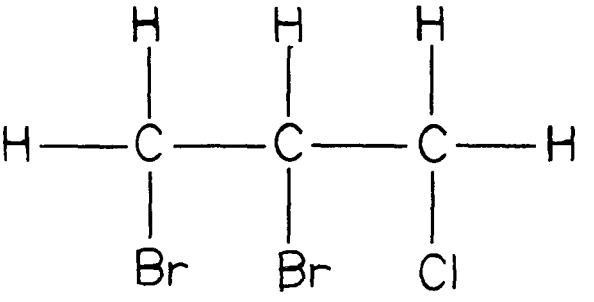
$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg dibromochloropropane/ml carbon disulfide gives an absorbance of approx. 0.007 in a 0.2 mm cell.)

Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Determination of Dibromochloropropane by Gas-Liquid Chromatography (TCD)

Dibromochloropropane is the trivial name for 1,2-dibromo-3-chloropropane, a registered soil fumigant and nematocide having the chemical structure:



Molecular formula: $C_3H_5Br_2Cl$

Molecular weight: 236.3

Boiling point: 196°C

Physical state, color, and odor: amber to dark brown dense liquid with a mildly pungent odor

Solubility: 1000 ppm in water; miscible with aliphatic and aromatic solvents

Stability: stable to hydrolysis in neutral or acid media; hydrolyzed by alkali to 2-bromoallyl alcohol; corrodes aluminum, magnesium, and tin alloys

Other names: Fumazone (Dow Chemical Co.), Nemagon (Shell Development Co.), DBCP, Nemafume, BBC 12, OS 1897

Reagents:

1. Dibromochloropropane standard of known % purity
2. Chloroform, pesticide or spectro grade

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 5' x 1/4" O.D. glass column packed with 20% SE-30 on Chromosorb W AW DMCS (or equivalent column)
3. Precision liquid syringe: 50 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	140°C
Injection temperature:	175°C
Detector temperature:	175°C
Carrier gas:	Helium
Flow rate:	40 ml/min

Operating conditions for filament current, column temperature, or gas flow should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.20 gram dibromochloropropane standard into a 10 ml volumetric flask and make to volume with chloroform. (final conc 20 mg/ml)

Preparation of Sample:

For technical material and liquid formulations, weigh a portion of sample equivalent to 0.20 gram dibromochloropropane into a 10 ml volumetric flask, make to volume with chloroform, and mix thoroughly. (final conc 20 mg dibromochloropropane/ml)

For dry formulations, weigh a portion of sample equivalent to 1.0 gram dibromochloropropane into a 125 ml screw-cap flask, add by pipette 50 ml chloroform, and shake for one hour. Allow to settle; filter or centrifuge if necessary, taking precautions to prevent evaporation. (final conc 20 mg dibromochloropropane/ml)

Determination:

Using a precision liquid syringe, alternately inject three 30-40 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

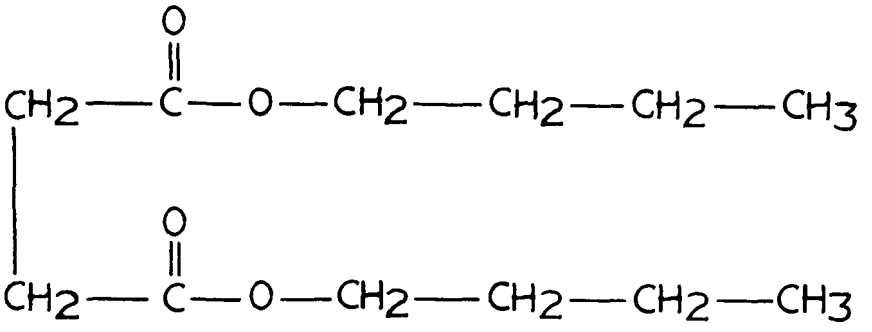
From the average peak height or peak area calculate the percent dibromochloropropane as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Eva Santos, EPA Region IX, San Francisco, California.

Determination of Dibutyl Succinate by Saponification and Titration

Dibutyl succinate is a registered insect repellent with the following chemical structure:



Molecular formula: $C_{12}H_{22}O_4$

Molecular weight: 230.3

Melting/boiling point: m.p.-29°C; b.p. 108°C at 4 mm Hg

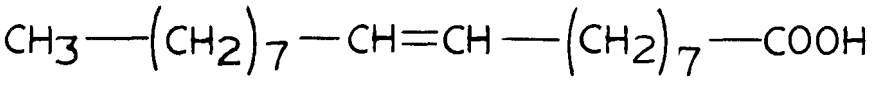
Physical state and color: colorless liquid

Solubility: practically insoluble in water but miscible with most organic solvents including petroleum oils

Stability: non-corrosive; hydrolyzed by alkalis

Other names: Tabutrex, renamed Tabatrex (Glen Chemical Co.)

Dibutyl succinate is normally formulated with oleic acid (cis-9-octadecenoic acid) to prolong activity. Oleic acid has the chemical structure:



Molecular formula: $C_{18}H_{34}O_2$ Molecular weight: 282.45

Colorless liquid; solidifies at 4°C to crystalline mass;

soluble in alcohol, benzene, chloroform, ether, fixed & volatile oils

Principle of the Method:

The total acidity in the sample is determined by titration with standard acid after saponification of the dibutyl succinate with an excess of standard alkali. Any free acid is determined by direct titration with standard alkali. The difference (as milliequivalents) is equal to the dibutyl succinate. The free acid is calculated as oleic acid.

Reagents:

1. Sodium (or potassium) hydroxide, 0.5N standard solution
2. Hydrochloric acid, 0.5N standard solution
3. Ethanolic potassium hydroxide, 0.5N standard solution in ethanol
4. Ethyl alcohol, neutralized to phenolphthalein
5. Phenolphthalein indicator solution

Equipment:

1. Alkali-resistant Erlenmeyer flask, 250-300 ml standard taper joint
2. Refluxing apparatus
3. Titrating apparatus
4. Usual laboratory glassware

Procedure:

Total acidity after hydrolysis:

Weigh a portion of sample equivalent to 0.3-0.5 gram dibutyl succinate into a 250-300 ml alkali-resistant Erlenmeyer standard taper flask and add 50.0 ml 0.5N alcoholic potassium hydroxide solution. To a second identical flask, add 50.0 ml of the same solution for a blank. Connect each flask to a reflux condenser and reflux 2 hours. Cool, add several drops of phenolphthalein indicator solution, and titrate each flask with 0.5N standard hydrochloric acid. The difference between the two titrations represents the total acidity after hydrolysis.

Free acidity before hydrolysis:

Weigh a portion of sample equivalent to 0.3-0.5 gram dibutyl succinate into a 250-300 ml Erlenmeyer flask. Add 50 ml neutralized alcohol, several drops of phenolphthalein solution, and titrate with 0.5N standard sodium (or potassium) hydroxide. The titration represents any free acid and is calculated as oleic acid.

Calculations:

A = milliequivalents of total acid after hydrolysis

A = (ml HCl for Blank-ml HCl for Sample)(N HCl)

B = milliequivalents of free acid before hydrolysis

B = (ml NaOH)(N NaOH)

$$\% \text{ Dibutyl succinate} = \frac{(A - B)(0.11515)(100)}{(\text{grams sample})}$$

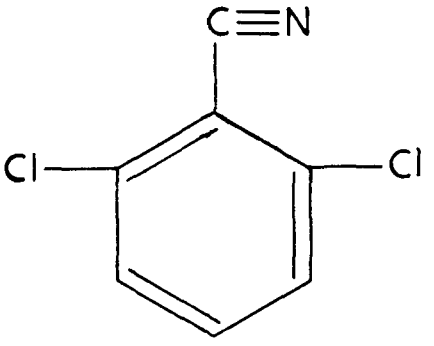
(milliequivalent weight of dibutyl succinate = 0.11515)

$$\% \text{ Oleic acid} = \frac{(B)(0.28245)(100)}{(\text{grams sample})}$$

(milliequivalent weight of oleic acid = 0.28245)

Determination of Dichlobenil by Infrared Spectroscopy

Dichlobenil is the accepted common name for 2,6-dichlorobenzonitrile, a registered herbicide having the chemical structure:



Molecular formula: $C_7H_3Cl_2N$

Molecular weight: 171.9

Melting point: 145-146°C for pure compound; the technical product is about 95% pure and has a m.p. 139 to 146°C

Physical state, color, and odor: white crystalline solid with an aromatic odor; technical is gray-white to yellow-brown

Solubility: very slightly soluble in water (18 ppm at 20°C); slightly soluble in most organic solvents

Stability: stable to heat and acids but is hydrolyzed by alkalis to 2,6-dichlorobenzamide; non-corrosive; compatible with other herbicides

Other names: Casoron (N.V. Phillips Duphar), 2,6-DBN, H133

Reagents:

1. Dichlobenil standard of known % purity
2. Carbon disulfide
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.1 gram dichlobenil standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml carbon disulfide by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.5 gram dichlobenil into a glass-stoppered flask or screw-cap tube. Add 50 ml carbon disulfide by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precautions to prevent evaporation. (final conc 10 dichlobenil/ml)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings, scan both the standard and sample from 835 cm^{-1} to 725 cm^{-1} (12.0 μ to 13.8 μ).

Determine the absorbance of standard and sample using the peak at 806.5 cm^{-1} (12.4 μ) and baseline from 819.7 cm^{-1} to 787.4 cm^{-1} (12.2 μ to 12.7 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent dichlobenil as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg dichlobenil/ml carbon disulfide gives an absorbance of approx. 0.017 in a 0.2 mm cell.)

Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services.

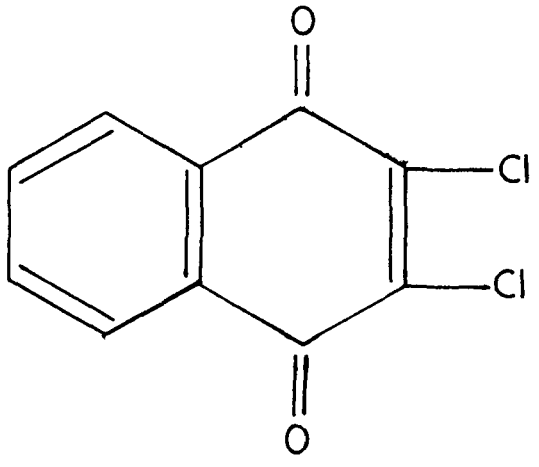
Eva Santos, EPA Region IX, San Francisco, California, submitted a similar method using:

solvent:	chloroform
conc:	10 mg/ml
scan range:	870 cm^{-1} to 720 cm^{-1} (11.5 μ to 13.9 μ)
analytical peak:	780.0 cm^{-1} (12.82 μ)
baseline:	819.7 cm^{-1} to 740.7 cm^{-1} (12.2 μ to 13.5 μ)

Any criticism, comparison, or suggestions as to preference, accuracy, or precision of using either of these peaks or using CS_2 or $CHCl_3$ will be appreciated.

Determination of Dichlone by Infrared Spectroscopy

Dichlone is the official common name for 2,3-dichloro-1,4-naphthoquinone, a registered fungicide having the chemical structure:



Molecular formula: $C_{10}H_4Cl_2O_2$

Molecular weight: 227.1

Melting point: 193°C (slowly sublimes above 32°C)

Physical state and color: yellow crystals or leaflets

Solubility: practically insoluble in water (0.1 ppm at 25°C); moderately soluble (about 4%) in xylene and O-dichlorobenzene; slightly soluble in acetone, benzene, ether, dioxane.

Stability: stable to light and acids but hydrolyzed by alkali; incompatible with petroleum oils, DNOC, and lime sulfur; non-corrosive

Other names: Phygon and Uniroyal (Uniroyal Inc.), USR 604

Reagents:

1. Dichlone standard of known % purity
2. Acetone, pesticide or spectro grade
3. Chloroform, pesticide or spectro grade
4. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Water bath 40°C
5. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps. These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Note! This method is applicable in presence of sulfur but not in presence of Ferbam.

Preparation of Standard:

Weigh 0.075 gram dichlone into a glass-stoppered flask or screw-cap bottle, add 50 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc. 1.5 mg/ml)

Preparation of Sample:

For 50% wettable powders or other high % formulations, weigh a portion of sample equivalent to 0.075 gram dichlone into a glass-stoppered flask or screw-cap bottle; add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 1.5 mg dichlone/ml)

For 1-4% dusts or other low % formulations, weigh a portion of sample equivalent to 0.03 gram dichlone into a glass-stoppered flask or screw-cap bottle; add 50 ml acetone by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. Evaporate a 25 ml aliquot over a water bath at 40°C using a gentle stream of air. Evaporate the last few ml at RT using air only. Dissolve in about 5 ml chloroform, transfer to a 10 ml volumetric flask, and make to volume with chloroform. Mix thoroughly and add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 1.5 mg dichlone/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1330 cm^{-1} to 1225 cm^{-1} (7.52 μ to 8.16 μ).

Determine the absorbance of standard and sample using the peak at 1275 cm^{-1} (7.84 μ) and basepoint at 1300 cm^{-1} (7.69 μ).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent dichlone as follows:

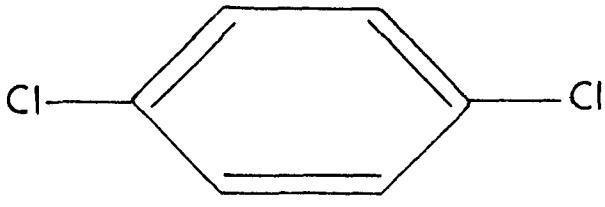
$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg dichlone/ml chloroform gives an absorbance of approx. 0.080 in a 0.2 mm cell.)

Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia, 23219.

Determination of p-Dichlorobenzene by Infrared Spectroscopy

p-Dichlorobenzene (or paradichlorobenzene) is the common name for 1,4-dichlorobenzene, a fumigant having the chemical structure:



Molecular formula: $C_6H_4Cl_2$

Molecular weight: 147.01

Melting point: 53°C

Boiling point: 173.4°C

Physical state, color, and odor: colorless crystals with a characteristic penetrating odor

Solubility: about 80 ppm in water at 25°C; slightly soluble in cold alcohol; readily soluble in organic solvents

Stability: stable; sublimes at ordinary temperatures; non-corrosive and non-staining

Other names: Paradow, Paracide, PDB, Santochlor

Reagents:

1. p-Dichlorobenzene standard of known % purity
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm KBr or NaCl cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.125 gram p-dichlorobenzene standard into a small glass-stoppered flask or screw-capped bottle. Add 50 ml chloroform by pipette and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 2.5 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.125 gram p-dichlorobenzene into a small glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 2.5 mg p-dichlorobenzene/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 870 cm^{-1} to 740 cm^{-1} (11.5 μ to 13.5 μ).

Determine the absorbance of standard and sample using the peak at 816 cm^{-1} (12.25 μ) and baseline from 855 cm^{-1} to 794 cm^{-1} (11.7 μ to 12.6 μ).

Calculation:

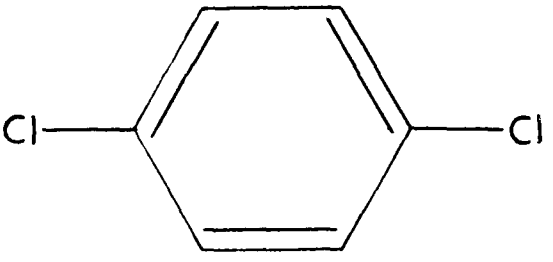
From the above absorbances and using the standard and sample concentrations, calculate the percent p-dichlorobenzene as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Method contributed by Nancy Frost, EPA Region IX, San Francisco, California.

Determination of p-Dichlorobenzene by Gas-Liquid Chromatography (TCD - Internal Standard)

p-Dichlorobenzene (or paradichlorobenzene) is the common name for 1,4-dichlorobenzene, a fumigant having the chemical structure:



Molecular formula: $C_6H_4Cl_2$

Molecular weight: 147.01

Melting point: 53°C

Boiling point: 173.4°C

Physical state, color, and odor: colorless crystals with a characteristic penetrating odor

Solubility: about 80 ppm in water at 25°C; slightly soluble in cold alcohol; readily soluble in organic solvents

Stability: stable; sublimes at ordinary temperatures; non-corrosive and non-staining

Other names: Paradow, Paracide, PDB, Santochlor

Reagents:

1. p-Dichlorobenzene standard of known % purity
2. DDVP standard of known % purity
3. Benzene, pesticide or spectro grade
4. Internal Standard solution - weigh 1.8 grams DDVP into a 50 ml volumetric flask; dissolve in and make to volume with benzene. (conc 36 mg DDVP/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 6' x 1/8" stainless steel column packed with 10% SE-30 on Diatoport S (or equivalent or suitable column)
3. Precision liquid syringe: 5 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	117°C
Injection temperature:	140°C
Detector temperature:	140°C
Filament current:	190 ma
Carrier gas:	Helium
Carrier gas pressure:	(not stated in method)
Carrier gas flow rate:	(not stated in method)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.088 gram p-dichlorobenzene standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 8.8 mg p-dichlorobenzene and 36 mg DDVP/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.088 gram p-dichlorobenzene into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the p-dichlorobenzene. For coarse or granular materials, shake mechanically for 10-15 minutes or shake by hand intermittently for 25-30 minutes. (final conc 8.8 mg p-dichlorobenzene and 36 mg DDVP/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within approx. 10 minutes and peak heights of from 1/2 to 3/4 full scale. The elution time of p-dichlorobenzene is approx. 1.3 minutes and that of DDVP approx. 4.5 minutes.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of p-dichlorobenzene and DDVP from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

* PDB = p-dichlorobenzene in following calculation formulas

$$RF = \frac{(\text{wt. DDVP})(\%\text{ purity DDVP})(\text{pk. ht. or area PDB})}{(\text{wt. PDB})(\%\text{ purity PDB})(\text{pk. ht. or area DDVP})}$$

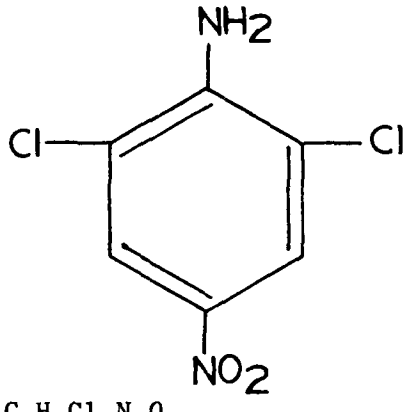
Determine the percent p-dichlorobenzene for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. DDVP})(\%\text{ purity DDVP})(\text{pk. ht. or area PDB})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area DDVP})(RF)} \quad (4-1)$$

Method submitted by Stelios Gerazounis, EPA Region II, New York, N. Y.

Determination of Dicloran in Dusts and Wettable Powder by Infrared Spectroscopy

Dicloran is the common name for 2,6-dichloro-4-nitroaniline, a registered fungicide having the chemical structure:



Molecular formula: $C_6H_4Cl_2N_2O_2$

Molecular weight: 207

Melting point: 192 to 194°C

Physical state, color, and odor: odorless, yellow crystalline solid; the technical product is brownish-yellow and is at least 90% pure.

Solubility: practically insoluble in water; slightly soluble in non-polar solvents; moderately soluble in polar solvents, e.g., acetone, 3.4 g/100 g at 20°C

Stability: stable to hydrolysis and to oxidation; non-corrosive; non-flammable; compatible with other pesticides

Other names: Allisan (Boots Company Ltd.), Botran (Upjohn Co.), DCNA, ditranil

Reagents:

1. Dicloran standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Ethyl ether, pesticide or spectro grade
4. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm KBr or NaCl cells
2. Mechanical shaker
3. Soxhlet extraction apparatus
4. Centrifuge or filtration apparatus
5. Rotary evaporator
6. Cotton or glass wool
7. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram dicloran standard into a small glass-stoppered flask or screw-cap bottle, add 25 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 4 mg/ml)

Preparation of Sample:

For high percent formulations (more than 10%), weigh a portion of sample equivalent to 0.2 gram dicloran into a glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 4 mg dicloran/ml)

For low percent (less than 10%) formulations, weigh a portion of sample equivalent to 0.2 gram dicloran into a Soxhlet extraction thimble, plug with cotton or glass wool, and extract with ethyl ether for 1-2 hours. Evaporate the ethyl ether

completely on a rotary evaporator. Dissolve the residue, transfer to a 50 ml volumetric flask, and make to volume with chloroform. Add a small amount of anhydrous sodium sulfate to clarify and dry the solution. (final conc 4 mg dicloran/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1250 cm^{-1} to 1042 cm^{-1} (8 μ to 9.6 μ).

Determine the absorbance of standard and sample using the peak at 1147 cm^{-1} (8.72 μ) and baseline from 1183 cm^{-1} to 1100 cm^{-1} (8.45 μ to 9.09 μ).

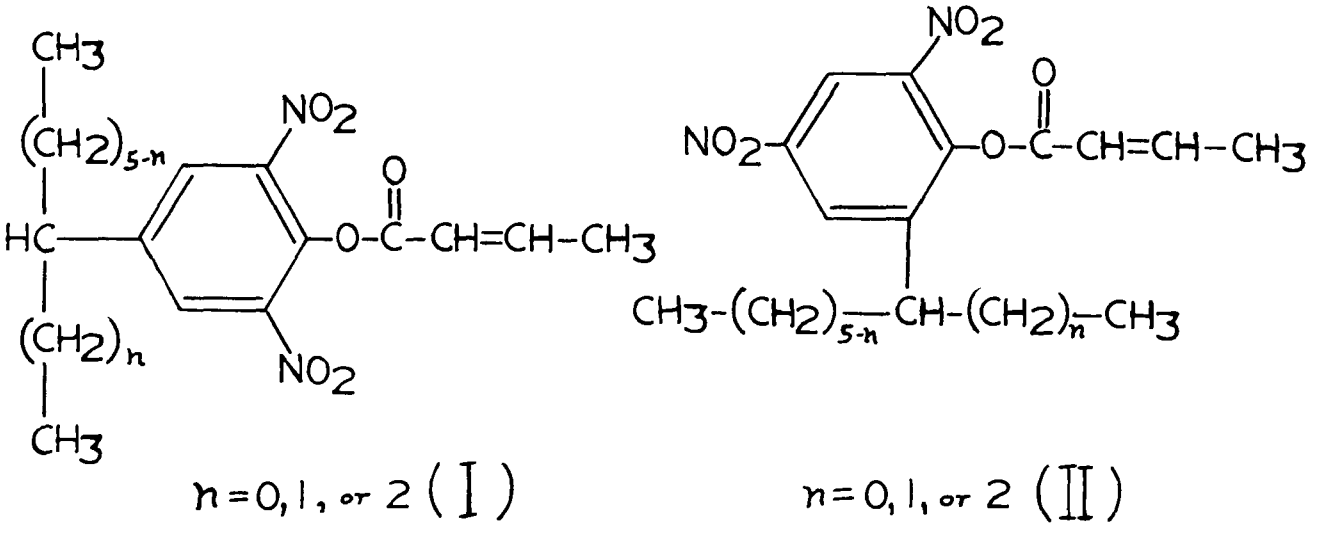
Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent dicloran as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Determination of Dinocap by Total Nitrogen Analysis

Dinocap is a common name for an isomeric mixture of 2,4-dinitro-6-octylphenyl crotonate (I) and 2,6-dinitro-4-octylphenyl crotonate (II), octyl being a mixture of 1-methylheptyl, 1-ethylhexyl, and 1-propylpentyl isomers. The chemical structures are:



n = 0, 1, or 2 (I) n = 0, 1, or 2 (II)

Dinocap is a registered acaricide and fungicide.

Molecular formula: $C_{18}H_{24}N_2O_6$

Molecular weight: 364

Boiling point: 138 to 140°C at 0.05 mm Hg

Physical state and color: dark brown liquid

Solubility: practically insoluble in water, soluble in most organic solvents

Stability: compatible with most other fungicides and insecticides but should not be used with oil-base sprays or with lime-sulfur

Other names: Karathane, Arathane (Rohm & Haas); Isocothan, Mildex

Principle of the Method:

Since the nitrogen is present in the nitro (oxidized) form, it must be converted to the amino (reduced) form before being determined by the regular Kjeldahl procedure. This is done by reacting the sample with salicylic acid and concentrated sulfuric acid to form nitro salicylic acid. The addition of a reducing agent such as zinc then reduces the nitro group to an amine group, forming amino salicylic acid. This compound is digested with boiling concentrated sulfuric acid in the presence of an oxidizing catalyst and forms ammonium sulfate from the amino-nitrogen. The solution is then made strongly alkaline and the released ammonia is distilled and absorbed in standard acid.

Reagents:

1. Concentrated sulfuric acid, reagent grade
2. Salicylic acid, reagent grade
3. Zinc dust, reagent grade
4. Mercuric oxide, red, reagent grade

   (Commercial packages called "Kel-pacs" are available containing various oxidizing catalysts and various amounts of potassium sulfate in small oxidizable plastic packets. One packet can be dropped into the flask, saving the weighing and transfer of the HgO and K_2SO_4.)
5. Potassium sulfate, reagent grade (see above)
6. Sodium or potassium sulfide, reagent grade
7. Granulated zinc, reagent grade

8. Kjeldahl sodium hydroxide solution (450 grams NaOH free from nitrates in one liter of water)
9. Phenolphthalein indicator solution
10. Sulfuric acid, 0.1N standard solution

    (An alternate procedure is to use 50 ml of a saturated boric acid solution that simply holds the ammonia which is titrated with standard acid. The procedure eliminates the need for standard alkali solution.)
11. Sodium hydroxide, 0.1N standard solution (see above)
12. Mixed methyl red indicator solution - dissolve 1.25 grams methyl red and 0.825 gram methylene blue in one liter of 90% ethyl alcohol. The color change is from purple in acid to green in basic solution.

Equipment:

1. 800 ml Kjeldahl flask
2. Kjeldahl digestion and distillation apparatus

    (Although a commercial Kjeldahl digestion and distillation apparatus is convenient, it is not essential. The digestion may be conducted over a flame in a hood while the distillation may utilize only a trap and condenser.)
3. Titration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Sample:

Most well mixed or homogeneous samples may be used directly for analysis; however, low percent formulations such as a 1% dust, or formulations containing any nitrogenous plant material should be extracted on a Soxhlet or by shaking with chloroform.

Reduction of NO_2 Group:

Weigh a portion of sample equivalent to 0.3-0.4 gram technical dinocap into an 800 ml Kjeldahl flask. Add 35 ml concentrated sulfuric acid containing 2 grams salicylic acid and allow to stand at least 30 minutes with frequent shaking.

Add 2 grams zinc dust slowly, shaking the contents of the flask during the addition. Heat over a low flame until frothing ceases, then heat until the acid boils briskly for about 5 minutes.

Digestion:

Add 0.7 gram mercuric oxide and 10 grams potassium sulfate (or one Kel-pac) and continue boiling until the liquid in the flask has been colorless for one hour. If the contents of the flask tend to become solid before this point is reached, add 10 ml more of sulfuric acid. To avoid decomposition of ammonium sulfate and subsequent loss of ammonia, do not allow the flame to reach any part of the flask not in contact with liquid. The flask may be lifted from the digestion rack and the acid swirled around the inside of the flask to wash undigested particles back into the acid. When digestion is complete, cool and add 200-300 ml water, making sure that the digestion mixture is completely dissolved.

Distillation:

Measure 50.00 ml of standard 0.1N sulfuric acid into a 500 ml Erlenmeyer wide-mouth flask, add several drops of mixed methyl red indicator solution, and place under the condenser of the distilling apparatus, making sure that the condenser tube extends beneath the surface of the acid in the flask. A glass tube attached by inert tubing to the condenser outlet tube is very convenient when later removing the receiving flask. If the indicator changes from acidic (purple) to basic (green), the determination must be repeated using less sample or more acid in the receiving flask.

Add 25 ml sodium or potassium sulfide solution and mix thoroughly; then add several pieces of granulated zinc.

(When using mercury as a catalyst, it must be precipitated with K or Na sulfide before the distillation process since it forms a complex substance with ammonia which is not readily decomposed by alkali.)

(Zinc in an alkaline solution slowly reacts to form a zincate and hydrogen: $Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2\uparrow$

This slow evolution of hydrogen keeps the solution stirred, thereby preventing superheating.

Pour about 110 ml of the Kjeldahl sodium hydroxide solution (or if extra acid was added, use 25 ml more alkali for each 10 ml acid added) slowly down the inclined neck of the flask so that it layers under the acid solution without mixing. A few drops of phenolphthalein may be added to be sure sufficient alkali is added to neutralize all the acid, remembering that a considerable excess of alkali will destroy the pink color.

Connect the flask to the condenser by means of a Kjeldahl connecting bulb, ignite the burner, and quickly mix the contents of the flask thoroughly with a rotary motion. It is advisable to begin the distillation with a small flame until the solution begins to boil; then increase the heat until the solution boils briskly. Distill 150-200 ml of the liquid (the first 150 ml usually contains all of the ammonia) into the receiving flask. Move the flask so that the tip of the delivery tube is above the level of the liquid and distill another 10 ml or so to wash the inside of the tube. Shut off heat, wash the outside of the delivery tube, and remove flask from apparatus.

Titration and Calculation:

Titrate the excess standard acid with standard 0.1N sodium hydroxide using mixed methyl red indicator. Reagents for this determination should be acid-free or a reagent blank should be run. Calculate the percent nitrogen as follows:

Using a blank:

$$\% = \frac{(\text{ml NaOH for blank} - \text{ml NaOH for sample})(\text{N of NaOH})(.01401)(100)}{(\text{grams of sample})}$$

Not using a blank:

$$\% = \frac{[(\text{ml } H_2SO_4)(\text{N of } H_2SO_4) - (\text{ml NaOH})(\text{N of NaOH})](.01401)(100)}{(\text{grams of sample})}$$

The % dinocap is found by dividing the percent nitrogen by the percent nitrogen in dinocap.

$$\% \text{ dinocap} = \frac{\% \text{ nitrogen in sample}}{6.6}$$

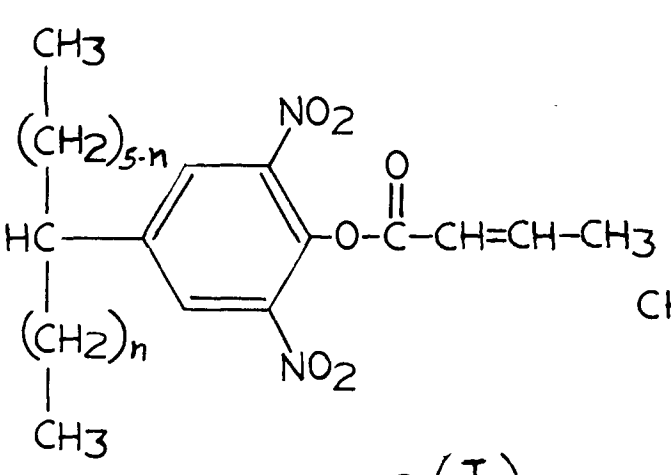
Technical dinocap contains from 6.6% to 7.2% nitrogen according to information received from the Rohm and Haas Company, March 1974.

January 1976

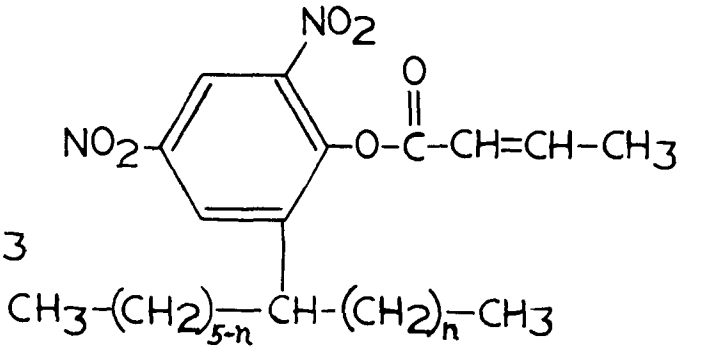
Dinocap EPA-2
(Tentative)

Determination of Dinocap by Infrared Spectroscopy

Dinocap is a common name for an isomeric mixture of 2,4-dinitro-6-octylphenyl crotonate (I) and 2,6-dinitro-4-octylphenyl crotonate (II), octyl being a mixture of 1-methylheptyl, 1-ethylhexyl, and 1-propylpentyl isomers. The chemical structures are:



n=0,1, or 2 (I)



n=0,1, or 2 (II)

Dinocap is a registered acaricide and fungicide.

Molecular formula: $C_{18}H_{24}N_2O_6$

Molecular weight: 364

Boiling point: 138 to 140°C at 0.05 mm Hg

Physical state and color: dark brown liquid

Solubility: practically insoluble in water, soluble in most organic solvents

Stability: compatible with most other fungicides and insecticides but should not be used with oil-base sprays or with lime-sulfur

Other names: Karathane, Arathane (Rohm & Haas); Isocothan, Mildex

Reagents:

1. Dinocap standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.1 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.1 gram dinocap standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg/ml)

Preparation of Sample:

For dusts, granules, and wettable powders, weigh a portion of sample equivalent to 0.5 gram dinocap into a 125 ml glass-stoppered or screw-cap Erlenmeyer flask. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly, shake on a mechanical shaker for 1 hour, allow to settle; filter or centrifuge if necessary, taking precaution to avoid evaporation. (final conc 10 mg dinocap/ml)

For emulsifiable concentrates and liquid formulations, weigh a portion of sample equivalent to 0.5 gram dinocap into a 125 ml glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and sufficient anhydrous sodium sulfate to clarify and dry the solution. Close tightly, shake a few minutes, add more sodium sulfate if needed, and shake vigorously on a mechanical shaker for one hour. Allow to settle; filter or centrifuge if necessary to get a clear chloroform solution, taking precaution to prevent evaporation. (final conc 10 mg dinocap/ml)

(There may be interference from the emulsifier in the sample; if so, another procedure must be used.)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings, scan both the standard and sample from 1430 cm^{-1} to 1250 cm^{-1} (7.0 μ to 8.0 μ).

Determine the absorbance of standard and sample using the peak at 1340 cm^{-1} (7.46 μ) and baseline from 1385 cm^{-1} to 1310 cm^{-1} (7.22 μ to 7.63 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent dinocap as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg dinocap/ml chloroform gives an absorbance of approx. 0.029 in a 0.1 mm cell.)

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

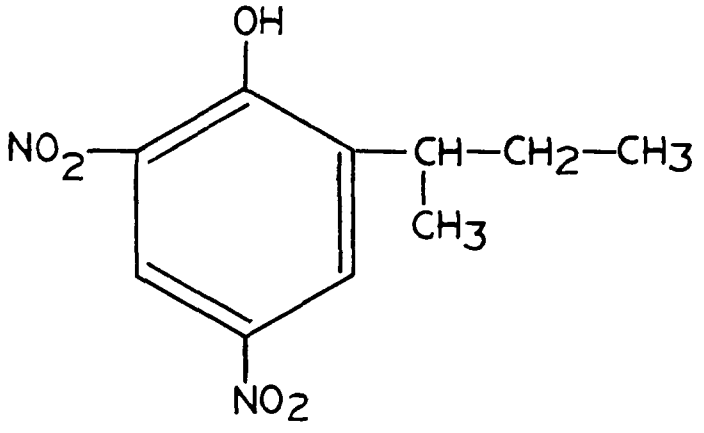
Note! This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Chemistry Lab. Any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated.

February 1976

Dinoseb EPA-1
(Tentative)

Determination of Dinoseb in Formulations by Infrared Spectroscopy

Dinoseb is the accepted common name for 2-sec-butyl-4,6-dinitrophenol, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_{12}N_2O_5$

Molecular weight: 240.2

Melting point: see below

Physical state, color, and odor: pure compound - yellow crystals mp 38 to 42°C; technical compound - orange-brown liquid of 95 to 98% purity and mp 30 to 40°C; pungent odor

Solubility: about 50 ppm in water; soluble in petroleum oils and most organic solvents; forms salts with inorganic and organic bases, some of which are water-soluble

Stability: corrosive to mild steel in the presence of water; combustible, flash point 177°C

Other names: Premerge (Dow), dinosebe (France), Bansanite, Chemox, Gebutox, DNBP, Dinitro, DN289, Kiloseb, Nitropone, Sinox

Reagents:

1. Dinoseb standard of known % purity
2. Carbon disulfide, ACS grade (or better)
3. Sulfuric acid, concentrated, ACS
4. Sodium hydroxide, 1% aqueous solution
5. Hydrochloric acid, concentrated, ACS
6. Ethyl ether, ACS (or better)
7. Sodium sulfate, anhydrous granular, ACS

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.1 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Water bath, 40°C, and a stream of dry air
5. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.1 gram dinoseb standard into a small glass-stoppered flask or screw-cap tube, add 10 ml carbon disulfide by pipette,

close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg/ml)

Preparation of Sample:

For oil solutions and emulsifiable concentrates, weigh a portion of sample equivalent to 0.5 gram dinoseb into a small glass-stoppered flask or screw-cap tube; add a few drops of concentrated sulfuric acid so that the sample is definitely acidic. Add 50 ml carbon disulfide by pipette, 1 gram anhydrous sodium sulfate, and shake on a mechanical shaker for several hours. Allow to settle; centrifuge or filter if necessary to get a clear solution. (conc 10 mg dinoseb/ml)

For liquid (water) formulations, weigh a portion of sample equivalent to 0.5 gram dinoseb (free phenol) into a small glass-stoppered flask or screw-cap tube, add by pipette 50 ml of 1% sodium hydroxide solution, and shake for one hour. Transfer a 25 ml aliquot (filter before aliquoting if necessary) to a 125 ml separatory funnel, dilute to 50 ml, and acidify with hydrochloric acid, adding several ml in excess. Extract with three 10 ml portions of carbon disulfide*, filtering each through a small cotton plug (moistened with carbon disulfide) into a 100 ml beaker. Evaporate to less than 25 ml and transfer quantitatively into a 25 ml volumetric flask. Make to volume and add a little anhydrous sodium sulfate to insure dryness. (final conc 10 mg dinoseb/ml)

* Ethyl ether is the recommended extraction solvent; however, it must be evaporated completely. The use of carbon disulfide has been suggested as an alternative procedure and if satisfactory is more convenient.

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings, scan both the standard and sample from 1430 cm^{-1} to 1280 cm^{-1} (7.0 μ to 7.8 μ).

Determine the absorbance of standard and sample using the peak at 1340 cm^{-1} (7.46 μ) and baseline 1390 cm^{-1} to 1290 cm^{-1} (7.19 μ to 7.75 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent dinoseb as follows:

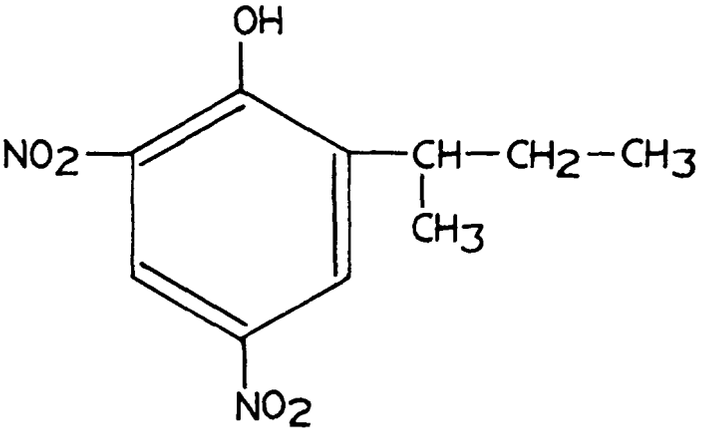
$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

This method has been given a tentative designation because of the alternative use of carbon disulfide instead of ethyl ether as extraction solvent.

Determination of Dinoseb in Formulations by Gas-Liquid Chromatography - TCD

Dinoseb is the accepted common name for 2-sec-butyl-4,6-dinitrophenol, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_{12}N_2O_5$

Molecular weight: 240.2

Melting point: see below

Physical state, color, and odor: pure compound - yellow crystals mp 38 to 42°C; technical compound - orange-brown liquid of 95 to 98% purity and mp 30 to 40°C; pungent odor

Solubility: about 50 ppm in water; soluble in petroleum oils and most organic solvents; forms salts with inorganic and organic bases, some of which are water-soluble

Stability: corrosive to mild steel in the presence of water; combustible, flash point 177°C

Other names: Premerge (Dow), dinosebe (France), Bansanite, Chemox, Gebutox, DNBP, Dinitro, DN289, Kiloseb, Nitropone, Sinox

Reagents:

1. Dinoseb standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sulfuric acid, concentrated, ACS
4. Sodium hydroxide, 1% aqueous solution
5. Hydrochloric acid, concentrated, ACS

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 5' x 1/4" glass column packed with 20% SE-30 on Chromosorb W, AW, DMCS (or equivalent column)
3. Precision liquid syringe: 50 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	220°C
Injection temperature:	250°C
Detector temperature:	250°C
Carrier gas:	Helium
Flow rate:	adjusted

Operating conditions for filament current, column temperature, or gas flow should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.15 gram dinoseb standard into a 10 ml volumetric flask; dissolve and make to volume with chloroform. (final conc 15 mg/ml)

Preparation of Sample:

For oil solutions and emulsifiable concentrates, weigh a portion of sample equivalent to 0.75 gram dinoseb into a small glass-stoppered flask or screw-cap tube; add a few drops of concentrated sulfuric acid so that the sample is definitely acidic. Add 50 ml chloroform by pipette, and shake on a mechanical shaker for several hours. Allow to settle; centrifuge or filter if necessary to get a clear solution. (conc 15 mg dinoseb/ml)

For liquid (water) formulations, weigh a portion of sample equivalent to 0.75 gram dinoseb (free phenol) into a small glass-stoppered flask or screw-cap tube, add by pipette 50 ml of 1% sodium hydroxide solution, and shake for one hour. Transfer a 25 ml aliquot (filter before aliquoting if necessary) to a 125 ml separatory funnel, dilute to 50 ml, and acidify with hydrochloric acid, adding several ml in excess. Extract with three 10 ml portions of chloroform, filtering each through a small cotton plug (moistened with chloroform) into a 100 ml beaker. Evaporate to less than 25 ml, transfer quantitatively into a 25 ml volumetric flask, and make to volume. (final conc 15 mg dinoseb/ml)

Determination:

Using a precision liquid syringe, alternately inject three 30-40 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent butylate as follows:

$$\% = \frac{\text{(pk. ht. or area sample)(wt. std injected)(\% purity of std)}}{\text{(pk. ht. or area standard)(wt. sample injected)}}$$

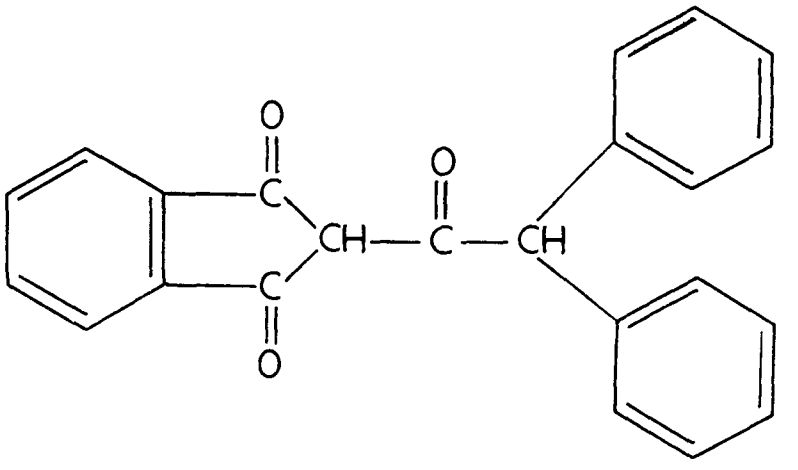
This method is based on a GLC method submitted by Eva Santos, EPA Region IX, San Francisco, California. The sample preparation is basically like that of Dinoseb EPA-1 IR method. Any suggestions, data, criticism, or comments about this method are most welcome.

July 1977 (U-1)
~~November 1975~~

Diphacinone EPA-1
(tentative) (U-1)

Determination of Diphacinone in Baits by Ultraviolet Spectroscopy

Diphacinone is the accepted common name for 2-(diphenylacetyl)-1,3-indandione, a registered rodenticide having the chemical structure:



Molecular formula: $C_{23}H_{16}O_3$

Molecular weight: 340.4

Melting point: 145°C

Physical state, color, and odor: yellow, odorless crystals

Solubility: slightly soluble in water and benzene; soluble in acetone and acetic acid. Forms a sodium salt which is sparingly soluble in water.

Stability: resists hydrolysis; stable toward mild oxidants; non-corrosive

Other names: Diphacin (Velsicol Chem. Corp.), diphacin (Turkey), Ramik, diphenadione

This method is suitable for products containing about 0.005% diphacinone. Although the absorption curves for diphacinone and pindone are similar, in the absence of strong interference, diphacinone can be identified by a maximum at 286 nm and pindone by a maximum at 283 nm.

Reagents:

1. Diphacinone standard of known % purity
2. Sodium pyrophosphate solutions, 1% and 2% - weigh 5.0 grams for 1% solution and 10.0 grams for 2% solution into a 500 ml volumetric flask; dissolve in and make to volume with distilled water (heating on a steam bath may be required for complete solution).
3. Ethyl ether, pesticide grade
4. Hexane, pesticide grade
5. Ethyl ether-hexane mixture - extract 200 ml hexane with three 20 ml portions of 1% sodium pyrophosphate solution. Prepare mixture by adding 20 ml ethyl ether to each 80 ml extracted hexane.
6. Hydrochloric acid, 50% solution - add 50 ml hydrochloric acid (specific gravity 1.19) to 50 ml distilled water.
7. Methanol, pesticide grade
8. Acidification Solution - mix equal volumes of methanol and 50% hydrochloric acid.

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm silica cells
2. Micro-mill or any suitable device for grinding or pulverizing sample
3. Bottles with teflon-lined or polyethylene screw caps in 2 oz, 4 oz, and 8 oz sizes
4. Mechanical shaker (wrist action preferred)

5. Centrifuge for bottles and 15-20 ml tubes
6. Syringe, 5 ml capacity with 4-inch needle
7. Usual laboratory glassware

Procedure:

Preparation of Standard:

Prepare a stock standard solution by weighing 0.04 gram diphacinone into a 100 ml volumetric flask; dissolve in and make to volume with 1% sodium pyrophosphate solution; mix well.

For a working standard solution, pipette 1 ml of the stock standard solution into a 100 ml volumetric flask and make to volume with 1% sodium pyrophosphate solution; mix well. (final conc 4 µg diphacinone/ml)

Pipette 25 ml of this working solution into a 4 oz screw-cap bottle and add 10 ml acidification solution. By pipette, add 50 ml ether-hexane solution and close tightly. Proceed as under Determination.

Preparation of Sample:

Weigh a portion of well-ground and mixed sample equivalent to 0.2 mg diphacinone into an 8 oz screw-cap bottle. (Sufficient sample should be weighed to yield 4 µg/ml in the final test solution. This is equivalent to 4 grams of 0.005% product or 0.8 gram of 0.025% product.)

Add 20 ml acidification solution; swirl and mix thoroughly for 2-3 minutes. Pipette 100 ml of the ether-hexane solution over the acidified sample and close tightly. Proceed as under Determination.

Determination:

Place standard and sample on a mechanical shaker (wrist action preferred) and shake vigorously for one hour. Allow to settle; transfer a 30 ml aliquot by pipette into a 2 oz screw-cap bottle. Add by pipette 15 ml 2% sodium pyrophosphate solution, close tightly, and shake on shaker for three minutes. Transfer to a 125 ml separatory funnel and separate the aqueous (bottom) layer into a 15-20 ml centrifuge tube. Centrifuge unstoppered (approx. 3400 RPM) for about 15 minutes, checking intermittently. Solution must be clear.

Sample solutions will have a narrow suspended emulsion layer. This layer may be drawn off using an aspirator fitted with a glass tube drawn into a fine tip; or, the clear solution below may be drawn into a 5 ml syringe through the emulsion layer with a four-inch needle.

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen at 0 and 100% transmission at 286 nm with 1% sodium pyrophosphate in each cell. Scan the standard and sample solutions from 360 nm to 200 nm with 1% sodium pyrophosphate solution in the reference cell. (Distilled water may be used as reference if desired.)

Calculations:

Measure the absorbance of standard and sample at 286 nm and calculate the percent diphacinone as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. standard in } \mu g/ml)(\% \text{ purity standard})}{(\text{abs. standard})(\text{conc. sample in } \mu g/ml)}$$

This method is basically method AM 0556, Velsicol, Analytical Research Division, Chicago, Illinois 60611, and is used with their permission.

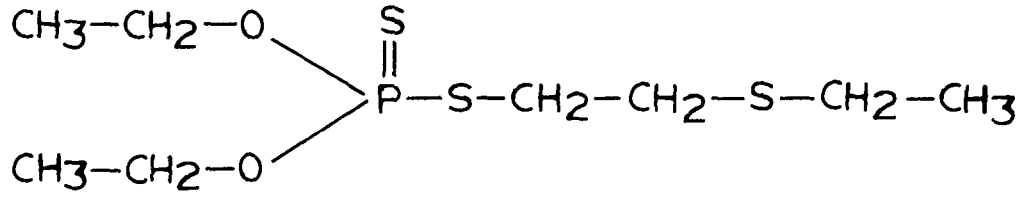
This method has been used successfully by EPA's New York and Beltsville Chemical Laboratories. A few changes in volume of aliquots were made for more convenience, and the basic format was changed to conform with the standard format of methods in this manual.

Some commercial products may present problems with this method because of interfering substances, but for most products this method has been found satisfactory.

Comments, criticisms, suggestions, etc. will be appreciated.

Determination of Disulfoton by Infrared Spectroscopy

Disulfoton is the common name for O,O-diethyl S-[2-(ethylthio) ethyl] phosphorodithioate, a registered insecticide and acaricide having the chemical structure:



Molecular formula: $C_8H_{19}O_2PS_3$

Molecular weight: 274.2

Boiling point: 62°C at 0.01 mm Hg

Physical state, color, and odor: colorless, oily liquid with a characteristic odor of sulfur compounds; the technical product is a dark yellowish oil.

Solubility: 25 ppm in water at RT; readily soluble in most organic liquids

Stability: relatively stable to hydrolysis below pH 8.0

Other names: Disyston (Di-Syston in US), Dithio-systox, S-276, Bayer 19639, (Bayer AG); thiodemeton; M-74 (USSR); Frumin AL; Solvirex

Reagents:

1. Disulfoton standard of known % purity
2. Carbon disulfide, pesticide or spectro grade
3. Acetone, pesticide or spectro grade (dried over sodium sulfate)
4. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm KBr cells (NaCl useful transmission up to 16 μ)
2. Mechanical shaker
3. Rotary evaporator
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.125 gram disulfoton standard into a 25 ml volumetric flask, dissolve in, and make to volume with carbon disulfide. Add a small amount of granular anhydrous sodium sulfate and shake. (final conc 5 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.5 gram disulfoton into a glass-stoppered or screw-capped 250 ml Erlenmeyer flask. Add, by pipette, 100 ml of mixed solvent (9+1 carbon disulfide + dry acetone), and shake on a mechanical shaker for one hour. (Be careful to avoid any loss of solvent around ground glass joint or screw cap.) Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. Pipette 25 ml into a standard taper 125 ml Erlenmeyer flask and evaporate on a rotary

evaporator to just dryness. Add 5 ml carbon disulfide and again evaporate to dryness. Dissolve in, quantitatively transfer to a 25 ml volumetric flask, and make to volume with carbon disulfide. Add a small amount of granular anhydrous sodium sulfate and shake. (final conc 5 mg disulfoton/ml)

IR Determination:

With carbon disulfide in the reference cell and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample solutions from 740 cm^{-1} to 590 cm^{-1} (13.5 μ to 17.0 μ). For a qualitative comparison, run a full scan.

Calculation:

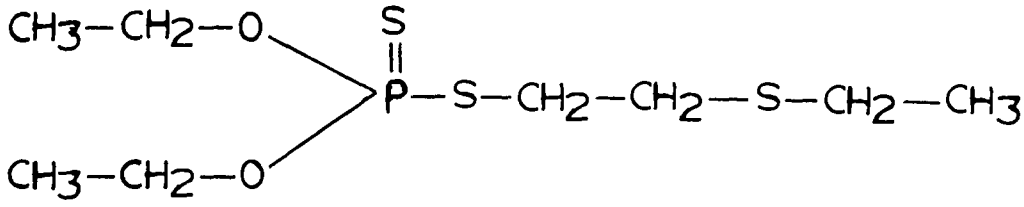
Measure the absorbance of standard and sample at 667 cm^{-1} (15.0 u) using a baseline from 730 cm^{-1} to 633 cm^{-1} (13.7 μ to 15.8 μ).

$$\% \text{ Disulfoton} = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Method submitted by Dean Hill, EPA Region IX, San Francisco, Calif.

Determination of Disulfoton by Gas-Liquid Chromatography (FID - Internal Standard)

Disulfoton is the common name for O,O-diethyl S-[2-(ethylthio) ethyl] phosphorodithioate, a registered insecticide and acaricide having the chemical structure:



Molecular formula: $C_8H_{19}O_2PS_3$

Molecular weight: 274.2

Boiling point: 62°C at 0.01 mm Hg

Physical state, color, and odor: colorless, oily liquid with a characteristic odor of sulfur compounds; the technical product is a dark yellowish oil.

Solubility: 25 ppm in water at RT; readily soluble in most organic liquids

Stability: relatively stable to hydrolysis below pH 8.0

Other names: Disyston (Di-Syston in US), Dithio-systox, S-276, Bayer 19639, (Bayer AG); thiodemeton; M-74 (USSR); Frumin AL; Solvirex

Reagents:

1. Disulfoton standard of known % purity
2. Alachlor standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.25 gram alachlor standard into a 100 ml volumetric flask, dissolve in, and make to volume with acetone. (conc 2.5 mg alachlor/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm I.D. glass, packed with 5% SE-30 80/100 mesh Chromosorb W HP (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	190°C
Injection temperature:	240°C
Detector temperature:	240°C
Carrier gas:	Nitrogen
Carrier gas flow rate:	adjusted for specific GC
Hydrogen flow rate:	adjusted for specific GC
Air flow rate:	adjusted for specific GC

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram disulfoton standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 2.5 mg disulfoton and 2.5 mg alachlor/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.05 gram disulfoton into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the disulfoton. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 2.5 mg disulfoton and 2.5 mg alachlor/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is disulfoton, then alachlor.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of disulfoton and alachlor from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. alachlor})(\%\text{ purity alachlor})(\text{pk. ht. or area disulfoton})}{(\text{wt. disulfoton})(\%\text{ purity disulfoton})(\text{pk. ht. or area alachlor})}$$

Determine the percent disulfoton for each injection of the sample-internal standard solution as follows and calculate the average:

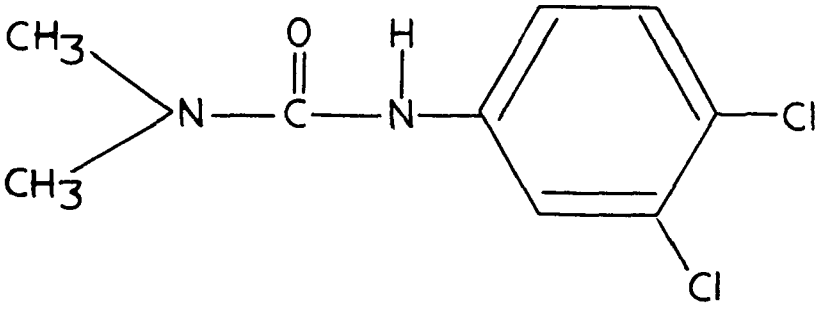
$$\% = \frac{(\text{wt. alachlor})(\%\text{ purity alachlor})(\text{pk. ht. or area disulfoton})(100)}{(\text{wt. sample})(\text{pk. ht. or area alachlor})(RF)}$$

Method submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Note! This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Chemistry Laboratory. Any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated.

Determination of Diuron by Alkaline Hydrolysis and Titration

Diuron is the common name for 3-(3,4-dichlorophenyl)-1,1-dimethyl-urea, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{10}Cl_2N_2O$

Molecular weight: 233.1

Melting point: 158 to 159°C

Physical state, color, and odor: Odorless, white, crystalline solid

Solubility: 42 ppm in water at 25°C; slightly soluble in hydrocarbons, about 5.3% in acetone at 27°C

Stability: decomposes at 180-190°C; non-corrosive; stable at ordinary temp. to oxidation and moisture, hydrolyzes at higher temp. and more acid or alkaline conditions

Other names: Karmex (DuPont), Di-on, Diurex, Vonduron, dichlorfenidim

Principle of the Method:

The diuron is hydrolyzed to 3,4-dichloroaniline, carbon dioxide (as carbonate), and dimethylamine. The dimethylamine is distilled and titrated. Volatile, moderately strong bases, or substances that hydrolyze to give them, interfere.

Reagents:

1. Potassium hydroxide, 20% solution
2. Hydrochloric acid, 0.1N standard solution
3. Sodium hydroxide, 0.1N standard solution
4. Ethyl alcohol, ACS
5. Glycerol, ACS

Equipment:

1. Distilling apparatus consisting of a 500 ml round-bottom flask with a thermometer well in the side and a 24/40 standard taper (ST) joint at the top. The flask is connected to the bottom of a vertical condenser which has its top connected to the top of a second vertical condenser by a horizontal tube with a right angle 24/40 ST joint on each end. The bottom of the second condenser is connected by 24/40 ST joint to the top of a delivery tube which has a narrow plain end extending almost to the bottom of a receiving beaker.
2. 500 ml size heating mantle with variable transformer control
3. Thermometer to 200°C
4. Potentiometric titrimeter
5. Usual laboratory glassware

Procedure:

Weigh a portion of sample equivalent to 0.4-0.5 gram diuron into the reaction flask, dissolve in 25 ml ethyl alcohol, and add 100 ml glycerol and 100 ml 20% potassium hydroxide solution. Attach immediately to the first condenser.

Pipette 50 ml of the 0.1N standard hydrochloric acid into the receiving beaker. Reflux at a moderate rate for 2-1/2 hours with water flowing through both condensers. Remove the water from the first condenser and distill until the temperature at the thermometer well reaches 175°C -- usually about 50 minutes. (The temperature rises rapidly at the end.)

Titration:

Remove the delivery tube and receiving beaker and rinse the delivery tube into the beaker. Titrate the excess standard acid with the 0.1N standard sodium hydroxide potentiometrically, using a glass electrode and a calomel electrode. The inflection point, which occurs at about pH 7.6, is taken as the endpoint.

With less accuracy, bromthymol blue may be used as an internal indicator.

Calculation:

Calculate the percentage of diuron as follows:

$$\% = \frac{(ml)(N)(.2331)(100)}{(g \text{ sample})}$$

where: .2331 is the milliequivalent weight of diuron

(1 ml 0.1N HCl = 0.02331 g diuron)

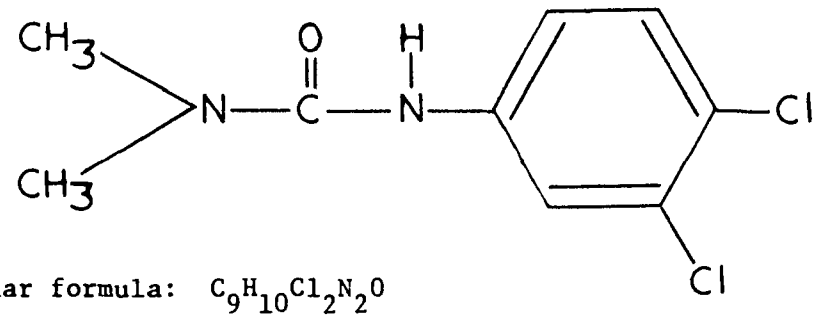
This method is based on Lowen and Baker, Anal. Chem. 24, 1475 (1952).

July 1975

Diuron EPA-2
(Tentative)

Determination of Diuron by High Pressure Liquid Chromatography

Diuron is the common name for 3-(3,4-dichlorophenyl)-1,1-dimethyl-urea, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{10}Cl_2N_2O$

Molecular weight: 233.1

Melting point: 158 to 159°C

Physical state, color, and odor: Odorless, white, crystalline solid

Solubility: 42 ppm in water at 25°C; slightly soluble in hydrocarbons, about 5.3% in acetone at 27°C

Stability: decomposes at 180-190°C; non-corrosive; stable at ordinary temp. to oxidation and moisture, hydrolyzes at higher temp. and more acid or alkaline conditions

Other names: Karmex (DuPont), Di-on, Diurex, Vonduron, dichlorfenidim

Reagents:

1. Diuron standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Methanol, pesticide or spectro grade

Equipment:

1. High pressure liquid chromatograph
2. High pressure liquid syringe or sample injection loop
3. Liquid chromatographic column 4 mm x 25 cm packed with Vydac Reverse Phase Hydrocarbon
4. Usual laboratory glassware

Operating conditions for Hewlett-Packard Model 1010B LC:

Mobile phase: 80% methanol + 20% water

Column temperature: ambient

Observed column pressure: 30-40 kg/cm^2 (425-570 PSI)

Flow rate: 3 ml/min

Detector: UV at 254 nm

Chart speed: 0.5 in/min

Injection: 10 µl

Conditions may have to be varied by the analyst for other instruments, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.02 gram diuron standard into a 100 ml volumetric flask; dissolve and make to volume with chloroform (final conc 0.2 mg/ml).

Preparation of Sample:

Weigh an amount of sample equivalent to 0.2 gram diuron in a 125 ml screw-cap Erlenmeyer flask, add 50 ml chloroform by pipette, close tightly, and shake for one hour. Let stand for 30 minutes or until clear (filter or centrifuge if necessary). Pipette 5 ml of the clear supernatant liquid into a 100 ml volumetric flask. Make to volume with chloroform and mix thoroughly (final conc 0.2 mg diuron/ml).

Determination:

Alternately inject three 10 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent diuron as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

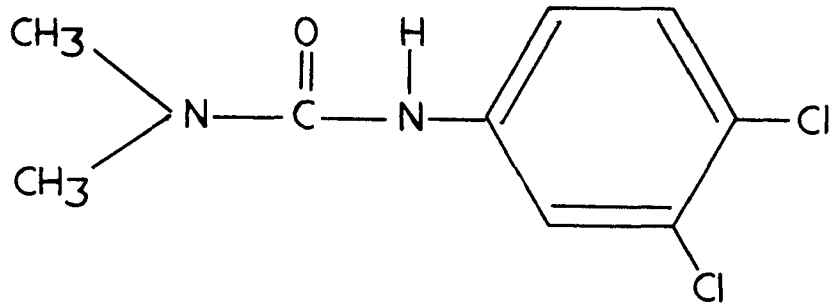
Method developed by Joseph B. Audino, Supervisor, Pesticide Formulation Laboratory, California Department of Food and Agriculture; and by Hoshihiko Kawano, Associate Chemist on sabbatical leave from the University of Hawaii.

November 1975

Diuron **EPA-3**
(Tentative)

Determination of Diuron by Ultraviolet Spectroscopy

Diuron is the common name for 3-(3,4-dichlorophenyl)-1,1-dimethyl-urea, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{10}Cl_2N_2O$

Molecular weight: 233.1

Melting point: 158 to 159°C

Physical state, color, and odor: Odorless, white, crystalline solid

Solubility: 42 ppm in water at 25°C; slightly soluble in hydrocarbons, about 5.3% in acetone at 27°C

Stability: decomposes at 180-190°C; non-corrosive; stable at ordinary temp. to oxidation and moisture, hydrolyzes at higher temp. and more acid or alkaline conditions

Other names: Karmex (DuPont), Di-on, Diurex, Vonduron, dichlorfenidim

Reagents:

1. Diuron standard of known % purity
2. Methanol, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm silica cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram diuron standard into a 100 ml volumetric flask, add 100 ml methanol by pipette, and mix thoroughly. Pipette 10 ml into a second 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette 5 ml into a third 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. (final conc 5 µg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram diuron into a 250 ml glass-stoppered or screw-cap flask, add 100 ml methanol by pipette, and shake on a mechanical shaker for 30 minutes. Allow to settle; centrifuge or filter if necessary, taking precautions to prevent evaporation. Pipette 10 ml into a 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette 5 ml of this solution into another 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. (final conc 5 µg diuron/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen at 0 and 100% transmission at 248 nm with

methanol in each cell. Scan both the standard and sample from 300 nm to 200 nm with methanol in the reference cell.

Measure the absorbance of standard and sample using the peak at 248 nm and a basepoint at 280 nm.

The absorbance is linear from 1 to 8 µg/ml.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent diuron as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

Method submitted by Mark Law, EPA, Beltsville Chemistry Laboratory, Beltsville, Md.

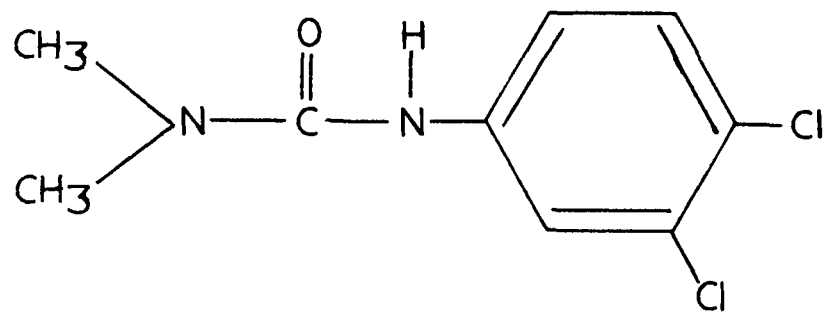
(This method is based on Monuron EPA-2.)

November 1975

Diuron EPA-4
(Tentative)

Determination of Diuron by Infrared Spectroscopy

Diuron is the common name for 3-(3,4-dichlorophenyl)-1,1-dimethyl-urea, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{10}Cl_2N_2O$

Molecular weight: 233.1

Melting point: 158 to 159°C

Physical state, color, and odor: odorless, white, crystalline solid

Solubility: 42 ppm in water at 25°C; slightly soluble in hydrocarbons, about 5.3% in acetone at 27°C

Stability: decomposes at 180-190°C; non-corrosive; stable at ordinary temp. to oxidation and moisture, hydrolyzes at higher temp. and more acid or alkaline conditions

Other names: Karmex (DuPont), Di-on, Diurex, Vonduron, dichlorfenidim

Reagents:

1. Diuron standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm KBr or NaCl cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.06 gram diuron standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 6 mg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.3 gram diuron into a glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precautions to prevent evaporation. (final conc 6 mg diuron/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings, scan both the standard and sample from 1500 cm^{-1} to 1300 cm^{-1} (6.67 μ to 7.7 μ).

Determine the absorbance of standard and sample using the peak at 1353 cm^{-1} (7.39 μ) and baseline from 1399 cm^{-1} to 1316 cm^{-1} (7.15 μ to 7.60 μ).

The absorbance is linear from 1 to 10 mg/ml.

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent diuron as follows:

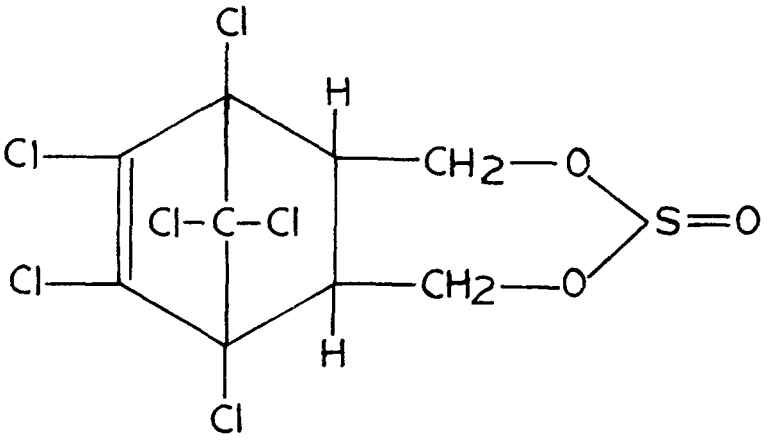
$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Method submitted by Mark Law, EPA, Beltsville Chemistry Laboratory, Beltsville, Md.

(This method is based on Monuron EPA-3.)

Determination of Endosulfan by Alkaline Hydrolysis

Endosulfan is the accepted common name for hexachlorohexahydro-methano-2,4,3-benzodioxathiepin-3-oxide, a registered pesticide having the chemical structure:



Molecular formula: $C_9H_6Cl_6O_3S$

Molecular weight: 406.9

Melting point: (see below)

Physical state, color, and odor: endosulfan is an odorless white crystalline solid mixture of two isomers with mp's of 106°C and 212°C; the technical product is a brownish crystalline solid, mp 70-100°C, with a 4:1 ratio of the above isomers. Both isomers are insecticidally active.

Solubility: practically insoluble in water, but soluble in most organic solvents

Stability: generally quite stable; decomposition catalyzed by iron; slowly hydrolyzed by water; sensitive to acid and bases; compatible with non-alkaline pesticides

Other names: Thiodan (Farwerke Hoechst), Beosit, Chlorthiepin, Cyclodan, Insectophene, Kop-Thiodan, Malix, Thifor, Thimul, Thionex, HOE 2671, NIA 5462, FMC 5462

Principle of the Method:

This determination is based on the alkaline hydrolysis of endosulfan to give sodium sulfite, which is reacted with an excess of acidified standard iodine solution. The excess iodine solution is titrated with standard sodium thiosulfate solution and the amount of endosulfan is calculated from the amount of iodine used by the sodium sulfite.

Reagents:

1. Methanol, ACS
2. n-Hexane, ACS
3. Sodium hydroxide pellets, ACS
4. Sulfuric acid solution, 1 + 4
5. Sodium hydroxide solution, 1 + 9
6. Phenolphthalein solution, 1% in alcohol
7. Standard 0.1N iodine solution
8. Standard 0.1N sodium thiosulfate solution
9. Starch solution, 0.2%

Equipment:

1. Iodine titration flasks
2. Refluxing apparatus
3. Mechanical shaker
4. Usual laboratory glassware

Procedure:

Preparation of Sample:

For liquid formulations and technical endosulfan, weigh a portion of sample equivalent to 0.2-0.3 gram of endosulfan into a standard taper 250 ml Erlenmeyer flask. Add 100 ml methanol and proceed directly with the hydrolysis.

For dusts and granules, weigh a portion of sample equivalent to 0.4-0.6 gram of endosulfan into a screw-capped or glass-stoppered flask, add 100 ml methanol, and shake for 15 minutes. Pipette 50 ml of clear liquid into a 250 ml standard taper Erlenmeyer flask, add an additional 50 ml methanol, and proceed with the hydrolysis.

If the methanol extract is highly colored, repeat the extraction on another portion of sample using hexane. Pipette 50 ml of the clear extract into a 250 ml standard taper Erlenmeyer flask, evaporate the hexane to near dryness over a hot water bath in a hood, cool, and add 100 ml methanol and proceed with the hydrolysis.

Hydrolysis:

Add 2-3 grams (15 pellets) of sodium hydroxide to the methanol solution of the sample and reflux gently for two hours. Wash down the condenser with 20 ml methanol and then with 50 ml distilled water. Remove from condenser, add a few drops of phenolphthalein solution, neutralize with 1 + 4 sulfuric acid solution to just colorless, and restore color with 1 + 9 sodium hydroxide to prevent loss of sulfite as SO_2.

Titration:

Add 40 ml of standard 0.1N iodine solution to a 500 ml glass-stoppered iodine flask using a pipette or burette, acidify with 1 ml 1 + 4 sulfuric acid, and while stirring with a magnetic stirrer, add the sulfite solution slowly. Rinse the flask with several small portions of distilled water until all the sulfite is transferred; the washing is complete when there is insufficient sulfite left in the flask to bleach one drop of 0.1N iodine solution. The final volume in the flask should be about 225-250 ml.

Titrate the excess iodine with standard 0.1N sodium thiosulfate solution using 10 ml 0.2% starch solution as indicator and titrating to the disappearance of the blue color.

Run a blank titration on 40 ml of standard 0.1N iodine solution using 175 ml distilled water and 1 ml 1 + 4 sulfuric acid.

Calculation:

The molecular weight of endosulfan is 406.95 and the milli-equivalent weight is 0.2305.

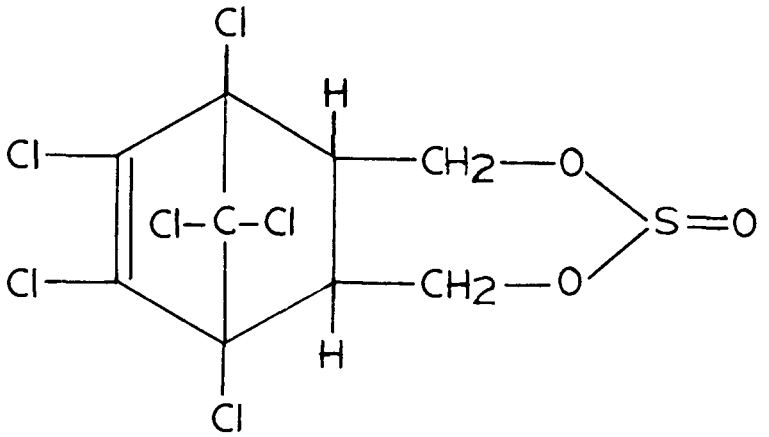
Net ml $Na_2S_2O_3$ used = ml $Na_2S_2O_3$ for blank - ml $Na_2S_2O_3$ for sample

$$\% \text{ endosulfan} = \frac{(\text{net ml } Na_2S_2O_3)(\text{N of } Na_2S_2O_3)(.2035)(100)}{(\text{grams of sample})(50/100 \text{ see note})}$$

Note: The factor (50/100) is not used for liquid formulations or technical endosulfan.

Determination of Endosulfan by Infrared Spectroscopy

Endosulfan is the accepted common name for hexachlorohexahydro-methano-2,4,3-benzodioxathiepin-3-oxide, a registered pesticide having the chemical structure:



Molecular formula: $C_9H_6Cl_6O_3S$

Molecular weight: 406.9

Melting point: (see below)

Physical state, color, and odor: endosulfan is an odorless white crystalline solid mixture of two isomers with mp's of 106°C and 212°C; the technical product is a brownish crystalline solid, mp 70-100°C, with a 4:1 ratio of the above isomers. Both isomers are insecticidally active.

Solubility: practically insoluble in water, but soluble in most organic solvents

Stability: generally quite stable; decomposition catalyzed by iron; slowly hydrolyzed by water; sensitive to acid and bases; compatible with non-alkaline pesticides

Other names: Thiodan (Farwerke Hoechst), Beosit, Chlorthiepin, Cyclodan, Insectophene, Kop-Thiodan, Malix, Thifor, Thimul, Thionex, HOE 2671, NIA 5462, FMC 5462

Reagents:

1. Endosulfan standard of known % purity
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm NaCl or KBr cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.06 gram endosulfan into a small glass-stoppered flask or screw-cap bottle, add 10 ml carbon disulfide by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 6 mg/ml)

Preparation of Sample:

For emulsifiable concentrates, weigh a portion of sample equivalent to 0.06 gram endosulfan into a 10 ml volumetric flask, make to volume with carbon disulfide, and mix well. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 6 mg endosulfan/ml)

For granular formulations, weigh a portion of sample equivalent to 0.3 gram endosulfan into a glass-stoppered flask or screw-cap bottle. Add 50 ml carbon disulfide by pipette and 1-2 grams anhydrous sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 6 mg endosulfan/ml)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan the standard and sample from 1250 cm^{-1} to 1110 cm^{-1} (8 μ to 9 μ).

Determine the absorbance of standard and sample using the peak at 1192 cm^{-1} (8.39 μ) and baseline from 1205 cm^{-1} to 1176 cm^{-1} (8.3 μ to 8.5 μ).

Calculation:

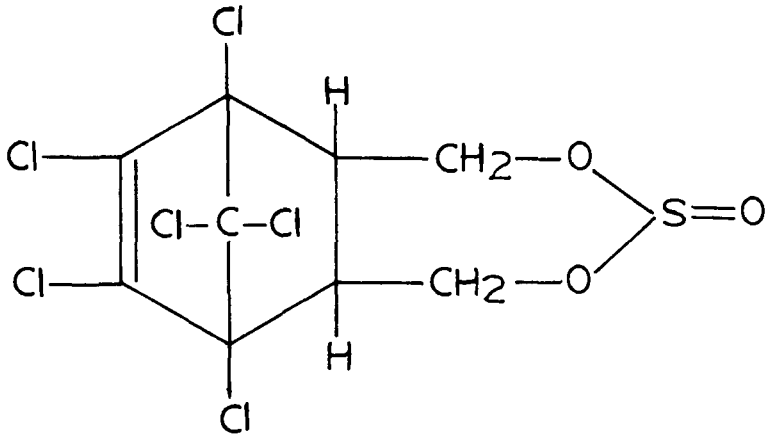
From the above absorbances and using the standard and sample concentrations, calculate the percent endosulfan as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Method submitted by M. Frost and M. Conti, EPA Region IX, San Francisco, California.

Determination of Endosulfan by Gas-Liquid Chromatography (TCD - Internal Standard)

Endosulfan is the accepted common name for hexachlorohexahydro-methano-2,4,3-benzodioxathiepin-3-oxide, a registered pesticide having the chemical structure:



Molecular formula: $C_9H_6Cl_6O_3S$

Molecular weight: 406.9

Melting point: (see below)

Physical state, color, and odor: endosulfan is an odorless white crystalline solid mixture of two isomers with mp's of 106°C and 212°C; the technical product is a brownish crystalline solid, mp 70-100°C, with a 4:1 ratio of the above isomers. Both isomers are insecticidally active.

Solubility: practically insoluble in water, but soluble in most organic solvents

Stability: generally quite stable; decomposition catalyzed by iron; slowly hydrolyzed by water; sensitive to acid and bases; compatible with non-alkaline pesticides

Other names: Thiodan (Farwerke Hoechst), Beosit, Chlorthiepin, Cyclodan, Insectophene, Kop-Thiodan, Malix, Thifor, Thimul, Thionex, HOE 2671, NIA 5462, FMC 5462

Reagents:

1. Endosulfan standard of known % purity
2. Aldrin standard of known HHDN content
3. Acetone, pesticide or spectro grade (chloroform could also be used)
4. Internal Standard solution - weigh 0.1 gram HHDN into a 50 ml volumetric flask; dissolve in and make to volume with acetone. (conc 2 mg HHDN/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 6' x 1/8" ID SS packed with 10% SE-30 on 60/80 mesh Diatoport S (or equivalent column)
3. Precision liquid syringe - 10 or 25 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	230°C
Injection temperature:	260°C
Detector temperature:	260°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas pressure:	30-40 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.08 gram endosulfan standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 4 mg endosulfan and 2 mg HHDN/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.08 gram endosulfan into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the endosulfan. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 4 mg endosulfan and 2 mg HHDN/ml)

Determination:

Inject 10-15 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is HHDN, then endosulfan.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of endosulfan and ~~dieldrin~~ HHDN from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. HHDN})(\%\text{ purity HHDN})(\text{pk. ht. or area endosulfan})}{(\text{wt. endosulfan})(\%\text{ purity endosulfan})(\text{pk. ht. or area HHDN})}$$

Determine the percent endosulfan for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. HHDN})(\%\text{ purity HHDN})(\text{pk. ht. or area endosulfan})\cancel{(100)}}{(\text{wt. sample})(\text{pk. ht. or area HHDN})(RF)}\ \text{ul}$$

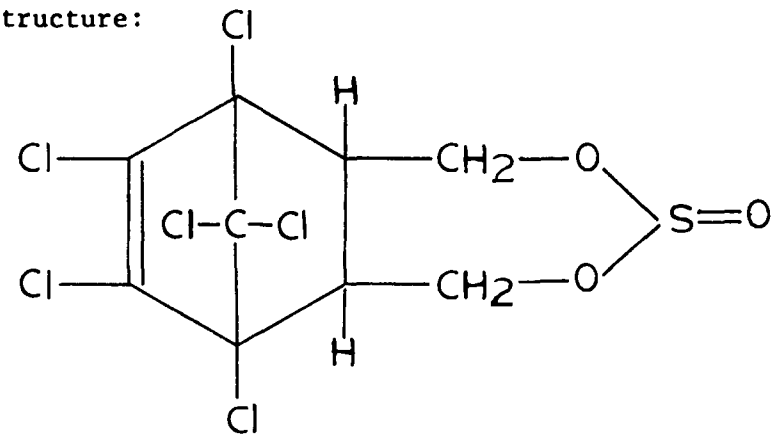
This method is based on EPA Experimental Method 62A submitted by G. Radan, EPA, Region II, New York, N. Y. Some changes and additions have been made in the write-up; therefore, any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated.

November 1975

Endosulfan EPA-4
(Tentative)

Determination of Endosulfan by Gas-Liquid Chromatography (FID - Internal Standard)

Endosulfan is the accepted common name for hexachlorohexahydro-methano-2,4,3-benzodioxathiepin-3-oxide, a registered pesticide having the chemical structure:



Molecular formula: $C_9H_6Cl_6O_3S$

Molecular weight: 406.9

Melting point: (see below)

Physical state, color, and odor: endosulfan is an odorless white crystalline solid mixture of two isomers with mp's of 106°C and 212°C; the technical product is a brownish crystalline solid, mp 70-100°C, with a 4:1 ratio of the above isomers. Both isomers are insecticidally active.

Solubility: practically insoluble in water, but soluble in most organic solvents

Stability: generally quite stable; decomposition catalyzed by iron; slowly hydrolyzed by water; sensitive to acid and bases; compatible with non-alkaline pesticides

Other names: Thiodan (Farwerke Hoechst), Beosit, Chlorthiepin, Cyclodan, Insectophene, Kop-Thiodan, Malix, Thifor, Thimul, Thionex, HOE 2671, NIA 5462, FMC 5462

Reagents:

1. Endosulfan standard of known % purity
2. Dieldrin standard of known HEOD content
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.15 gram HEOD into a 50 ml volumetric flask, dissolve in, and make to volume with acetone. (conc 3 mg HEOD/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm ID glass column packed with 5% OV-210 on 80/100 mesh Chromosorb W HP (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	180°
Injection temperature:	230°
Detector temperature:	230°
Carrier gas:	Nitrogen
Carrier gas pressure:	40-60 psi
Hydrogen pressure:	20 psi
Air pressure:	30 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.12 gram endosulfan standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 6 mg endosulfan and 3 mg HEOD/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.12 gram endosulfan into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the endosulfan. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 6 mg endosulfan and 3 mg HEOD/ml)

Determination:

Inject 2-4 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is endosulfan, then HEOD (see note).

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of endosulfan and HEOD from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. HEOD})(\%\text{ purity HEOD})(\text{pk. ht. or area endosulfan})}{(\text{wt. endosulfan})(\%\text{ purity endosulfan})(\text{pk. ht. or area HEOD})}$$

Determine the percent endosulfan for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. HEOD})(\%\text{ purity HEOD})(\text{pk. ht. or area endosulfan})\cancel{(100)}}{(\text{wt. sample})(\text{pk. ht. or area HEOD})(RF)} \quad (4-1)$$

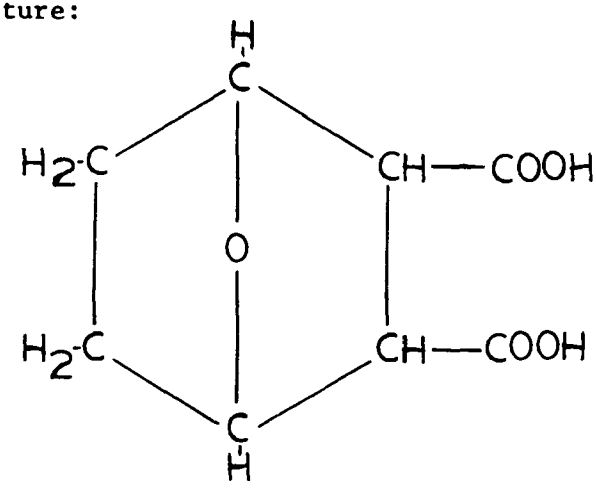
Note! Endosulfan consists of two isomers (I and II) which elute before and after the HEOD. Calculate results using isomer I (1st peak); however, if results are low, calculate using the total of isomers I and II (both peaks). The ratio of isomers I and II varies considerably among various samples and standards. Endosulfan II and parathion are not completely separated on this column, but this does not seem to affect either the endosulfan II or parathion results significantly.

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Chemistry Lab. Any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated.

Determination of Endothall in Formulations (Oxidation and Acid-Base Titration)

Endothall is the accepted common name for 7-oxabicyclo (2.2.1) heptane-2,3-dicarboxylic acid, a registered herbicide having the chemical structure:



Molecular formula: $C_8H_{10}O_5$

Molecular weight: 186.2

Melting point: 144°C (some decomposition, see below)

Physical state, color, and odor: white, odorless, crystalline solid

Solubility: solubility in grams per 100 ml at 25°C is: 10 in water, 7 in acetone, 0.1 in benzene, 7.6 in dioxane, 28 in methanol

Stability: stable to light; stable to about 90°C, after which it undergoes a slow conversion to the anhydride; stable in acid, non-flammable; non-corrosive to metals

Other names: Endothal (Pennwalt), endothal (Europe except Italy), Accelerate, Aquathol, Des-i-cate, Herbicide 273, Herbicide 283, Hydout, Hydrothol, Tri-Endothal

Principle of the Method:

The sample is neutralized with sulfuric acid (because of residual sodium hydroxide from manufacturing). It is then evaporated and ashed to convert the carboxylic acid to carbonate which is determined acidimetrically. Salts of carboxylic acids other than endothall interfere. If ammonium sulfate is present, it must be volatilized.

Reagents:

1. Sodium hydroxide, 0.1N standardized solution
2. Sulfuric acid, 0.1N standardized solution
3. Phenolphthalein indicator solution
4. Sodium hydroxide pellets, ACS

Equipment:

1. Platinum evaporating dish
2. Steam bath and/or drying oven
3. Muffle furnace
4. Filtration apparatus
5. Titration apparatus
6. Usual laboratory glassware

Procedure:

Weigh a portion of sample equivalent to 0.25-0.30 gram endothall acid (0.31-0.37 gram disodium salt) into a platinum evaporating dish. Wet dry samples with a few ml water.

(If ammonium sulfate is present, add 1 gram sodium hydroxide, mix well, and evaporate to dryness.)

Neutralize carefully with 0.1N sulfuric acid to just colorless with phenolphthalein. Evaporate and ash at approx. 525°C. Cool, extract with hot water, and filter through paper into a 500 ml Erlenmeyer flask, washing with water. Return the paper to the platinum crucible, dry, and ash completely. Cool, dissolve the residue in water, and add to the extract in the Erlenmeyer flask.

Add 50 ml exactly 0.1N sulfuric acid solution and boil 20 minutes to remove carbon dioxide. Cool, and titrate with 0.1N sodium hydroxide solution to the phenolphthalein endpoint.

Calculate the endothall as follows:

$$\% = \frac{(\text{ml } H_2SO_4)(\text{N } H_2SO_4) - (\text{ml NaOH})(\text{N NaOH})(0.0931)(100)}{(\text{grams sample})}$$

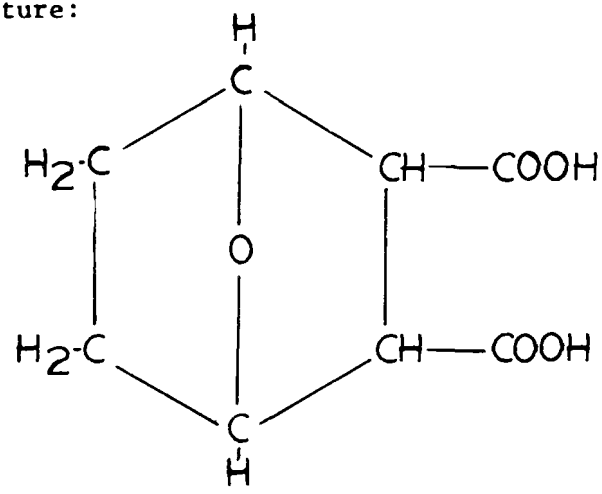
milliequivalent weight endothall acid = 0.0931

milliequivalent weight endothall, disodium salt = 0.1151

% endothall acid X 1.236 = % endothall disodium salt

Determination of Endothall by Gas-Liquid Chromatography (FID)

Endothall is the accepted common name for 7-oxabicyclo (2.2.1) heptane-2,3-dicarboxylic acid, a registered herbicide having the chemical structure:



Molecular formula: $C_8H_{10}O_5$

Molecular weight: 186.2

Melting point: 144°C (some decomposition, see below)

Physical state, color, and odor: white, odorless, crystalline solid

Solubility: solubility in grams per 100 ml at 25°C is: 10 in water, 7 in acetone, 0.1 in benzene, 7.6 in dioxane, 28 in methanol

Stability: stable to light; stable to about 90°C, after which it undergoes a slow conversion to the anhydride; stable in acid, non-flammable; non-corrosive to metals

Other names: Endothal (Pennwalt), endothal (Europe except Italy), Accelerate, Aquathol, Des-i-cate, Herbicide 273, Herbicide 283, Hydout, Hydrothol, Tri-Endothal

This method applies to the salts of endothall, e.g., mono (N,N-dimethylalklamine salt) as well as to the free acid.

Reagents:

1. Endothall standard of known % purity
2. Acetonitrile, pesticide or spectro grade
3. 3M Sulfuric acid, ACS

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 5' x 1/4" O.D. glass, packed with 3% SE-30 on 60/80 Chromosorb W AW DMCS (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	130°C
Injection temperature:	180°C
Detector temperature:	180°C
Carrier gas:	Nitrogen
Carrier gas flow rate:	40 ml/min
Hydrogen flow rate:	adjusted for specific GC
Air flow rate:	adjusted for specific GC

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.075 gram endothall standard into a small glass-stoppered flask or screw-cap bottle, add 8 drops 3M sulfuric acid, 25 ml acetonitrile by pipette, and shake to dissolve. (conc 3 μg/μl)

Preparation of Sample:

For technical material and liquid formulations, weigh a portion of sample equivalent to 0.075 gram endothall into a 25 ml volumetric flask, add 8 drops 3M sulfuric acid, make to volume with acetonitrile, and mix thoroughly. (final conc 3 μg endothall/μl)

For dry formulations, weigh a portion of sample equivalent to 0.150 gram of endothall into a 125 ml screw-cap flask, add 8 drops 3M sulfuric acid, 50 ml acetonitrile by pipette, and shake for one hour. Allow to settle; filter or centrifuge if necessary taking precautions to prevent evaporation. (final conc 3 μg endothall/μl)

Determination:

Using a precision liquid syringe, alternately inject three 5 μl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent endothall as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Florida Department of Agriculture and Consumer Services, Mayo Building, Tallahassee, Florida 32304.

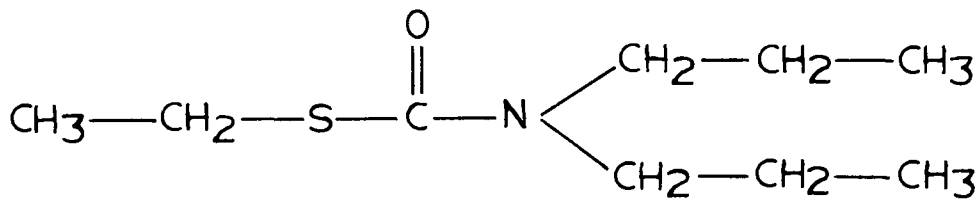
This method has been designated as tentative since some data has been suggested by EPA's Beltsville Chemistry Laboratory. Any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated.

October 1975

EPTC EPA-1
(Tentative)

Determination of EPTC by Gas-Liquid Chromatography (TCD - Internal Standard)

EPTC is the common name for S-ethyl dipropylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{19}NOS$

Molecular weight: 189.3

Boiling point: 127°C at 20 mm Hg (235°C by extrapolation)

Physical state, color, and odor: Light yellow-colored liquid with an amine odor

Solubility: 365 ppm in water at 20°C; miscible with acetone, benzene, ethanol, isopropanol, kerosene, methanol, methyl isobutyl ketone, toluene, and xylene

Stability: stable, non-corrosive

Other names: Eptam (Stauffer), Eradicane, Knoxweed

Reagents:

1. EPTC standard of known % purity
2. 2-ethyl-1,3-hexanediol standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.5 gram ethyl hexanediol into a 50 ml volumetric flask, dissolve in, and make to volume with acetone. (conc 10 mg/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. 6' x 1/4" glass column packed with 10% SE-30 on 100/120 mesh Diatoport S (or equivalent column)
3. Precision liquid syringe - 5 or 10 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	130°C
Injection temperature:	225°C
Detector temperature:	150°C
Filament current:	200 ma
Carrier gas:	Helium
Flow rate:	30 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram EPTC standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 10 mg EPTC and 10 mg ethyl hexanediol/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.25 gram EPTC into a small glass-stoppered flask or screw-cap bottle. Add by pipette 25 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the EPTC. For coarse or granular materials, shake mechanically for 10-15 minutes or shake by hand intermittently for 25-30 minutes. (final conc 10 mg EPTC and 10 mg ethyl hexanediol/ml)

Determination:

Inject 2-3 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within approx. 10 minutes and peak heights of from 1/2 to 3/4 full scale. The elution time of ethyl hexanediol is approx. 2 minutes and that of EPTC approx. 4 minutes.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of EPTC and ethyl hexanediol from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

IS = internal standard = ethyl hexanediol

$$RF = \frac{(\text{wt. IS})(\%\text{ purity IS})(\text{pk. ht. or area EPTC})}{(\text{wt. EPTC})(\%\text{ purity EPTC})(\text{pk. ht. or area IS})}$$

Determine the percent EPTC for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. x \% purity IS})(\text{pk. ht. or area EPTC})(\sout{100})}{(\text{wt. sample})(\text{pk. ht. or area IS})(\text{RF})} \quad (1-1)$$

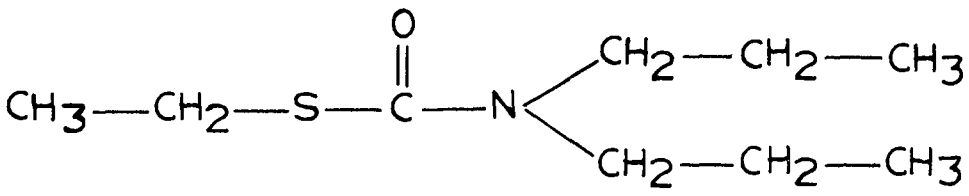
Method submitted by George Radan, EPA Region II, New York, N. Y.

July 1975

EPTC EPA-2
(Tentative)

Determination of EPTC by High Pressure Liquid Chromatography ("Normal Phase")

EPTC is the common name for S-ethyl dipropylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{19}NOS$

Molecular weight: 189.3

Boiling point: 127°C at 20 mm Hg (235°C by extrapolation)

Physical state, color, and odor: Light yellow-colored liquid with an amine odor

Solubility: 365 ppm in water at 20°C; miscible with acetone, benzene, ethanol, isopropanol, kerosene, methanol, methyl isobutyl ketone, toluene, and xylene

Stability: stable, non-corrosive

Other names: Eptam (Stauffer), Eradicane, Knoxweed

Reagents:

1. EPTC standard of known % purity
2. Chloroform
3. Dichloromethane
4. Hexane
5. Methanol

All solvents should be pesticide or spectro grade.

Equipment:

1. High pressure liquid chromatograph
2. High pressure liquid syringe or sample injection loop
3. Liquid chromatographic column, 4 mm I.D. x 25 cm packed with LiChrosorb Si 60 - 10 μ (or equivalent column)
4. Usual laboratory glassware

Operating conditions for Hewlett-Packard Model 1010B LC:

Mobile phase: 40 ml methanol in 2000 ml of a mixture containing 80% dichloromethane and 20% hexane

Column temperature: ambient

Observed column pressure: 30 kg/cm^2 (425 PSI)

Flow rate: 3 ml/min

Detector: UV at 240 nm

Chart speed: 0.5 in/min

Injection: 10 μl

Conditions may have to be varied by the analyst for other instruments, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.02 gram EPTC standard into a 10 ml volumetric flask; dissolve and make to volume with chloroform (final conc 2 mg/ml).

Preparation of Sample:

Weigh an amount of sample equivalent to 0.2 gram EPTC into a 100 ml volumetric flask, make to volume with chloroform, and mix thoroughly (final conc 2 mg EPTC/ml).

Determination:

Alternately inject three 10 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

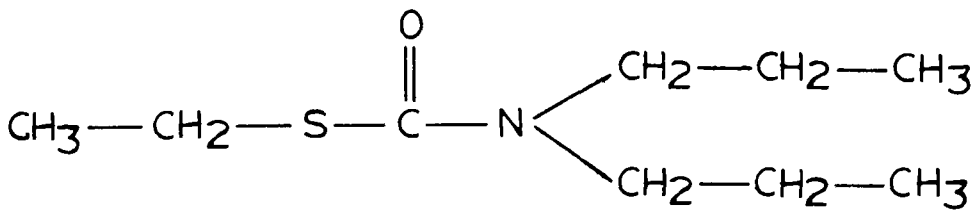
From the average peak height or peak area calculate the percent EPTC as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method developed by Joseph B. Audino, Supervisor, Pesticide Formulation Laboratory, California Department of Food and Agriculture; and by Yoshihiko Kawano, Associate Chemist on sabbatical leave from the University of Hawaii.

Determination of EPTC by Gas-Liquid Chromatography (FID - Internal Standard)

EPTC is the common name for S-ethyl dipropylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{19}NOS$

Molecular weight: 189.3

Boiling point: 127°C at 20 mm Hg (235°C by extrapolation)

Physical state, color, and odor: Light yellow-colored liquid with an amine odor

Solubility: 365 ppm in water at 20°C; miscible with acetone, benzene, ethanol, isopropanol, kerosene, methanol, methyl isobutyl ketone, toluene, and xylene

Stability: stable, non-corrosive

Other names: Eptam (Stauffer), Eradicane, Knoxweed

Reagents:

1. EPTC standard of known % purity
2. Butylate standard of known % purity
3. Carbon disulfide, pesticide or spectro grade

Reagents (Cont.)

4. Chloroform, pesticide or spectro grade
5. Methanol, pesticide or spectro grade
6. Internal Standard solution - weigh 0.25 gram butylate into a 50 ml volumetric flask, dissolve in, and make to volume with a solvent mixture consisting of 80% carbon disulfide + 15% chloroform + 5% methanol. (conc 5 mg butylate/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 2 mm glass column packed with 3% OV-1 on 60/80 Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	120°C
Injection temperature:	225°C
Detector temperature:	250°C
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi
Hydrogen pressure:	20 psi
Air pressure:	30 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.08 gram EPTC standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 4 mg EPTC and 5 mg butylate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.08 gram EPTC into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the EPTC. For coarse or granular materials, shake mechanically for 10-15 minutes or shake by hand intermittently for 25-30 minutes. (final conc 4 mg EPTC and 5 mg butylate/ml)

Determination:

Inject 2-3 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is EPTC 1st and butylate 2nd.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of EPTC and butylate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{\text{(wt. butylate)(\% purity butylate)(pk. ht. or area EPTC)}}{\text{(wt. EPTC)(\% purity EPTC)(pk. ht. or area butylate)}}$$

Determine the percent EPTC for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{\text{(wt. butylate)(\% purity butylate)(pk. ht. or area EPTC)}\ \cancel{(100)}}{\text{(wt. sample)(pk. ht. or area butylate)(RF)}} \quad (4\text{-}1)$$

Method submitted by Division of Regulatory Services, Kentucky Agricultural Experiment Station, University of Kentucky, Lexington, Kentucky 40506.

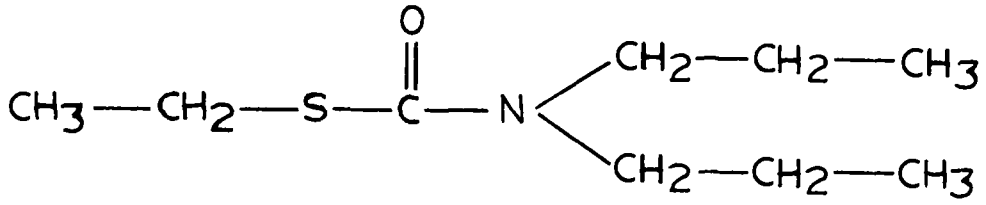
(See EPA-4 for a similar method submitted by Virginia State Laboratories.)

October 1975

EPTC **EPA-4**
(Tentative)

Determination of EPTC by Gas-Liquid Chromatography (FID - Internal Standard)

EPTC is the common name for S-ethyl dipropylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{19}NOS$

Molecular weight: 189.3

Boiling point: 127°C at 20 mm Hg (235°C by extrapolation)

Physical state, color, and odor: Light yellow-colored liquid with an amine odor

Solubility: 365 ppm in water at 20°C; miscible with acetone, benzene, ethanol, isopropanol, kerosene, methanol, methyl isobutyl ketone, toluene, and xylene

Stability: stable, non-corrosive

Other names: Eptam (Stauffer), Eradicane, Knoxweed

Reagents:

1. EPTC standard of known % purity
2. Vernolate standard of known % purity
3. Carbon disulfide, pesticide or spectro grade
4. Chloroform, pesticide or spectro grade
5. Methanol, pesticide or spectro grade
6. Internal Standard solution - weigh 0.2 gram vernolate into a 50 ml volumetric flask, dissolve in, and make to volume with a solvent mixture consisting of 80% carbon disulfide + 15% chloroform + 5% methanol. (conc 4 mg vernolate/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm ID glass column packed with 5% SE-30 on 80/100 Chromosorb W HP (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	130°
Injection temperature:	200°
Detector temperature:	200°
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi
Hydrogen pressure:	20 psi
Air pressure:	30 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram EPTC standard into a small glass-stoppered flask or screw-cap tube. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 2.5 mg EPTC and 4 mg vernolate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.05 gram EPTC into a small glass-stoppered flask or screw-cap tube. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the EPTC. For coarse or granular materials, shake or tumble mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 2.5 mg EPTC and 4 mg vernolate/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is EPTC, then vernolate.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of EPTC and vernolate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. vernolate})(\%\text{ purity vernolate})(\text{pk. ht. or area EPTC})}{(\text{wt. EPTC})(\%\text{ purity EPTC})(\text{pk. ht. or area vernolate})}$$

Determine the percent EPTC for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. vernolate})(\%\text{ purity vernolate})(\text{pk. ht. or area EPTC})(100)}{(\text{wt. sample})(\text{pk. ht. or area vernolate})(RF)}$$ (4-1)

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

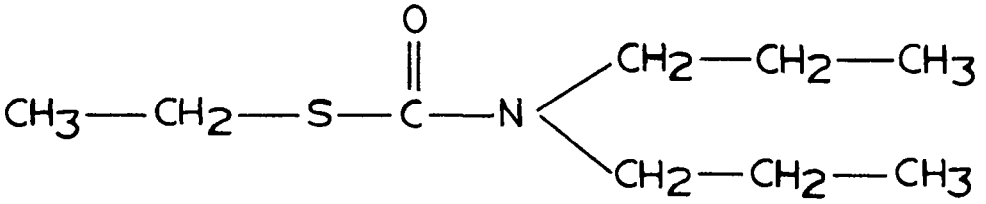
Note! This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Chemistry Lab. Any comments, criticism, suggestion, data, etc. concerning this method will be appreciated.

October 1975

EPTC **EPA-5**
(Tentative)

Determination of EPTC by Gas-Liquid Chromatography (TCD - Internal Standard)

EPTC is the common name for S-ethyl dipropylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{19}NOS$

Molecular weight: 189.3

Boiling point: 127°C at 20 mm Hg (235°C by extrapolation)

Physical state, color, and odor: Light yellow-colored liquid with an amine odor

Solubility: 365 ppm in water at 20°C; miscible with acetone, benzene, ethanol, isopropanol, kerosene, methanol, methyl isobutyl ketone, toluene, and xylene

Stability: stable, non-corrosive

Other names: Eptam (Stauffer), Eradicane, Knoxweed

Reagents:

1. EPTC standard of known % purity
2. Vernolate standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.25 gram vernolate into a 25 ml volumetric flask, dissolve in, and make to volume with acetone. (conc 10 mg vernolate/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 5' x 1/4" glass column packed with 5% PEG-1540 on 60/80 Chromosorb W AW DMCS (or equivalent column)
3. Precision liquid syringe: 25 or 50 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	160°C
Injection temperature:	200°C
Detector temperature:	200°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas flow rate:	30 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.08 gram EPTC standard into a small glass-stoppered flask or screw-cap tube. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 8 mg EPTC and 10 mg vernolate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.08 gram EPTC into a small glass-stoppered flask or screw-cap tube. Add by pipette 10 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the EPTC. For coarse or granular materials, shake or tumble mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 8 mg EPTC and 10 mg vernolate/ml)

Determination:

Inject 10-15 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is EPTC, then vernolate.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of EPTC and vernolate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. vernolate})(\%\text{ purity vernolate})(\text{pk. ht. or area EPTC})}{(\text{wt. EPTC})(\%\text{ purity EPTC})(\text{pk. ht. or area vernolate})}$$

Determine the percent EPTC for each injection of the sample-internal standard solution as follows and calculate the average:

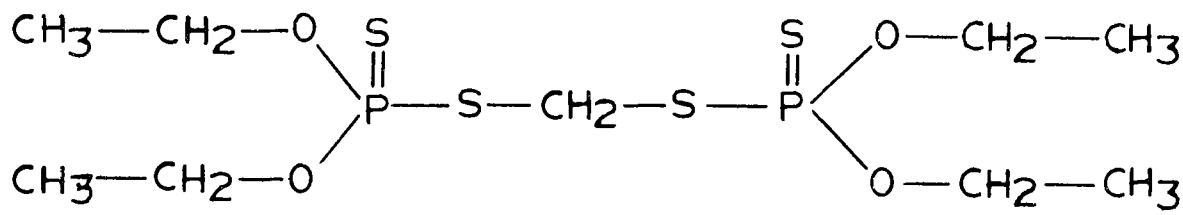
$$\% = \frac{(\text{wt. vernolate})(\%\text{ purity vernolate})(\text{pk. ht. or area EPTC})(100)}{(\text{wt. sample})(\text{pk. ht. or area vernolate})(RF)} \quad (4-1)$$

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Note! This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Lab. Any comments, criticism, suggestion, data, etc. concerning this method will be appreciated.

Determination of Ethion in Solid Formulations by Infrared Spectroscopy

Ethion is the accepted common name for O,O,O',O'-tetraethyl S,S'-methylene bisphosphorodithioate, a registered insecticide having the chemical structure:



Molecular formula: $C_9H_{22}O_4P_2S_4$

Molecular weight: 384.48

Boiling point: 164 to 165°C at 0.3 mm Hg; solidifies at -12 to -15°C

Physical state, color, and odor: pure form is an odorless, colorless liquid; technical product is a yellow to amber liquid

Solubility: very slightly soluble in water; poorly soluble in aliphatic solvents; highly soluble in aromatic solvents

Stability: slowly oxidizes in air; subject to hydrolysis by both acids and alkalis

Other names: NIA 1240 and Nialate (FMC Corp.), diethion, Ethodan

Reagents:

1. Ethion standard of known % purity
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps. These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.10 gram ethion standard into a 10 ml volumetric flask; make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.40 gram ethion into a glass-stoppered flask or screw-cap tube. Add 100 ml carbon disulfide by pipette and 1-2 grams anhydrous sodium sulfate.

Close tightly and shake for one hour. Allow to settle; centrifuge of filter if necessary, taking precaution to prevent evaporation. Evaporate a 25 ml aliquot to about 5 ml, transfer to a 10 ml volumetric flask, and make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg ethion/ml)

Determination:*

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 714 cm^{-1} to 595 cm^{-1} (14.0 μ to 16.8 μ).

Determine the absorbance of standard and sample using the peak at 647 cm^{-1} (15.45 μ) and baseline from 701 cm^{-1} to 615 cm^{-1} (14.25 μ to 16.25 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent ethion as follows:

$$\% = \frac{\text{(abs. sample)(conc. std in mg/ml)(\% purity std)}}{\text{(abs. std)(conc. sample in mg/ml)}}$$

(A concentration of 1 mg ethion/ml carbon disulfide gives an absorbance of approx. 0.04 in a 0.2 mm cell.)

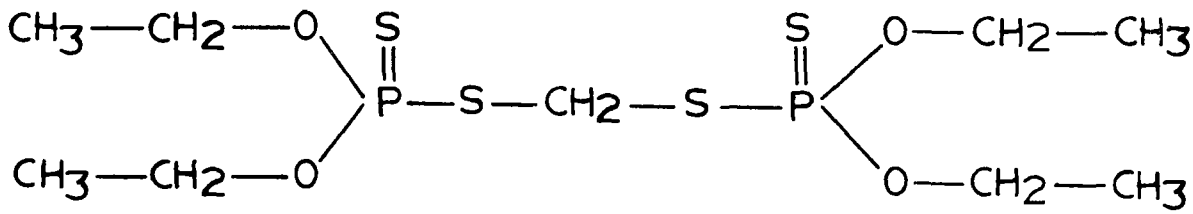
Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services.

* Eva Santos, EPA Region IX, San Francisco, California, has contributed a similar method using:

958 cm^{-1} (10.44 μ) analytical absorption band
981 cm^{-1} (10.19 μ) basepoint

Determination of Ethion by Gas-Liquid Chromatography (TCD)

Ethion is the accepted common name for O,O,O',O'-tetraethyl S,S'-methylene bisphosphorodithioate, a registered insecticide having the chemical structure:



Molecular formula: $C_9H_{22}O_4P_2S_4$

Molecular weight: 384.48

Boiling point: 164 to 165°C at 0.3 mm Hg; solidifies at -12 to -15°C

Physical state, color, and odor: pure form is an odorless, colorless liquid; technical product is a yellow to amber liquid

Solubility: very slightly soluble in water; poorly soluble in aliphatic solvents; highly soluble in aromatic solvents

Stability: slowly oxidizes in air; subject to hydrolysis by both acids and alkalis

Other names: NIA 1240 and Nialate (FMC Corp.), diethion, Ethodan

Reagents:

1. Ethion standard of known % purity
2. Chloroform, pesticide or spectro grade

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 5' x 1/4" glass column packed with 10% QF-1 on Chromosorb W, AW, DMCS (or equivalent column)
3. Precision liquid syringe: 50 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	210°C
Injection temperature:	240°C
Detector temperature:	240°C
Filament current:	200 ma
Carrier gas:	Helium
Flow rate:	100 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.2 gram ethion standard into a 10 ml volumetric flask; dissolve and make to volume with chloroform. (final conc 20 mg/ml)

Preparation of Sample:

For technical material and liquid formulations, weigh a portion of sample equivalent to 0.20 gram ethion into a 10 ml volumetric flask, make to volume with chloroform, and mix thoroughly. (final conc 20 mg ethion/ml)

For dry formulations, weigh a portion of sample equivalent to 1.0 gram ethion into a glass-stoppered flask or screw-cap bottle, add by pipette 50 ml chloroform, close tightly, and shake for one hour. Allow to settle; filter or centrifuge if necessary, taking precautions to prevent evaporation. (final conc 20 mg ethion/ml)

Determination:

Using a precision liquid syringe, alternately inject three 30-40 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent ethion as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity std})}{(\text{pk. ht. or area std})(\text{wt. sample injected})}$$

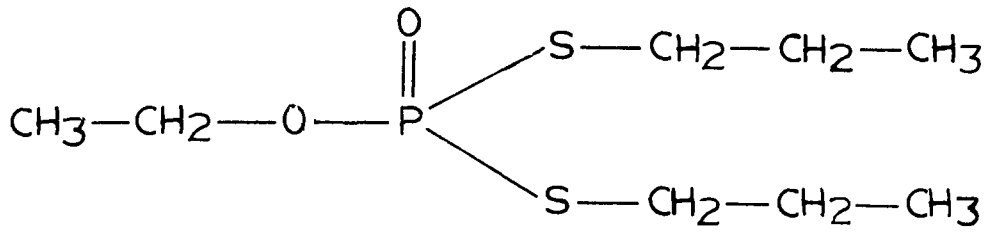
Method submitted by Eva Santos, EPA Region IX, San Francisco, California.

December 1975

Ethoprop EPA-1
(Tentative)

Determination of Ethoprop by Infrared Spectroscopy

Ethoprop is a common name for O-ethyl-S,S-dipropyl phosphorodithioate, a registered nematocide and soil insecticide having the chemical structure:



Molecular formula: $C_8H_{19}O_2PS_2$

Molecular weight: 242.3

Melting point: 86 to 91°C at 0.2 mm Hg

Physical state, color, and odor: clear yellowish liquid with a strong mercaptan odor

Solubility: insoluble in water; soluble in most organic solvents

Stability: very stable in acid aqueous media from 25 to 100°C; hydrolyzed in basic media moderately fast at 25°C and rapidly at 100°C; thermal stability is good for 8 hours at 150°C

Other names: Mocap (Mobil), prophos (discontinued because of conflict), VC 9-104

Reagents:

1. Ethoprop standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording, with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker
3. Filtration apparatus or centrifuge
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram ethoprop into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg/ml)

Preparation of Sample:

For dusts, granules, and wettable powders, weigh a portion of sample equivalent to 0.5 gram ethoprop into a 125 ml glass-stoppered or screw-cap Erlenmeyer flask. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly, shake on a mechanical shaker for 1 hour, allow to settle, filter or centrifuge if necessary, taking precaution to avoid evaporation. (final conc 10 mg ethoprop/ml)

For emulsifiable concentrates, weigh a portion of sample equivalent to 0.5 gram ethoprop into a 125 ml glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and sufficient anhydrous sodium sulfate to clarify the solution (after shaking). Close tightly and shake vigorously on a mechanical shaker for one hour. Allow to settle; filter or centrifuge if necessary to get a clear chloroform solution, taking precaution to prevent evaporation. (final conc 10 mg ethoprop/ml)

(There may be interference from the emulsifier in the sample; if so, another procedure must be used.)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1100 cm^{-1} to 900 cm^{-1} (9.1 μ to 11.1 μ).

Determine the absorbance of standard and sample using the peak at 1012 cm^{-1} (9.9 μ) and baseline from 1070 cm^{-1} to 970 cm^{-1} (9.35 μ to 10.3 μ).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent ethoprop as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Method submitted by Mark W. Law, EPA Beltsville Chemistry Laboratory, Beltsville, Md.

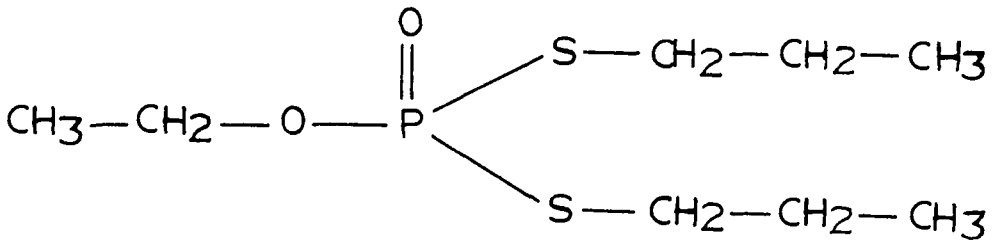
Any criticisms, suggestions, data, etc. on the use of this method will be appreciated.

December 1975

Ethoprop EPA-2
(Tentative)

Determination of Ethoprop by Gas-Liquid Chromatography (TCD - Internal Standard)

Ethoprop is a common name for O-ethyl-S,S-dipropyl phosphorodithioate, a registered nematocide and soil insecticide having the chemical structure:



Molecular formula: $C_8H_{19}O_2PS_2$

Molecular weight: 242.3

Melting point: 86 to 91°C at 0.2 mm Hg

Physical state, color, and odor: clear yellowish liquid with a strong mercaptan odor

Solubility: insoluble in water; soluble in most organic solvents

Stability: very stable in acid aqueous media from 25 to 100°C; hydrolyzed in basic media moderately fast at 25°C and rapidly at 100°C; thermal stability is good for 8 hours at 150°C

Other names: Mocap (Mobil), prophos (discontinued because of conflict), VC 9-104

Reagents:

1. Ethoprop standard of known % purity
2. Diazinon standard of known % purity
3. Chloroform, pesticide or spectro grade
4. Internal Standard solution - weigh 0.5 gram diazinon into a 50 ml volumetric flask and make to volume with chloroform. (conc 10 mg diazinon/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 6' x 1/8" I.D. SS packed with 10% SE 30 on 60/80 Diatoport S (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	200°C
Injection temperature:	225°C
Detector temperature:	225°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas flow:	adjusted for particular GC

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.16 gram ethoprop standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 8 mg ethoprop and 10 mg diazinon/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.16 gram ethoprop into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the ethoprop. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 8 mg ethoprop and 10 mg diazinon/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is ethoprop, then diazinon.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of ethoprop and diazinon from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{\text{(wt. diazinon)(\% purity diazinon)(pk. ht. or area ethoprop)}}{\text{(wt. ethoprop)(\% purity ethoprop)(pk. ht. or area diazonon)}}$$

Determine the percent ethoprop for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{\text{(wt. diazinon)(\% purity diazinon)(pk. ht. or area ethoprop)}\cancel{(100)}}{\text{(wt. sample)(pk. ht. or area diazinon)(RF)}} \quad (4!)$$

Method submitted by Stelios Gerazounis, EPA Region II, New York, N. Y.

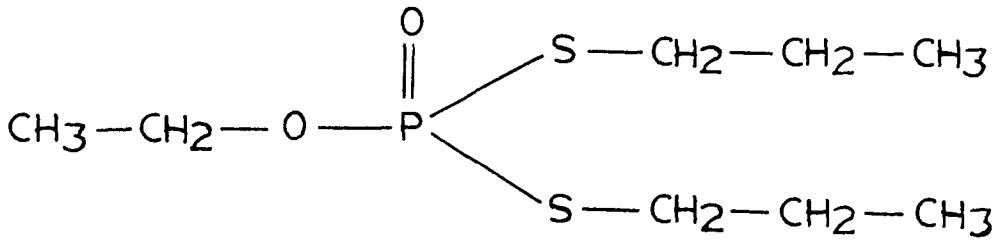
This method was designated as EPA Experimental Method No. 34 and was based on data from the Virginia Department of Agriculture. Some changes have been made and data added in this write-up; therefore, any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated.

December 1975

Ethoprop EPA-3
(Tentative)

Determination of Ethoprop by Gas-Liquid Chromatography (FID - Internal Standard)

Ethoprop is a common name for O-ethyl-S,S-dipropyl phosphorodithioate, a registered nematocide and soil insecticide having the chemical structure:



Molecular formula: $C_8H_{19}O_2PS_2$

Molecular weight: 242.3

Melting point: 86 to 91°C at 0.2 mm Hg

Physical state, color, and odor: clear yellowish liquid with a strong mercaptan odor

Solubility: insoluble in water; soluble in most organic solvents

Stability: very stable in acid aqueous media from 25 to 100°C; hydrolyzed in basic media moderately fast at 25°C and rapidly at 100°C; thermal stability is good for 8 hours at 150°C

Other names: Mocap (Mobil), prophos (discontinued because of conflict), VC 9-104

Reagents:

1. Ethoprop standard of known % purity
2. Diazinon standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.25 gram diazinon into a 50 ml volumetric flask and make to volume with acetone. (conc 5 mg diazinon/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm ID glass column packed with 5% SE-30 on 80/100 Chromosorb W HP (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	180°C
Injection temperature:	230°C
Detector temperature:	230°C
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi (adjust for specific GC)
Hydrogen pressure:	20 psi (adjust for specific GC)
Air pressure:	30 psi (adjust for specific GC)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.06 gram ethoprop standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 3 mg ethoprop and 5 mg diazinon/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.06 gram ethoprop into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the ethoprop. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 3 mg ethoprop and 5 mg diazinon/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is ethoprop, then diazinon.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of ethoprop and diazinon from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. diazinon})(\%\text{ purity diazinon})(\text{pk. ht. or area ethoprop})}{(\text{wt. ethoprop})(\%\text{ purity ethoprop})(\text{pk. ht. or area diazinon})}$$

Determine the percent ethoprop for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. diazinon})(\%\text{ purity diazinon})(\text{pk. ht. or area ethoprop})(100)}{(\text{wt. sample})(\text{pk. ht. or area diazinon})(RF)} \quad (4\text{-}1)$$

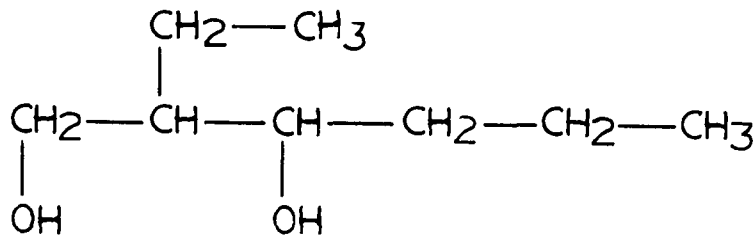
Method submitted by Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

This method has been designated as tentative since it is based on an experimental method from Virginia.

Variable results are sometimes obtained on duplicate runs of 10% granular formulations, probably due to the small sample size used and the non-uniform size of the granules. A larger sample with corresponding increase in internal standard solution solvent or a Soxhlet extraction may be necessary.

Determination of Ethyl Hexanediol by Acetylation and Titration

Ethyl hexanediol is a common name (Ent. Soc. Am.) for 2-ethyl-1,3-hexanediol, a registered insect repellent having the chemical structure:



Molecular formula: $C_8H_{18}O_2$

Molecular weight: 146.2

Boiling point: 244°C; the technical product has a distillation range of 240 to 250°C

Physical state, color, and odor: colorless liquid; the technical product has a faint odor of witch hazel

Solubility: slightly soluble in water; miscible with alcohol, chloroform, ether; will not dissolve nylon, rayon

Stability: stable under normal conditions; both hydroxyl groups can be esterified, the secondary group with difficulty; it is without chemical or solvent action on clothing and most plastics

Other names: ethohexadiol (USP), Rutgers 6-12, 6-12 Insect Repellent, ethyhexylene glycol

Principle of the Method:

A known amount of acetic anhydride is reacted with the hydroxyl groups of ethyl hexanediol and the excess is titrated with sodium hydroxide.

This method will determine the hydroxyl groups in alcohols, glycols, and phenols and the amino groups in primary and secondary amines. If any of these substances are present, they must be removed prior to analysis. Water, except in very small amounts, interferes by reacting with the acetylating reagent.

Reagents:

1. Acetic anhydride, ACS
2. Pyridine, ACS, preferably freshly redistilled
3. Acetylating reagent - mix 25 ml acetic anhydride with 75 ml pyridine
4. Mixed indicator - mix one part 0.1% neutral (to NaOH) cresol red with 3 parts 0.1% neutral (to NaOH) thymol blue
5. Alcohol sodium hydroxide, 0.5N standardized solution - prepare from 50% sodium hydroxide solution and aldehyde-free ethanol (or methanol)

Equipment:

1. Iodine flasks, 300 ml
2. Steam bath
3. Titration apparatus
4. Usual laboratory glassware

Procedure:

Weigh a portion of sample equivalent to 0.7 gram ethyl hexanediol into a 300 ml iodine flask, add exactly 10 ml acetylating reagent by pipette, stopper the flask, and add 1-2 ml pyridine to the well around the stopper. Add 10 ml acetylating reagent to a second flask for a blank, and treat exactly as the sample.

Heat the flasks on a steam bath for at least one hour, using the maximum heat that is practical. Cool; add 10 ml water to the well of the flask,allowing it to wash down the sides of the loosened stopper and flask. Mix thoroughly to bring the water into contact with all of the acetylating reagent.

Add a few drops of the mixed indicator and titrate with 0.5N alcohol sodium hydroxide solution to a blue endpoint.

Calculation:

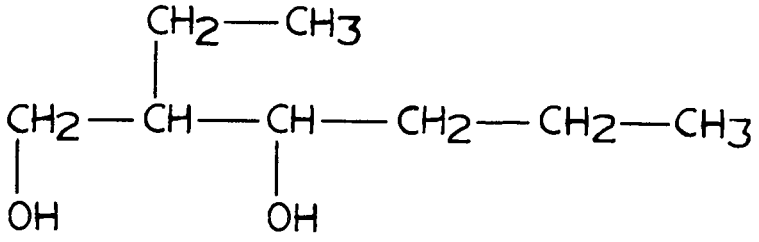
Calculate the percent ethyl hexanediol as follows:

$$\% = \frac{(\text{ml NaOH for blank} - \text{ml NaOH for sample})(\text{N NaOH})(0.07311)(100)}{(\text{grams sample})}$$

0.07311 = milliequivalent weight ethyl hexanediol

Determination of Ethyl Hexanediol by Gas-Liquid Chromatography (TCD - Internal Standard)

Ethyl hexanediol is a common name (Ent. Soc. Am.) for 2-ethyl-1,3-hexanediol, a registered insect repellent having the chemical structure:



Molecular formula: $C_8H_{18}O_2$

Molecular weight: 146.2

Boiling point: 244°C; the technical product has a distillation range of 240 to 250°C

Physical state, color, and odor: colorless liquid; the technical product has a faint odor of witch hazel

Solubility: slightlv soluble in water; miscible with alcohol, chloroform, ether; will not dissolve nylon, rayon

Stability: stable under normal conditions; both hydroxyl groups can be esterified, the secondary group with difficulty; it is without chemical or solvent action on clothing and most plastics

Other names: ethohexadiol (USP), Rutgers 6-12, 6-12 Insect Repellent, ethyhexylene glycol

Reagents:

1. 2-Ethyl-1,3-hexanediol of known % purity
2. o-Dichlorobenzene, commercial grade or better
3. Isopropanol, pesticide or spectro grade
4. Internal Standard solution - weigh 0.5 gram o-dichlorobenzene into a 50 ml volumetric flask; dissolve in and make to volume with isopropanol. (conc 10 mg o-dichlorobenzene/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 6' x 1/8" stainless steel, packed with 10% SE-30 on Diatoport S (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	120°C
Injection temperature:	150°C
Detector temperature:	150°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas pressure:	40 psi (adjust for specific GC)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.25 gram ethyl hexanediol standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 25 mg ethyl hexanediol and 10 mg o-dichlorobenzene/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.25 gram ethyl hexanediol into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution. Close tightly and shake thoroughly. (final conc 25 mg ethyl hexanediol and 10 mg o-dichlorobenzene/ml)

Determination:

Inject 1 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is o-dichlorobenzene, then ethyl hexanediol.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of ethyl hexanediol and o-dichlorobenzene from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

I.S. = Internal Standard = o-dichlorobenzene

$$RF = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area ethyl hexanediol})}{(\text{wt. ethyl hexanediol})(\%\text{ purity ethyl hexanediol})(\text{pk. ht. or area I.S.})}$$

Determine the percent ethyl hexanediol for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area ethyl hexanediol})(100)}{(\text{wt. sample})(\text{pk. ht. or area I.S.})(RF)} \qquad (4\text{-}1)$$

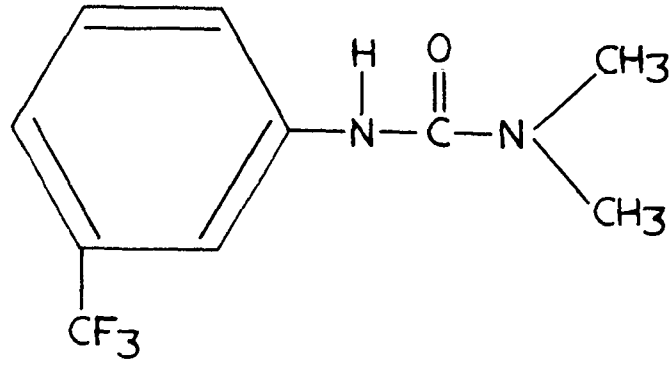
Note: a 1/4" column can be used at 130°C with very similar results.

Method submitted by George Radan, EPA, Region II, New York, N. Y.

This method is designated as tentative since it is based on EPA's Experimental Method No. 35 and some of the data has been suggested by EPA's Beltsville, Md. Chemical Laboratory.

Determination of Fluometuron by Infrared Spectroscopy

Fluometuron is the accepted common name for 1,1-dimethyl-3-(α,α,α-trifluoro-m-tolyl) urea, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_{11}F_3N_2O$

Molecular weight: 232.2

Melting point: 163 to 164.5°C (The technical product is about 96% pure and has a m.p. of about 155°C)

Physical state, color, and odor: odorless, white, crystalline solid

Solubility: 90 ppm in water at 25°C; soluble in acetone, ethanol, isopropanol

Stability: stable, non-corrosive, compatible with other herbicides

Other names: Cotoran (CIBA-GEIGY), Lanex (Nor-Am), C-2059, CIBA-2059

Reagents:

1. Fluometuron standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm NaCl or KBr cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram fluometuron standard into a small glass-stoppered flask or screw-cap bottle, add 50 ml chloroform by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 2 mg/ml)

Preparation of Sample:

For wettable powders and dusts: Weigh an amount of sample equivalent to 0.1 gram fluometuron into a glass-stoppered flask or screw-cap tube. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle, centrifuge or filter if necessary, taking precautions to prevent evaporation. (final conc 2 mg fluometuron/ml)

For suspensions (MSMA-fluometuron suspensions containing about 13.7% fluometuron): Weigh an amount of sample equivalent to 0.1 gram of fluometuron (0.7 gm for 13.7% fluometuron) into a 125 ml Erlenmeyer flask that contains 5 g Na_2SO_4. Pipette 50 ml chloroform into the flask. Shake the sample on a mechanical shaker for one hour. Transfer a portion of the $CHCl_3$ extract to a centrifuge tube and centrifuge for five minutes or until the solution is clear. If the chloroform layer has a small insoluble layer on top,

remove the insoluble layer with a medicine dropper. Perform the same procedure on the standard as on the sample if this extraction procedure is used. (conc 2 mg fluometuron/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings, scan both the standard and sample from 1410 cm^{-1} to 1300 cm^{-1} (7.1 μ to 7.7 μ).

Determine the absorbance of standard and sample using the peak at 1335 cm^{-1} (7.49 μ) and baseline from 1355 cm^{-1} to 1300 cm^{-1} (7.38 μ to 7.69 μ).

Calculation:

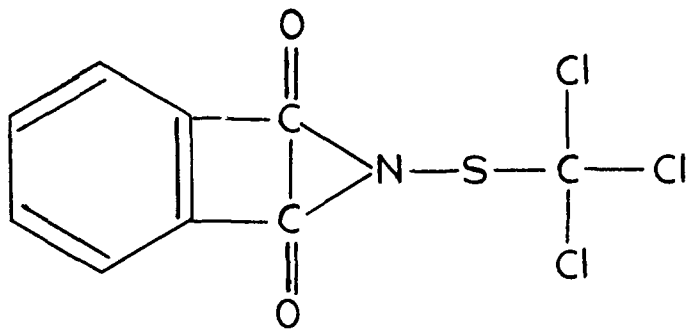
From the above absorbances and using the standard and sample solution concentrations, calculate the percent fluometuron as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Method submitted by Mississippi State Chemical Laboratory, Box CR, Mississippi State, Mississippi 39762.

Determination of Folpet by Infrared Spectroscopy

Folpet is the acceptable common name for N-(trichloromethylthio) phthalimide, a registered fungicide having the chemical formula:



Molecular formula: $C_9H_4Cl_3NO_2S$

Molecular weight: 296.6

Melting point: 177°C

Physical state and color: white crystals

Solubility: insoluble in water (1 ppm at RT); slightly soluble in organic solvents

Stability: stable when dry; slowly hydrolyzes in water at ordinary temperatures, rapidly at high temperatures or under alkaline conditions; not compatible with alkaline pesticides; non-corrosive, but decomposition products are.

Other names: Phaltan (Chevron), Folpan, thiophal

Reagents:

1. Folpet standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.1 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps. These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.06 gram folpet standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 6 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.3 gram folpet into a glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 6 mg folpet/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1900 cm^{-1} to 1650 cm^{-1} (5.26 μ to 6.1 μ).

Determine the absorbance of standard and sample using the peak at 1755 cm^{-1} (5.70 μ) and basepoint at 1850 cm^{-1} (5.41 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent of folpet as follows:

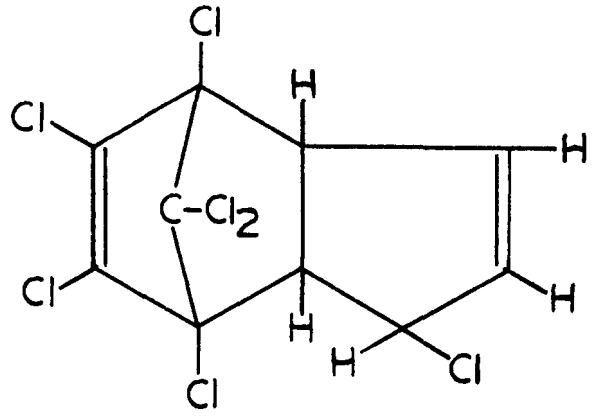
$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg folpet/ml chloroform gives an absorbance of approx. 0.06 in a 0.1 mm cell.)

Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services.

Determination of Heptachlor by Infrared Spectroscopy

Heptachlor is the accepted common name for heptachlorotetrahydro-4,7-methanoindene (and related compounds), a registered insecticide having the chemical structure:



Molecular formula: $C_{10}H_5Cl_7$

Molecular weight: 373.5

Melting point: 95 to 96°C

Physical state, color, and odor: white crystalline solid with a mild camphor odor; the technical product contains about 72% heptachlor and 28% related compounds and is a soft waxy solid with a melting range of 46 to 74°C

Solubility: practically insoluble in water; soluble in most organic solvents

Stability: stable to light, moisture, air, and to moderate heat; not readily dehydrochlorinated, but susceptible to oxidation to heptachlor epoxide; compatible with most commonly used insecticides and fertilizers

Other names: Velsicol 104, E3314 (Velsicol Chem. Corp.); Drinox; Heptamul; H-34; 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene

Reagents:

1. Heptachlor standard of known % purity
2. Carbon disulfide, pesticide or spectro grade
3. Acetone, pesticide or spectro grade (dried over sodium sulfate)
4. Pentane (b.p. 20-40°C), pesticide or spectro grade
5. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm KBr or NaCl cells
2. Mechanical shaker
3. Soxhlet extraction apparatus
4. Centrifuge or filtration apparatus
5. Rotary evaporator
6. Cotton or glass wool
7. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.25 gram heptachlor standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml carbon disulfide by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 25 mg/ml)

Preparation of Sample:

For extraction by shaking (formulations over 10%), weigh a portion of sample equivalent to 0.5 gram heptachlor into a 125 ml glass-stoppered or screw-cap Erlenmeyer flask, add by pipette 50 ml of mixed solvent (9+1, carbon disulfide + dry acetone), close tightly, and shake for 30 minutes. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. Pipette 25 ml into a 125 ml standard tapered flask, and evaporate to just dryness under vacuum on a rotary evaporator. Add 5 ml carbon disulfide and evaporate to dryness (to remove the last traces of acetone). Dissolve in, quantitatively transfer to a 10 ml volumetric flask, and make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 25 mg heptachlor/ml)

For Soxhlet extraction, weigh a portion of sample equivalent to 0.25 gram heptachlor into a Soxhlet thimble, plug with cotton or glass wool, and extract with pentane for two hours. Evaporate to just dryness on a rotary evaporator. Add 5 ml carbon disulfide and again evaporate to dryness. Dissolve in, quantitatively transfer to a 10 ml volumetric flask, and make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 25 mg heptachlor/ml)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 700 cm^{-1} to 625 cm^{-1} (14.3 μ to 16.0 μ).

Determine the absorbance of standard and sample using the peak at 658 cm^{-1} (15.2 μ) and baseline from 673 cm^{-1} to 637 cm^{-1} (14.85 μ to 15.7 μ).

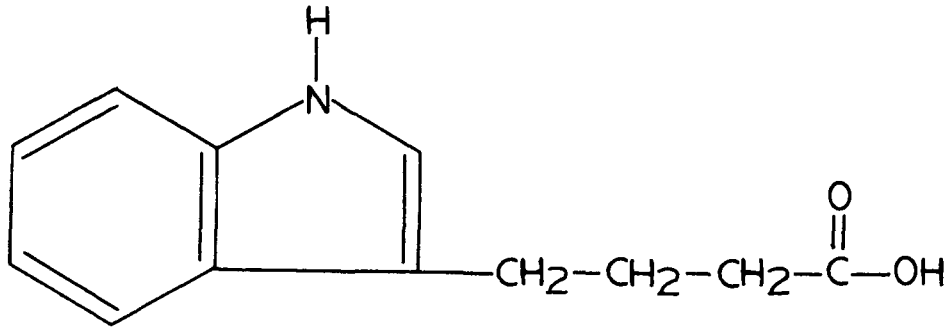
Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent heptachlor as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Determination of Indolebutyric acid by Ultraviolet Spectroscopy

Indolebutyric acid is 4-(3-indolyl)-butyric acid, a registered plant growth regulator having the chemical structure:



Molecular formula: $C_{12}H_{13}NO_2$

Molecular weight: 203.2

Melting point: 124°C

Physical state, color, and odor: white crystalline solid; slight characteristic odor

Solubility: practically insoluble in water and chloroform; soluble in alcohol, ether, acetone, and other organic solvents; forms water-soluble alkaline salts

Stability: stable in alkaline medium

Other names: Hormodin, Seradix, 3-indolebutyric acid, indole-3-butyric acid

Reagents:

1. Indolebutyric acid standard of known % purity
2. Ethanol, pesticide or spectro grade
3. Sodium hydroxide solution, 0.5% in ethanol

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm silica cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram indolebutyric acid into a 100 ml volumetric flask, dissolve in, and make to volume with 0.5% NaOH in ethanol solution. Mix thoroughly and pipette 10 ml into a second 100 ml volumetric flask. Make to volume with 0.5% NaOH in ethanol solution and mix thoroughly. Pipette 20 ml of this second solution into a third 100 ml volumetric flask, make to volume with water, and mix thoroughly. (final conc 20 µg indolebutyric acid/ml and 20 ml 0.5% NaOH in ethanol/100 ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.01 gram indolebutyric acid into a 250 ml glass-stoppered or screw-cap Erlenmeyer flask, add by pipette 100 ml 0.5% NaOH in ethanol solution, and shake for 3 hours. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. Pipette 20 ml of the clear solution into a 100 ml volumetric flask and make to volume with water. (final conc 20 µg indolebutyric acid/ml and 20 ml 0.5% NaOH in ethanol/100 ml)

Preparation of blank solution for reference cell:

Pipette 20 ml 0.5% NaOH in ethanol solution into a 100 ml volumetric flask, make to volume with water, and mix thoroughly.

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 280 nm with the blank solution in each cell. Scan both the standard and sample from 360 nm to 250 nm with the blank solution in the reference cell. Measure the absorbance of both standard and sample at 280 nm.

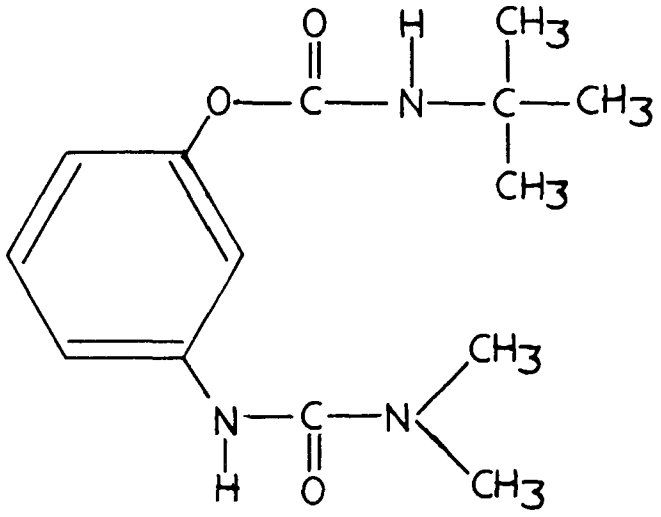
Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent indolebutyric acid as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

Determination of Karbutilate in Solid Formulations by Infrared Spectroscopy

Karbutilate is the accepted common name for m-(3,3-dimethylureido) phenyl tert-butylcarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{14}H_{21}N_3O_3$

Molecular weight: 279.4

Melting point: 176 to 176.5°C

Physical state and color: white crystalline solid

Solubility: at RT -- 325 ppm in water; less than 3% in isopropanol or xylene; 20 to 25% in dimethylformamide or dimethyl sulfoxide

Stability: stable and non-corrosive

Other names: Tandex (Niagara - FMC Corp.); NIA 11092; tert-butyl-carbamic acid, ester with 3-(m-hydroxyphenyl)-1,1-dimethylurea

Reagents:

1. Karbutilate standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.08 gram karbutilate standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 8 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.4 gram karbutilate into a glass-stoppered flask or screw-cap tube. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 8 mg karbutilate/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1925 cm^{-1} to 1650 cm^{-1} (5.2 μ to 6.0 μ).

Determine the absorbance of standard and sample using the peak at 1745 cm^{-1} (5.73 μ) and basepoint at 1840 cm^{-1} (5.43 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent karbutilate as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg karbutilate/ml chloroform gives an absorbance of approx. 0.05 in a 0.2 mm cell.)

Method* contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services.

* based on Niagara test method #10 7/69

Beltsville Chemistry Lab, EPA, Technical Services Division, Beltsville, Md. suggests the following:

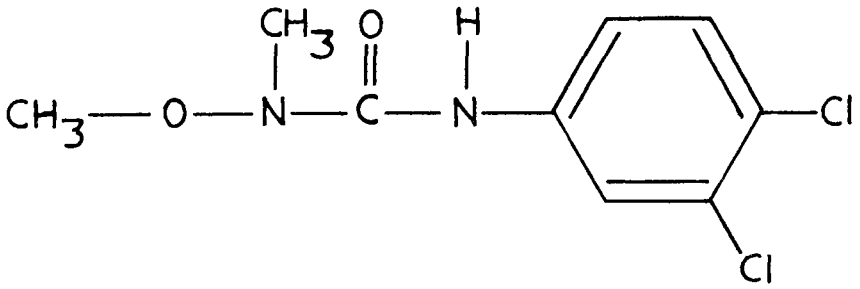
scan range:	2000 cm^{-1} to 1600 cm^{-1} (5 μ to 6.25 μ)
analytical peak:	as above
baseline:	along shoulder from about 2000 cm^{-1} to 1800 cm^{-1} (5 μ to 5.56 μ)

July 1975

Linuron EPA-1
(Tentative)

Determination of Linuron by High Pressure Liquid Chromatography

Linuron is the common name for 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{10}Cl_2N_2O_2$

Molecular weight: 249.1

Melting point: 93 to 94°C

Physical state, color, and odor: odorless, white, crystalline solid

Solubility: 75 ppm in water at 25°C; slightly soluble in aliphatic hydrocarbons, moderately soluble in ethanol and common aromatic solvents, soluble in acetone

Stability: stable at its m.p. and in solution; slowly decomposed by acids and bases in moist soil; non-corrosive

Other names: Lorox (DuPont), Afalon, Sarclex, HOE 2810

Reagents:

1. Linuron standard of known % purity
2. Chloroform
3. Hexane
4. Methanol
5. Methylene chloride

All solvents should be pesticide or spectro grade.

Equipment:

1. High pressure liquid chromatograph
2. High pressure liquid syringe or sample injection loop
3. Liquid chromatographic column 4 mm I.D. x 25 cm packed with LiChrosorb Si 60 - 10 μ (or equivalent column)
4. Usual laboratory glassware

Operating conditions for Hewlett-Packard Model 1010B LC:

Mobile phase: 40 ml methanol in 2000 ml of a solution containing 80% methylene chloride and 20% hexane

Column temperature: ambient

Observed column pressure: 3 kg/cm^2 (425 PSI)

Flow rate: 3 ml/min

Detector: UV at 254 nm

Chart speed: 0.5 in/min

Injection: 10 μl

Conditions may have to be varied by the analyst for other instruments, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.01 gram linuron standard into a 50 ml volumetric flask; dissolve and make to volume with chloroform (final conc 0.2 mg/ml).

Preparation of Sample:

Weigh an amount of sample equivalent to 0.02 gram linuron into a 100 ml volumetric flask, make to volume with chloroform and mix thoroughly (final conc 0.2 mg linuron/ml).

Determination:

Alternately inject three 10 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

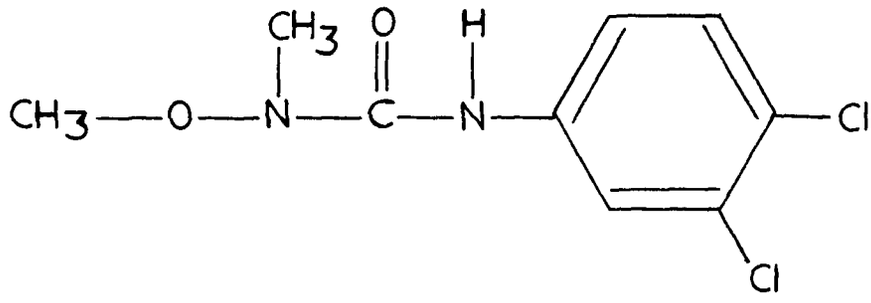
From the average peak height or peak area calculate the percent linuron as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method developed by Joseph B. Audino, Supervisor, Pesticide Formulation Laboratory, California Department of Food and Agriculture; and by Yoshihiko Kawano, Associate Chemist on sabbatical leave from the University of Hawaii.

Determination of Linuron by Infrared Spectroscopy

Linuron is the common name for 3-(3,4-dichlorophenyl)-1-methoxy -1-methylurea, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{10}Cl_2N_2O_2$

Molecular weight: 249.1

Melting point: 93 to 94°C

Physical state, color, and odor: odorless, white, crystalline solid

Solubility: 75 ppm in water at 25°C; slightly soluble in aliphatic hydrocarbons, moderately soluble in ethanol and common aromatic solvents, soluble in acetone

Stability: stable at its m.p. and in solution; slowly decomposed by acids and bases in moist soil; non-corrosive

Other names: Lorox (DuPont), Afalon, Sarclex, HOE 2810

Reagents:

1. Linuron standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps. These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.20 gram linuron standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 20 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 1.0 gram linuron into a glass-stoppered flask or screw-cap tube. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 20 mg linuron/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1370 cm^{-1} to 1250 cm^{-1} (7.3 μ to 8.0 μ).

Determine the absorbance of standard and sample using the peak at 1290 cm^{-1} (7.75 μ) and basepoint at 1258 cm^{-1} (7.95 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent linuron as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg linuron/ml chloroform gives an absorbance of approx. 0.01 in a 0.2 mm cell.)

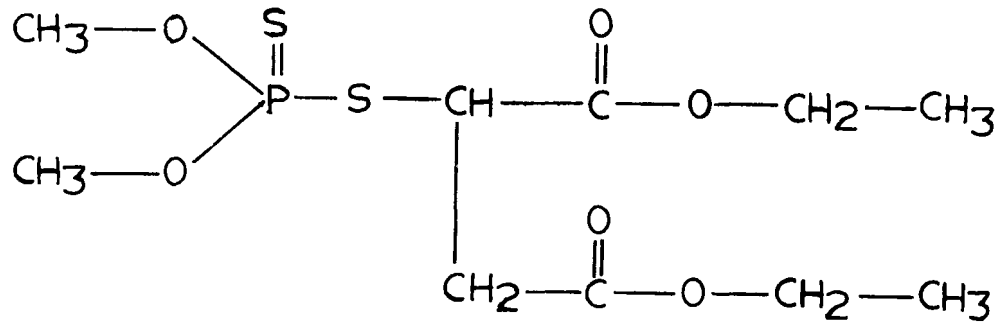
Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services.

December 1975

Malathion EPA-1
(Tentative)

Determination of Malathion by High Pressure Liquid Chromatography

Malathion is the official common name for 0,0-dimethyl dithiophosphate of diethyl mercaptosuccinate, a registered insecticide having the chemical structure:



Molecular formula: $C_{10}H_{19}O_6PS_2$

Molecular weight: 330.4

Melting/boiling point: m.p. 2.85°C, b.p. 156 to 157°C at 0.7 mm Hg with slight decomposition

Physical state, color, and odor: clear colorless to amber liquid, technical grade 95% with a garlic-like odor

Solubility: 145 ppm in water; limited solubility in petroleum oils but miscible with most organic solvents; light petroleum oil (30-60°C) is soluble in malathion to the extent of 35%

Stability: rapidly hydrolyzed at pH above 7.0 or below 5.0 but is stable in aqueous solutions buffered at pH 5.26; incompatible with alkaline pesticides and is corrosive to iron, hence lined containers must be used.

Other names: EI 4049 and Cythion (American Cyanamid), mercaptothion (So. Africa), carbofos (USSR), Emmatos, For-Mal, Fyfanon, Karbofos, Kop-Thion, Kypfos, Malaspray, Malamar, MLT, Zithiol

Reagents:

1. Malathion standard of known % purity
2. Methanol, ACS

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm. If a variable wavelength UV detector is available, other wavelengths may be useful to increase sensitivity or eliminate interference. 235 nm has been found very good for malathion.
2. Suitable column such as:
   a. DuPont ODS Permaphase, 1 meter x 2.1 mm ID
   b. Perkin-Elmer ODS Sil-X II-RP, 1/2 meter x 2.6 mm ID
3. High pressure liquid syringe or sample injection loop
4. Usual laboratory glassware

Operating Conditions:

Mobile phase:	30% methanol + 70% water
Column temperature:	55°C
Chart speed:	5 min/inch or equivalent
Flow rate:	0.5 to 1.5 ml/min (Perkin-Elmer 1/2 meter column)
Pressure:	700 psi (DuPont 1 meter column)
Attenuation:	Adjusted

Conditions may have to be varied by the analyst for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram malathion standard into a small glass-stoppered flask or vial, add 10 ml methanol by pipette, dissolve and mix well. (final conc 5 μg/μl)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.5 gram malathion into a glass-stoppered flask or vial, add 100 ml methanol by pipette, and shake thoroughly to dissolve the malathion. With granules or dust, shake for 30 minutes on a mechanical shaker or shake by hand intermittently for one hour. Allow any solid matter to settle; filter or centrifuge if necessary. (final conc 5 μg malathion/μl)

Determination:

Using a high pressure liquid syringe or sample injection loop, alternately inject three 5 μl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

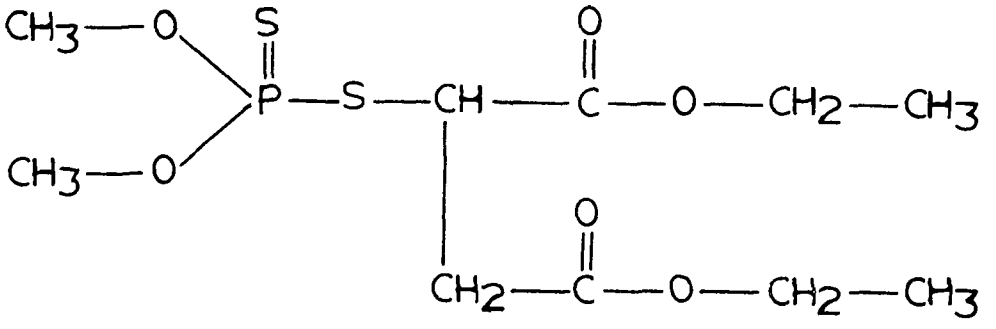
From the average peak height or peak area calculate the percent malathion as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Elmer H. Hayes, EPA, Beltsville, Md.

Determination of Malathion by Infrared Spectroscopy

Malathion is the official common name for O,O-dimethyl dithiophosphate of diethyl mercaptosuccinate, a registered insecticide having the chemical structure:



Molecular formula: $C_{10}H_{19}O_6PS_2$

Molecular weight: 330.4

Melting/boiling point: m.p. 2.85°C, b.p. 156 to 157°C at 0.7 mm Hg with slight decomposition

Physical state, color, and odor: clear colorless to amber liquid, technical grade 95% with a garlic-like odor

Solubility: 145 ppm in water; limited solubility in petroleum oils but miscible with most organic solvents; light petroleum oil (30-60°C) is soluble in malathion to the extent of 35%

Stability: rapidly hydrolyzed at pH above 7.0 or below 5.0 but is stable in aqueous solutions buffered at pH 5.26; incompatible with alkaline pesticides and is corrosive to iron, hence lined containers must be used.

Other names: EI 4049 and Cythion (American Cyanamid), mercaptothion (So. Africa), carbofos (USSR), Emmatos, For-Mal, Fyfanon, Karbofos, Kop-Thion, Kypfos, Malaspray, Malamar, MLT, Zithiol

Reagents:

1. Malathion standard of known % purity
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.1 gram malathion standard into a 10 ml volumetric flask and make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate to insure dryness and shake thoroughly. (conc 10 mg/ml)

Preparation of Sample:

For dusts, granules, and wettable powders, weigh a portion of sample equivalent to 0.5 gram malathion into a 125 ml glass-stoppered or screw-cap Erlenmeyer flask. Add 50 ml carbon disulfide by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly, shake on a mechanical shaker for 1 hour, allow to settle and filter or centrifuge if necessary, taking precaution to avoid evaporation. (final conc 10 mg malathion/ml)

For emulsifiable concentrates, weigh a portion of sample equivalent to 0.5 gram malathion into a small beaker, place on a steam bath, and evaporate the solvent with a current of air. Add about 5 ml of carbon disulfide and evaporate again. Extract the cooled residue with carbon disulfide, transfer to a 50 ml volumetric flask, and make to volume. Add a small amount of anhydrous sodium sulfate to insure dryness and shake thoroughly. (final conc 10 mg malathion/ml)

An alternative procedure, especially where interfering components cannot be removed by evaporation, is to prepare a compensating solution containing approximately the same concentration of interfering materials as is expected in the sample. This solution is used in the reference cell of double beam instruments.

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings, scan both the standard and sample from 685 cm^{-1} to 550 cm^{-1} (14.5 μ to 18.0 μ).

Determine the absorbance of standard and sample using the peak at 657.9 cm^{-1} (15.2 μ) and basepoint 625 cm^{-1} (16.0 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent malathion as follows:

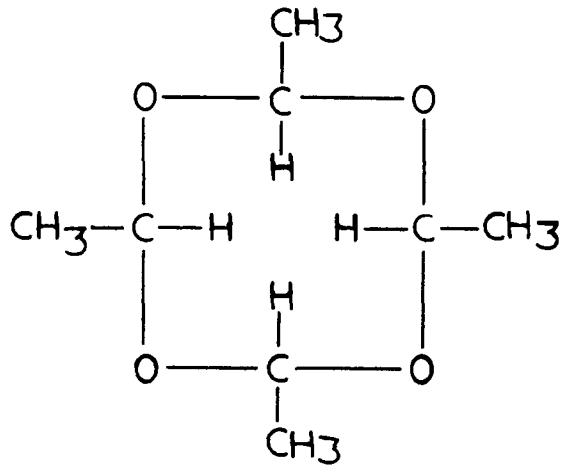
$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg malathion/ml carbon disulfide gives an absorbance of approx. 0.025 in a 0.2 mm cell.)

Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Determination of Metaldehyde by Iodimetric Titration

Metaldehyde is a registered molluscicide (attractant and toxicant for slugs and snails). Chemically, it is a polymerization of acetaldehyde; it is thought to be a stereoisomer of the eight-membered ring:



Molecular formula: $(CH_3CHO)_n$

Molecular weight: $(44.1)_n$

Melting point: in sealed tube, 246°C; sublimes at 110 to 120°C with partial depolymerization

Physical state, color, and odor: white crystalline flammable material with a powdery appearance and mild characteristic odor

Solubility: practically insoluble in water (200 ppm at 17°C); low solubility in ethanol (1.8% at 70°C) and ether; soluble in benzene and chloroform

Stability: combustible (burns with a non-smoky flame, thus it is used as a solid fuel); subject to depolymerization and sublimation: avoid soldered tinplate containers and high temperature

Other names: Antimilace, Meta, metacetaldehyde

Reagents:

1. Sulfuric acid, 1N solution
2. Sodium metabisulfite, 2.5% solution - dissolve 25 grams $Na_2S_2O_5$ in water and make to one liter.
3. Iodine, 0.1N standard solution - dissolve 12.7 grams iodine and 25.4 grams potassium iodide in water and make to one liter. Standardize against an arsenic primary standard.
4. Iodine, 1N solution - dissolve 63.5 grams iodine and 127 grams potassium iodide in water and make to 500 ml. (This solution need not be standardized.)
5. Starch indicator, 1% solution - boil 1 gram soluble starch in 100 ml water a few minutes; cool; store in bottle with 1 drop of mercury as preservative.
6. Sodium bicarbonate, powder

(All reagents should be ACS grade.)

Equipment:

1. 150 ml round-bottom distilling flask (with side arm bent vertically downward - see below)
2. Spiral condenser fitted with a 1 mm delivery tube long enough to reach the bottom of a 100 ml graduated cylinder
3. Thermometer 0 —100°C
4. Heating mantle or water bath for 60-70°C
5. Compressed air
6. Steam generator
7. Titration apparatus
8. Usual laboratory glassware

Procedure:

Apparatus assembly:

Bend the side outlet tube of a 150 ml distilling flask vertically downward so that it can be attached to the top of a vertical spiral condenser. To the bottom of the condenser, attach a delivery tube long enough to reach just to the bottom of a 100 ml graduated cylinder - the tip should be about 1 mm internal diameter. The bulb of the distilling flask should be placed in either a water bath or heating mantle so that a temperature of 60-70°C can be maintained for one hour. Fit a thermometer and an air inlet tube through a two-hole stopper in the neck of the flask so that both reach nearly to the bottom. The air inlet tube should have a fitting that can be changed from compressed air to steam.

Distillation:

Weigh a portion of sample equivalent to 0.1 gram metaldehyde, transfer to the distilling flask, add 50 ml of 1N sulfuric acid solution, and shake or swirl thoroughly so that all the sample is wet by the acid solution. Place 40 ml of 2.5% sodium bisulfite solution into a 100 ml graduated cylinder and place under the condenser with the delivery tube extending almost to the bottom. Attach the distillation flask to the assembled apparatus and heat at 60-70°C with an air flow of about four bubbles per second. After one hour, disconnect the air supply and immediately attach a steam generator and distill 50 ml into the bisulfite solution. Transfer the distillate and bisulfite solution to a 200 ml volumetric flask, make to volume with water, and mix well.

Titration:

Transfer 100 ml of the distillate-bisulfite solution to a 500 ml Erlenmeyer flask, add a few ml starch indicator, titrate the excess bisulfite solution by adding about 5 ml of the 1N iodine solution,

and complete titration with 0.1N iodine solution to the exact blue-violet endpoint. If exact endpoint is passed, add a little bisulfite solution and re-titrate with 0.1N iodine to the exact endpoint. Neutralize the solution with sodium bicarbonate powder and then add 5-10 grams in excess. When the solution becomes colorless, immediately titrate with the 0.1N iodine solution to a blue-violet color which remains for one minute after the addition of 1 drop of the iodine solution.

The amount of 0.1N iodine solution used between the two endpoints is used to calculate the amount of metaldehyde in the sample.

Calculation:

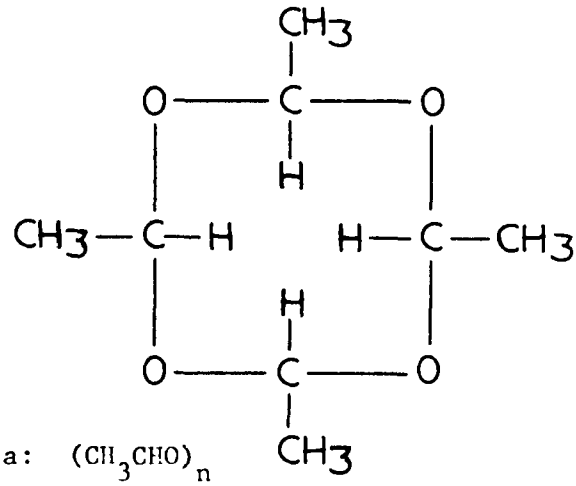
$$\% \text{ metaldehyde} = \frac{(\text{ml } I_2)(\text{N } I_2)(0.02203)(200/100)(100)}{(\text{grams sample})}$$

milliequivalent weight of metaldehyde = 0.02203

1 ml 0.1000N iodine solution = 0.0022 gram metaldehyde

Determination of Metaldehyde by Gas-Liquid Chromatography (TCD - Internal Standard)

Metaldehyde is a registered molluscicide (attractant and toxicant for slugs and snails). Chemically, it is a polymerization of acetaldehyde; it is thought to be a stereoisomer of the eight-membered ring:



Molecular formula: $(CH_3CHO)_n$

Molecular weight: $(44.1)_n$

Melting point: in sealed tube, 246°C; sublimes at 110 to 120°C with partial depolymerization

Physical state, color, and odor: white crystalline flammable material with a powdery appearance and mild characteristic odor

Solubility: practically insoluble in water (200 ppm at 17°C); low solubility in ethanol (1.8% at 70°C) and ether; soluble in benzene and chloroform

Stability: combustible (burns with a non-smoky flame, thus it is used as a solid fuel); subject to depolymerization and sublimation: avoid soldered tinplate containers and high temperature

Other names: Antimilace, Meta, metacetaldehyde

Reagents:

1. Metaldehyde standard of known % purity
2. Octyl alcohol standard of known % purity
3. Chloroform, pesticide or spectro grade
4. Internal Standard solution - weigh 0.25 gram octyl alcohol into a 100 ml volumetric flask, make to volume with chloroform, and mix well. (conc 2.5 mg octyl alcohol/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 4' x 1/4" O.D. glass column packed with 3% XE-60 on Chromosorb G AW DMCS (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	90°C
Injection temperature:	140°C
Detector temperature:	140°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas flow rate:	30 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.14 gram metaldehyde standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 14 mg metaldehyde and 2.5 mg octyl alcohol/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.35 gram metaldehyde into a small glass-stoppered flask or screw-cap bottle. Add by pipette 25 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the metaldehyde. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 14 mg metaldehyde and 2.5 mg octyl alcohol/ml)

Determination:

Inject 4-6 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is octyl alcohol, then metaldehyde.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of metaldehyde and octyl alcohol from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. octyl alcohol})(\%\text{ purity octyl alcohol})(\text{pk. ht. or area metaldehyde})}{(\text{wt. metaldehyde})(\%\text{ purity metaldehyde})(\text{pk. ht. or area octyl alcohol})}$$

Determine the percent metaldehyde for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. octyl alcohol})(\%\text{ purity octyl alcohol})(\text{pk. ht. or area metaldehyde})(100)}{(\text{wt. sample})(\text{pk. ht. or area octyl alcohol})(RF)} \quad (4-1)$$

Method submitted by Stelios Gerazounis, EPA, Region II, New York, N.Y.

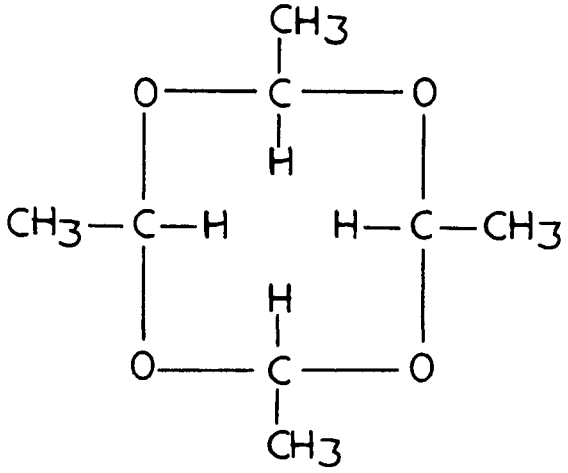
Some additional information and a few changes have been made in this write-up; therefore, any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated.

November 1975

Metaldehyde EPA-3
(Tentative)

Determination of Metaldehyde by Infrared Spectroscopy

Metaldehyde is a registered molluscicide (attractant and toxicant for slugs and snails). Chemically, it is a polymerization of acetaldehyde; it is thought to be a stereoisomer of the eight-membered ring:



Molecular formula: $(CH_3CHO)_n$

Molecular weight: $(44.1)_n$

Melting point: in sealed tube, 246°C; sublimes at 110 to 120°C with partial depolymerization

Physical state, color, and odor: white crystalline flammable material with a powdery appearance and mild characteristic odor

Solubility: practically insoluble in water (200 ppm at 17°C); low solubility in ethanol (1.8% at 70°C) and ether; soluble in benzene and chloroform

Stability: combustible (burns with a non-smoky flame, thus it is used as a solid fuel); subject to depolymerization and sublimation: avoid soldered tinplate containers and high temperature

Other names: Antimilace, Meta, metacetaldehyde

Reagents:

1. Metaldehyde standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.06 gram metaldehyde standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 6 mg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.3 gram metaldehyde into a glass-stoppered flask or screw-cap tube. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precautions to prevent evaporation. (final conc 6 mg metaldehyde/ml)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings, scan both the standard and sample from 1250 cm^{-1} to 1110 cm^{-1} (8.0 μ to 9.0 μ).

Determine the absorbance of standard and sample using the peak at 1164 cm^{-1} (8.59 μ) and basepoint 1140 cm^{-1} (8.77 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent metaldehyde as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

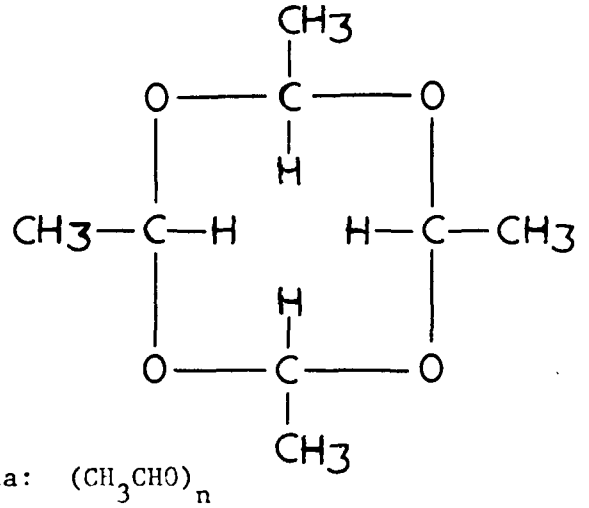
Method submitted by E. Greer, EPA, Region IX, San Francisco, California.

November 1975

Metaldehyde EPA-4
(Tentative)

Determination of Metaldehyde by Gas-Liquid Chromatography (TCD)

Metaldehyde is a registered molluscicide (attractant and toxicant for slugs and snails). Chemically, it is a polymerization of acetaldehyde; it is thought to be a stereoisomer of the eight-membered ring:



Molecular formula: $(CH_3CHO)_n$

Molecular weight: $(44.1)_n$

Melting point: in sealed tube, 246°C; sublimes at 110 to 120°C with partial depolymerization

Physical state, color, and odor: white crystalline flammable material with a powdery appearance and mild characteristic odor

Solubility: practically insoluble in water (200 ppm at 17°C); low solubility in ethanol (1.8% at 70°C) and ether; soluble in benzene and chloroform

Stability: combustible (burns with a non-smoky flame, thus it is used as a solid fuel); subject to depolymerization and sublimation: avoid soldered tinplate containers and high temperature

Other names: Antimilace, Meta, metacetaldehyde

Reagents:

1. Metaldehyde standard of known % purity
2. Chloroform, pesticide or spectro grade

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 5' x 1/4" O.D. glass column packed with 20% SE-30 on Chromosorb W AW DMCS (or equivalent column)
3. Precision liquid syringe: 50 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	120°C
Injection temperature:	160°C
Detector temperature:	160°C
Carrier gas:	Helium
Flow rate:	30 ml/min

Operating conditions for filament current, column temperature, or gas flow should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.06 gram metaldehyde standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, and shake to dissolve. (final conc 6 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.3 gram metaldehyde into a small glass-stoppered flask or screw-cap bottle. Add by pipette 50 ml chloroform, close tightly, and shake thoroughly to dissolve and extract the metaldehyde. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 6 mg metaldehyde/ml)

Determination:

Using a precision liquid syringe, alternately inject three 5-10 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent metaldehyde as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

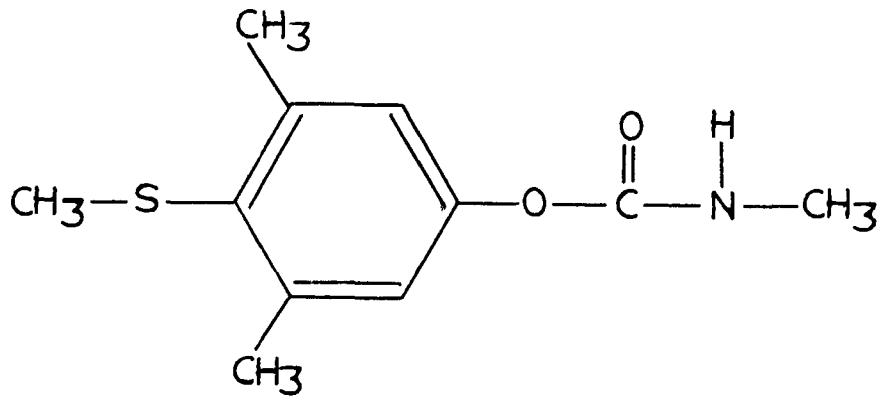
Method submitted by Eva Santos, EPA Region IX, San Francisco, California.

December 1975

Methiocarb EPA-1
(Tentative)

Determination of Methiocarb in Solid Formulations by Infrared Spectroscopy

Methiocarb is a common name (BSI) for 4-(methylthio)-3,5-xylyl N-methylcarbamate, a registered insecticide and acaricide having the chemical structure:



Molecular formula: $C_{11}H_{15}NO_2S$

Molecular weight: 225.3

Melting point: 121°C

Physical state, color, and odor: white crystalline powder with a mild milk-like odor

Solubility: insoluble in water; soluble in acetone and alcohol; soluble in most organic solvents

Stability: unstable in highly alkaline media (hydrolyzed by alkalis)

Other names: Mesurol, Bay 37344, H 321, (Bayer AG); mercaptodimethur, metmercapturon, Draza

Reagents:

1. Methiocarb standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording, with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker
3. Soxhlet extraction apparatus
4. Cotton or glass wool
5. Centrifuge or filtration apparatus
6. Rotary evaporator
7. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.07 gram methiocarb standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 7 mg/ml)

Preparation of Sample:

For high percent formulations (more than 10%), weigh a portion of sample equivalent to 0.35 gram methiocarb into a glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 7 mg methiocarb/ml)

For low percent (less than 10%) formulations, weigh a portion of sample equivalent to 0.35 gram methiocarb into a Soxhlet extraction thimble, plug with cotton or glass wool, and extract with chloroform for three hours. Evaporate to about 25 ml on a rotary evaporator, quantitatively transfer to a 50 ml volumetric flask, and make to volume with chloroform. Add a small amount of anhydrous sodium sulfate to clarify and dry the solution. (final conc 7 mg methiocarb/ml)

IR Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1880 cm^{-1} to 1625 cm^{-1} (5.32 μ to 6.15 μ).

Determine the absorbance of standard and sample using the peak at 1748 cm^{-1} (5.72 μ) and a baseline from 1835 cm^{-1} to 1667 cm^{-1} (5.45 μ to 6.00 μ).

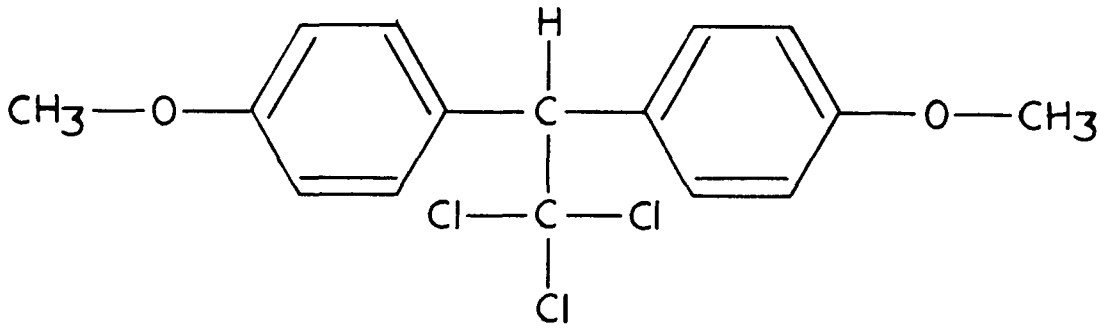
Calculation:

From the above absorbances, calculate the percent methiocarb as follows:

$$\% = \frac{\text{(abs. sample)(conc. std in mg/ml)(\% purity std)}}{\text{(abs. std)(conc. sample in mg/ml)}}$$

Determination of Technical Methoxychlor by Infrared Spectroscopy

Methoxychlor, technical is the official name for 2,2-bis (p-methoxyphenyl)-1,1,1-trichloroethane 88% and related compounds 12%; it is a registered insecticide having the chemical structure:



Molecular formula: $C_{16}H_{15}Cl_3O_2$

Molecular weight: 345.5

Physical state, color, and odor: pure p,p' isomer forms colorless crystals; technical product is a gray flaky powder containing 88% p,p' isomer with the bulk of the remainder being the o,p isomer

Melting point: pure p,p' isomer 89°C; technical 70 to 85°C

Solubility: practically insoluble in water; moderately soluble in ethanol and petroleum oils; readily soluble in most aromatic solvents

Stability: resistant to heat and oxidation; susceptible to dehydrochlorination by alcoholic alkali and heavy metal catalyst

Other names: Marlate (DuPont), Moxie, 1,1,1-trichloro-2,2-bis(p-methoxyphenyl)ethane

Reagents:

1. Methoxychlor, technical standard (minimum 88% p,p' isomer)
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm KBr or NaCl cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.16 gram technical methoxychlor standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml carbon disulfide by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 16 mg/ml)

Preparation of Sample:

Weigh an amount of sample (dusts and wettable powders) equivalent to 1.6 grams technical methoxychlor into a glass-stoppered flask or screw-cap bottle. Add 100 ml carbon disulfide by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 16 mg tech. methoxychlor/ml)

(Aerosols, emulsifiable concentrates, and oil solutions may be tried by this method; however, interfering substances are most likely to be present.)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical setting for the particular IR instrument being used, scan both the standard and sample from 870 cm^{-1} to 740 cm^{-1} (11.5 μ to 13.5 μ).*

Determine the absorbance of standard and sample using the peak at 795.5 cm^{-1} (12.57 μ) and basepoint at 772.2 cm^{-1} (12.95 μ).*

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent technical methoxychlor as follows:

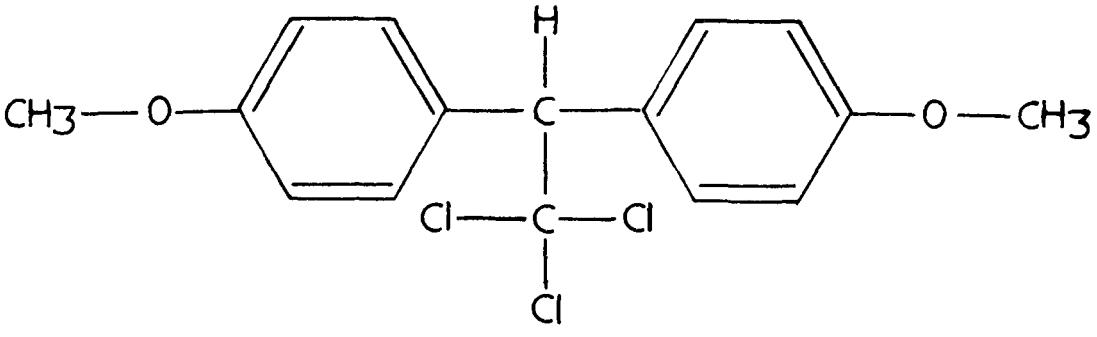
$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Method contributed by M. Conti and N. Frost, EPA Region IX, San Francisco, California.

* Absorption bands at 1250 cm^{-1} (8.0 μ), 1179 cm^{-1} (8.48 μ), 1042 cm^{-1} (9.6 μ), or 752 cm^{-1} (13.3 μ) may also be used when interference from other ingredients is present; however, the linearity should be checked.

Determination of Methoxychlor by Gas-Liquid Chromatography (FID - Internal Standard)

Methoxychlor, technical is the official name for 2,2-bis (p-methoxyphenyl)-1,1,1-trichloroethane 88% and related compounds 12%; it is a registered insecticide having the chemical structure:



Molecular formula: $C_{16}H_{15}Cl_3O_2$

Molecular weight: 345.5

Physical state, color, and odor: pure p,p' isomer forms colorless crystals; technical product is a gray flaky powder containing 88% p,p' isomer with the bulk of the remainder being the o,p isomer

Melting point: pure p,p' isomer 89°C; technical 70 to 85°C

Solubility: practically insoluble in water; moderately soluble in ethanol and petroleum oils; readily soluble in most aromatic solvents

Stability: resistant to heat and oxidation; susceptible to dehydrochlorination by alcoholic alkali and heavy metal catalyst

Other names: Marlate (DuPont), Moxie, 1,1,1-trichloro-2,2-bis(p-methoxyphenyl) ethane

Reagents:

1. Methoxychlor standard of known % purity
2. Dieldrin standard of known HEOD content
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.2 gram HEOD into a 50 ml volumetric flask; dissolve in and make to volume with acetone. (conc 4 mg HEOD/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm ID glass column packed with 5% OV-210 on 80/100 mesh Chromosorb W HP (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	190°C
Injection temperature:	240°C
Detector temperature:	240°C
Carrier gas:	Nitrogen
Carrier gas pressure:	40-60 psi
Hydrogen pressure:	20 psi
Air pressure:	30 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram methoxychlor standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 5 mg methoxychlor and 4 mg HEOD/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram methoxychlor into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the methoxychlor. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 5 mg methoxychlor and 4 mg HEOD/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is HEOD, then methoxychlor.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of methoxychlor and HEOD from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. HEOD})(\%\text{ purity HEOD})(\text{pk. ht. or area methoxychlor})}{(\text{wt. methoxychlor})(\%\text{ purity methoxychlor})(\text{pk. ht. or area HEOD})}$$

Determine the percent methoxychlor for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. HEOD})(\%\text{ purity HEOD})(\text{pk. ht. or area methoxychlor})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area HEOD})(RF)} \quad (4-1)$$

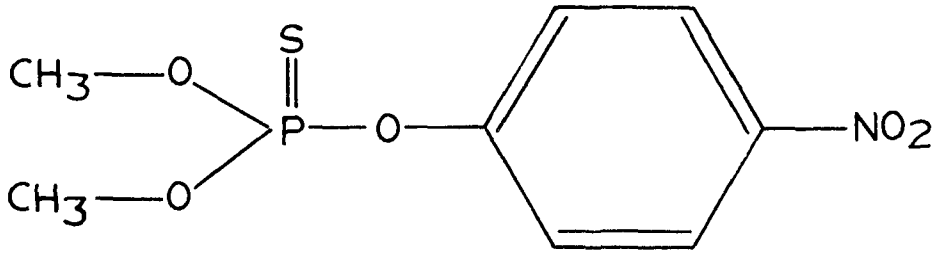
Note! MG-264 interferes with dieldrin under these conditions.

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Chemistry Lab. Any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated.

Determination of Methyl Parathion by High Pressure Liquid Chromatography

Methyl parathion is the common (US) name (parathion-methyl, ISO and BSI) for O,O-dimethyl O-p-nitrophenyl phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_8H_{10}NO_5PS$

Molecular weight: 263.2

Melting point: 35-36°C

Physical state and color: white crystalline solid; the technical product is a light to dark tan liquid of about 80% purity, crystallizing at about 29°C.

Solubility: 55-60 ppm in water at 25°C; slightly soluble in light petroleum and mineral oils; soluble in most other organic solvents

Stability: hydrolyzed by alkalis; compatible with most non-alkaline pesticides; isomerizes on heating; it is a good methylating agent.

Other names: Dalf (Bayer); Metacide, Nitrox 80 (Chemagro); parathion-methyl (ISO and BSI); Metaphos (USSR); dimethyl parathion; E601; Folidol M; Fosferno M50; Gearphos; Metron; Partron M; Tekwaisa; Wofatox

Reagents:

1. Methyl parathion standard of known % purity
2. Methanol, pesticide or spectro grade

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm. If a variable wavelength UV detector is available, other wavelengths may be useful to increase sensitivity or eliminate interference.
2. Suitable column such as:
   a. DuPont ODS Permaphase, 1 meter x 2.1 mm ID
   b. Perkin-Elmer ODS Sil-X 11 RP, 1/2 meter x 2.6 mm ID
3. High pressure liquid syringe or sample injection loop
4. Usual laboratory glassware

Operating Conditions:

Mobile phase:	20% methanol + 80% water
Column temperature:	50-55°C
Chart speed:	5 min/inch or equivalent
Flow rate:	0.5 to 1.5 ml/min (Perkin-Elmer 1/2 meter column)
Pressure:	700 psi (DuPont 1 meter column)
Attenuation:	Adjusted

Conditions may have to be varied by the analyst for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram methyl parathion standard into a small glass-stoppered flask or vial, add 100 ml methanol by pipette, dissolve and mix well. (final conc 1 mg methyl parathion/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.1 gram methyl parathion into a glass-stoppered flask or vial, add 100 ml methanol by pipette, and shake thoroughly to dissolve the methyl parathion. Allow any solid matter to settle; filter or centrifuge if necessary. (final conc 1 mg methyl parathion/ml)

Determination:

Alternately inject three 10 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

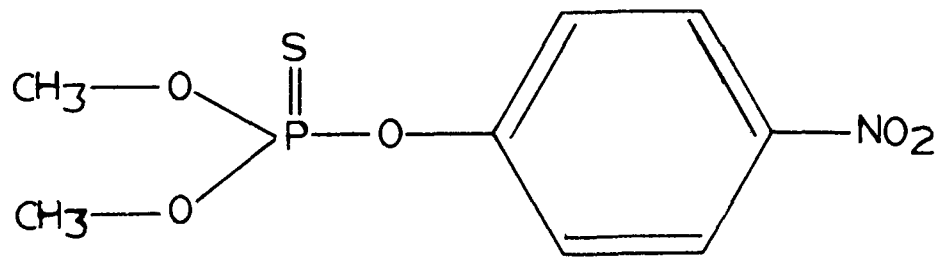
From the average peak height or peak area calculate the percent methyl parathion as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Elmer H. Hayes, EPA, Beltsville, Md.

Determination of Methyl Parathion by Infrared Spectroscopy

Methyl parathion is the common (US) name (parathion-methyl, ISO and BSI) for O,O-dimethyl O-p-nitrophenyl phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_8H_{10}NO_5PS$

Molecular weight: 263.2

Melting point: 35-36°C

Physical state and color: white crystalline solid; the technical product is a light to dark tan liquid of about 80% purity, crystallizing at about 29°C.

Solubility: 55-60 ppm in water at 25°C; slightly soluble in light petroleum and mineral oils; soluble in most other organic solvents

Stability: hydrolyzed by alkalis; compatible with most non-alkaline pesticides; isomerizes on heating; it is a good methylating agent.

Other names: Dalf (Bayer); Metacide, Nitrox 80 (Chemagro); parathion-methyl (ISO and BSI); Metaphos (USSR); dimethyl parathion; E601; Folidol M; Fosferno M50; Gearphos; Metron; Partron M; Tekwaisa; Wofatox

Reagents:

1. Methyl parathion standard of known % purity
2. Acetone, pesticide or spectro grade
3. Carbon disulfide, pesticide or spectro grade
4. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram methyl parathion into a small glass-stoppered flask or screw-cap bottle, add 10 ml carbon disulfide by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg methyl parathion/ml)

Preparation of Sample:

For emulsifiable concentrates, weigh a portion of sample equivalent to 0.1 gram methyl parathion into a 10 ml volumetric flask, make to volume with carbon disulfide, and mix well. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg methyl parathion/ml)

For granular formulations, weigh a portion of sample equivalent to 0.2 gram methyl parathion into a glass-stoppered flask or screw-cap bottle. Add 100 ml acetone by pipette and 1-2 grams anhydrous sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. Evaporate a 50 ml aliquot to dryness on a water bath using a gentle stream of dry air; evaporate the last one or two ml with air only. Add 5 ml carbon disulfide and evaporate again to remove all traces of acetone. Dissolve in about 4-5 ml carbon disulfide, transfer to a 10 ml volumetric flask, and make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg methyl parathion/ml)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan the standard and sample from 1350 cm^{-1} to 1110 cm^{-1} (7.4 μ to 9.0 μ).

Determine the absorbance of standard and sample using the peak at 1234.6 cm^{-1} (8.10 μ) and baseline from 1274 cm^{-1} to 1198 cm^{-1} (7.85 μ to 8.35 μ).

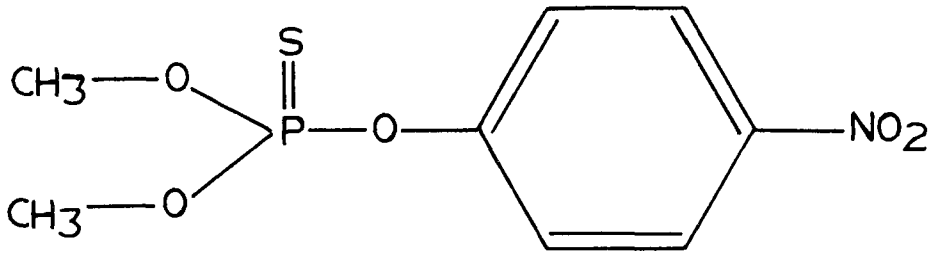
Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent methyl parathion as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Determination of Methyl Parathion in Dusts and Wettable Powder by Colorimetric (Visible) Spectroscopy

Methyl parathion is the common (US) name (parathion-methyl, ISO and BSI) for O,O-dimethyl O-p-nitrophenyl phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_8H_{10}NO_5PS$

Molecular weight: 263.2

Melting point: 35-36°C

Physical state and color: white crystalline solid; the technical product is a light to dark tan liquid of about 80% purity, crystallizing at about 29°C.

Solubility: 55-60 ppm in water at 25°C; slightly soluble in light petroleum and mineral oils; soluble in most other organic solvents

Stability: hydrolyzed by alkalis; compatible with most non-alkaline pesticides; isomerizes on heating; it is a good methylating agent.

Other names: Dalf (Bayer); Metacide, Nitrox 80 (Chemagro); parathion-methyl (ISO and BSI); Metaphos (USSR); dimethyl parathion; E601; Folidol M; Fosferno M50; Gearphos; Metron; Partron M; Tekwaisa; Wofatox

Principle of the Method:

The methyl parathion is extracted with alcohol and hydrolyzed with potassium hydroxide in the presence of hydrogen peroxide (this prevents reduction of the nitro group) to potassium p-nitrophenate, which is determined colorimetrically. Any free p-nitrophenol present is determined on a portion of the extract before hydrolysis. A high free p-nitrophenol content may indicate product decomposition, especially if the methyl parathion assay is low.

Reagents:

1. p-Nitrophenol of known % purity
2. 95% Ethanol, ACS
3. Ethanol, 50% in water
4. Potassium hydroxide, 1N solution in ethanol
5. Hydrogen peroxide, 30%

Equipment:

1. UV-VIS spectrophotometer, double beam ratio recording with matched 1 cm cells (a photoelectric colorimeter with a filter giving maximum transmission between 400-450 nm may be used)
2. Reflux apparatus
3. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.06 gram p-nitrophenol into a 100 ml volumetric flask; dissolve and make to volume with 95% ethanol. Pipette 10 ml into a second 100 ml volumetric flask and make to volume with 95%

ethanol. Pipette 5 ml into a third 100 ml volumetric flask, add by pipette 5 ml 1N potassium hydroxide solution, and make to volume with 95% ethanol. The final concentration will be 3 µg/ml.

Preparation of Sample:

Weigh a portion of sample equivalent to 0.012 gram methyl parathion into a 250 ml glass-stoppered flask. Add by pipette 100 ml 95% ethanol and shake periodically for about ten minutes. Filter 25-50 ml into a glass-stoppered flask or bottle. If necessary, extract a larger sample and aliquot, using 95% ethanol as the solvent.

Determination:

Standard:

With the UV-VIS spectrophotometer at the optimum quantitative settings, balance the pen for 0 and 100% at 405 nm with 50% ethanol in both cells. Set the instrument to scan from 500 nm to 350 nm. Scan the standard p-nitrophenol solution between these wavelengths using 50% ethanol in the reference cell.

Free p-nitrophenol:

To measure the free p-nitrophenol, pipette 10 ml of the filtered sample solution into a 100 ml volumetric flask and make to volume with 50% ethanol. Add 5 drops of 1N potassium hydroxide solution, mix, and immediately (within 2 minutes of adding the alkali) scan from 500 nm to 350 nm. This is the absorbance due to the free p-nitrophenol in the sample.

Methyl parathion (as p-nitrophenol):

To determine the methyl parathion (as p-nitrophenol), pipette 5 ml of the filtered sample solution into a 125 ml standard taper Erlenmeyer flask. Add 5 ml 1N potassium

hydroxide solution by pipette, 2 ml of 30% hydrogen peroxide, a few glass beads, and reflux for at least 30 minutes. Cool, transfer to a 100 ml volumetric flask with 50% ethanol, and make to volume with the 50% ethanol. Scan between 500 nm and 350 nm. This is the uncorrected total absorbance due to the free p-nitrophenol and to the p-nitrophenol from the methyl parathion. The concentration of this solution is 6 µg methyl parathion/ml or approx. 3 µg p-nitrophenol/ml.

Calculation:

Using the absorbance due to the free p-nitrophenol (FPNP), calculate the percent present as follows:

$$\% = \frac{(\text{abs. FPNP})(\text{wt. std})(1/100)(10/100)(5/100)(100)}{(\text{abs. std})(\text{wt. sample})(1/100)(10/100)}$$

Using the absorbance from the uncorrected total p-nitrophenol (UTPNP), calculate the percent as follows:

$$\% = \frac{(\text{abs. UTPNP})(\text{wt. std})(1/100)(10/100)(5/100)(100)}{(\text{abs. std})(\text{wt. sample})(1/100)(5/100)}$$

The percent p-nitrophenol due to the methyl parathion is found by subtracting the free p-nitrophenol from the uncorrected total p-nitrophenol.

% p-nitrophenol = % uncorrected total p-nitrophenol - % free p-nitrophenol

The % methyl parathion is then found by dividing this % p-nitrophenol by .5285 or multiplying by 1.892.

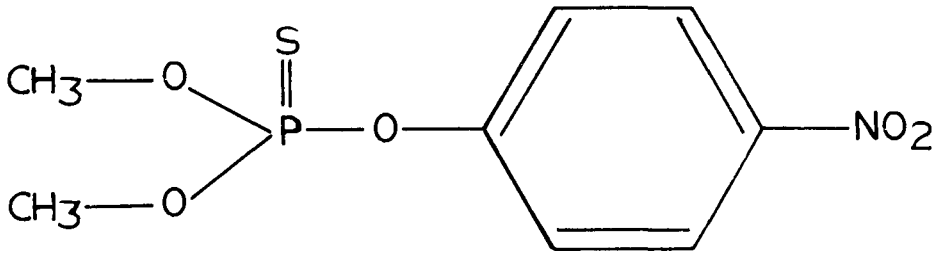
$$\% \text{ Methyl Parathion} = \frac{(\% \text{ p-nitrophenol})}{(.5285)} \text{ or } (1.892)(\% \text{ p-nitrophenol})$$

Methyl parathion = 52.85% p-nitrophenol

% methyl parathion = % p-nitrophenol X 1.892

Determination of Methyl Parathion in Emulsifiable Concentrates by Gas-Liquid Chromatography (FID - Internal Standard)

Methyl parathion is the common (US) name (parathion-methyl, ISO and BSI) for O,O-dimethyl O-p-nitrophenyl phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_8H_{10}NO_5PS$

Molecular weight: 263.2

Melting point: 35-36°C

Physical state and color: white crystalline solid; the technical product is a light to dark tan liquid of about 80% purity, crystallizing at about 29°C.

Solubility: 55-60 ppm in water at 25°C; slightly soluble in light petroleum and mineral oils; soluble in most other organic solvents

Stability: hydrolyzed by alkalis; compatible with most non-alkaline pesticides; isomerizes on heating; it is a good methylating agent.

Other names: Dalf (Bayer); Metacide, Nitrox 80 (Chemagro); parathion-methyl (ISO and BSI); Metaphos (USSR); dimethyl parathion; E601; Folidol M; Fosferno M50; Gearphos; Metron; Partron M; Tekwaisa; Wofatox

Reagents:

1. Methyl parathion standard of known % purity
2. p,p'-DDE standard of known % purity
3. Carbon disulfide, pesticide or spectro grade
4. Internal Standard solution - weigh 0.125 gram p,p'-DDE into a 25 ml volumetric flask, dissolve in, and make to volume with carbon disulfide. (conc 5 mg DDE/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 1/4" OD glass column packed with a 1:1 mixture of 10% DC-200 and 15% QF-1 on 80/100 mesh Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 10 or 50 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	190°C
Injection temperature:	215°C
Detector temperature:	260°C
Carrier gas:	Nitrogen
Carrier gas flow rate:	90 ml/min
Hydrogen flow rate:	Adjust for specific GC
Air flow rate:	Adjust for specific GC

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.08 gram methyl parathion standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 8 mg methyl parathion and 5 mg DDE/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.08 gram methyl parathion into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the methyl parathion. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 8 mg methyl parathion and 5 mg DDE/ml)

Determination:

Inject 2-3 µl of standard and adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is methyl parathion, then DDE.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of methyl parathion and DDE from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{\text{(wt. DDE)(\% purity DDE)(pk. ht. or area methyl parathion)}}{\text{(wt. methyl parathion)(\% purity methyl parathion)(pk. ht. or area DDE)}}$$

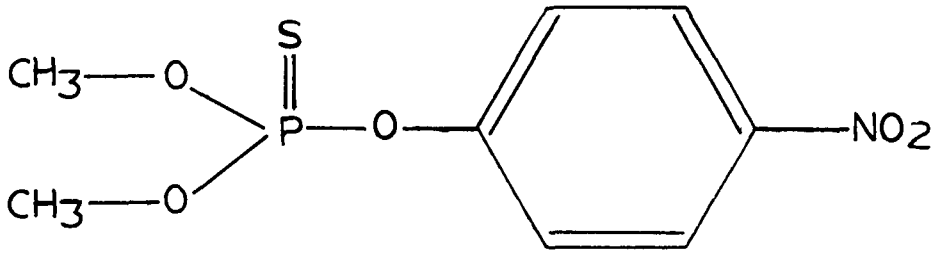
Determine the percent methyl parathion for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{\text{(wt. DDE)(\% purity DDE)(pk. ht. or area methyl parathion)}\cancel{(100)}}{\text{(wt. sample)(pk. ht. or area DDE)(RF)}} \quad (4-1)$$

Method submitted by Mississippi State Chemical Laboratory, Box CR, Mississippi State, Mississippi 39762.

Determination of Methyl Parathion by Gas-Liquid Chromatography (FID - Internal Standard)

Methyl parathion is the common (US) name (parathion-methyl, ISO and BSI) for O,O-dimethyl O-p-nitrophenyl phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_8H_{10}NO_5PS$

Molecular weight: 263.2

Melting point: 35-36°C

Physical state and color: white crystalline solid; the technical product is a light to dark tan liquid of about 80% purity, crystallizing at about 29°C.

Solubility: 55-60 ppm in water at 25°C; slightly soluble in light petroleum and mineral oils; soluble in most other organic solvents

Stability: hydrolyzed by alkalis; compatible with most non-alkaline pesticides; isomerizes on heating; it is a good methylating agent.

Other names: Dalf (Bayer); Metacide, Nitrox 80 (Chemagro); parathion-methyl (ISO and BSI); Metaphos (USSR); dimethyl parathion; E601; Folidol M; Fosferno M50; Gearphos; Metron; Partron M; Tekwaisa; Wofatox

Reagents:

1. Methyl parathion standard of known % purity
2. Dieldrin standard of known HEOD content
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.15 gram HEOD into a 25 ml volumetric flask; dissolve in and make to volume with acetone. (conc 6 mg HEOD/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 4 mm ID glass column packed with 3% OV-1 on 60/80 mesh Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	175°C
Injection temperature:	250°C
Detector temperature:	250°C
Carrier gas:	Nitrogen
Carrier gas pressure:	(not stated in method)(40-60 psi)
Hydrogen pressure:	32 psi
Air pressure:	29 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.06 gram methyl parathion standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 6 mg methyl parathion and 6 mg HEOD/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.06 gram methyl parathion into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the methyl parathion. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 6 mg methyl parathion and 6 mg HEOD/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is methyl parathion, then HEOD.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of methyl parathion and HEOD from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{\text{(wt. HEOD)(\% purity HEOD)(pk. ht. or area methyl parathion)}}{\text{(wt. methyl parathion)(\% purity methyl parathion)(pk. ht. or area HEOD)}}$$

Determine the percent methyl parathion for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{\text{(wt. HEOD)(\% purity HEOD)(pk. ht. or area methyl parathion)}\cancel{(100)}}{\text{(wt. sample)(pk. ht. or area HEOD)(RF)}} \quad (4\text{-}1)$$

The above method was submitted by Division of Regulatory Services, Kentucky Agricultural Experiment Station, University of Kentucky, Lexington, Kentucky 40506.

A similar method (data below) was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Column: 4' x 2 mm ID glass packed with 5% SE-30 on 80/100 mesh Chromosorb W HP

Column temp: 180°

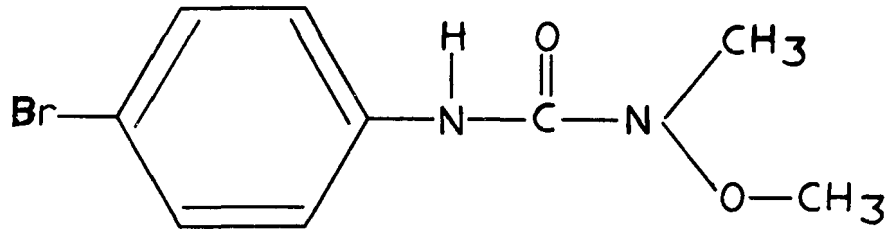
Internal standard: Alachlor 2 mg/ml

Methyl parathion conc: 2 mg/ml

Comments, criticisms, suggestions, data, etc. concerning this method are invited and are welcome.

Determination of Metobromuron by Infrared Spectroscopy

Metobromuron is the accepted common name for 3-(p-bromophenyl)-1-methoxy-1-methylurea, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{11}BrN_2O_2$

Molecular weight: 259

Melting point: 95.5 to 96°C

Physical state and color: white crystalline solid

Solubility: 330 ppm in water at RT; very soluble in acetone, chloroform, ethanol

Stability: stable; non-corrosive; good compatibility

Other names: Patoran (CIBA), C-3126

Reagents:

1. Metobromuron standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm KBr or NaCl cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram metobromuron standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.5 gram metobromuron into a glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precautions to prevent evaporation. (final conc 10 metobromuron/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings, scan both the standard and sample from 1430 cm^{-1} to 1250 cm^{-1} (7.0 μ to 8.0 μ).

Determine the absorbance of standard and sample using the peak at 1387 cm^{-1} (7.21 μ) and basepoint 1351 cm^{-1} (7.40 μ).

An alternate peak at 1305 cm^{-1} (7.66 μ) with the same basepoint could be used. Both give a linear absorption curve over the 3-13 mg/ml range.

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent metobromuron as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Method submitted by Eva Santos, EPA Region IX, San Francisco, California.

David Persch, EPA Region II, New York, N. Y. submitted a similar method using:

scan range: 2000 cm^{-1} to 1430 cm^{-1} (5.0 μ to 7.0 μ)

analytical peak: 1683.5 cm^{-1} (5.94 μ)

basepoint: 1818 cm^{-1} (5.5 μ)

The absorption curve is linear for 2-16 mg/ml.

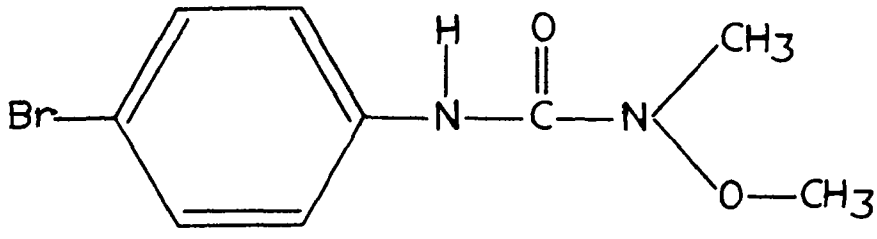
Comments on these analytical bands (or others) are most welcome.

November 1975

Metobromuron EPA-2
(Tentative)

Determination of Metobromuron by Gas-Liquid Chromatography (FID)

Metobromuron is the accepted common name for 3-(p-bromophenyl)-1-methoxy-1-methylurea, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{11}BrN_2O_2$

Molecular weight: 259

Melting point: 95.5 to 96°C

Physical state and color: white crystalline solid

Solubility: 330 ppm in water at RT; very soluble in acetone, chloroform, ethanol

Stability: stable; non-corrosive; good compatibility

Other names: Patoran (CIBA), C-3126

Reagents:

1. Metobromuron standard of known % purity
2. Acetone, pesticide or spectro grade

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 2' x 4 mm ID glass column packed with 2% SE-52 on 70/80 mesh Anakrom ABS (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	165°C
Injection temperature:	200°C
Detector temperature:	200°C
Carrier gas:	Nitrogen
Carrier gas pressure:	40 psi
Hydrogen pressure:	20 psi
Air pressure:	30 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram metobromuron standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml acetone by pipette, close tightly, and shake to dissolve. (final conc 10 mg metobromuron/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.5 gram metobromuron into a glass-stoppered flask or screw-cap bottle, add 50 ml acetone by pipette, close tightly, and shake for one hour. Allow to settle; filter or centrifuge if necessary, taking precautions to prevent evaporation. (final conc 10 mg metobromuron/ml)

Determination:

Using a precision liquid syringe, alternately inject three 3-4 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

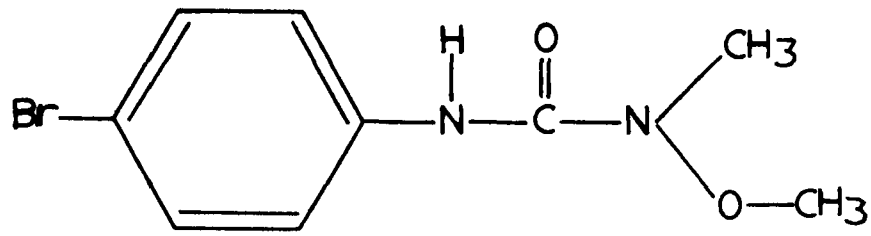
From the average peak height or peak area calculate the percent metobromuron as follows:

$$\% = \frac{\text{(pk. ht. or area sample)(wt. std injected)(\% purity std)}}{\text{(pk. ht. or area std)(wt. sample injected)}}$$

This method is based on a modification of EPA's Experimental Method (No. 47) which was adapted from a method from Ciba. Comments, suggestions, data, results, etc. on this method are most welcome.

Determination of Metobromuron by Gas-Liquid Chromatography (TCD - Internal Standard)

Metobromuron is the accepted common name for 3-(p-bromophenyl)-1-methoxy-1-methylurea, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{11}BrN_2O_2$

Molecular weight: 259

Melting point: 95.5 to 96°C

Physical state and color: white crystalline solid

Solubility: 330 ppm in water at RT; very soluble in acetone, chloroform, ethanol

Stability: stable; non-corrosive; good compatibility

Other names: Patoran (CIBA), C-3126

Reagents:

1. Metobromuron standard of known % purity
2. Aldrin standard of known HHDN content
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.2 gram HHDN into a 25 ml volumetric flask, dissolve in, and make to volume with acetone. (conc 8 mg HHDN/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 4' x 1/4" O.D. glass column packed with 4% SE-30 on 60/80 mesh Diatoport S (or equivalent column)
3. Precision liquid syringe: 10 or 25 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	165°C
Injection temperature:	200°C
Detector temperature:	200°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas pressure:	30-40 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram metobromuron standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 5 mg metobromuron and 8 mg HHDN/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.05 gram metobromuron into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the metobromuron. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 5 mg metobromuron and 8 mg HHDN/ml)

Determination:

Inject 5-15 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is metobromuron, then HHDN.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of metobromuron and HHDN from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. HHDN})(\%\text{ purity HHDN})(\text{pk. ht. or area metobromuron})}{(\text{wt. metobromuron})(\%\text{ purity metobromuron})(\text{pk. ht. or area HHDN})}$$

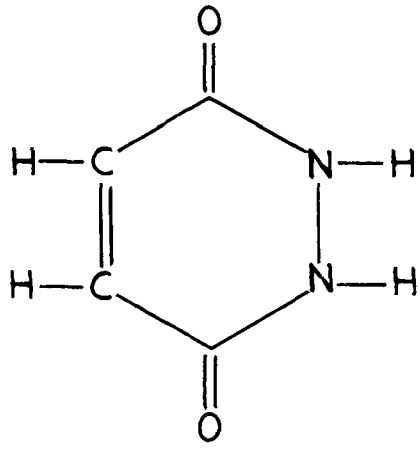
Determine the percent metobromuron for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. HHDN})(\%\text{ purity HHDN})(\text{pk. ht. or area metobromuron})\cancel{(100)}}{(\text{wt. sample})(\text{pk. ht. or area HHDN})(RF)} \quad (4\text{-}1)$$

This method is based on EPA Experimental Method No. 47B submitted by G. Radan, EPA, Region II, New York, N. Y. Some changes have been made in this write-up; therefore, any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated.

Determination of MH in Water-Soluble Formulations by Ultraviolet Spectroscopy

MH is the common name for 1,2-dihydro-pyridazinedione, a registered growth retardant and selective herbicide having the chemical structure:



Molecular formula: $C_4H_4N_2O_2$

Molecular weight: 112.1

Melting point: 296 to 298°C; the technical product is at least 97% pure and has a m.p. of at least 292°C.

Physical state, color, and odor: odorless, white crystalline powder

Solubility: at 25°C is 0.6% in water, 0.1% in ethanol or acetone, 2.4% in dimethylformamide

Stability: stable to hydrolysis; decomposed by strong acids with release of nitrogen. Behaves as a mono-basic acid and forms salts with alkali metals and amines; these salts are water-soluble but are precipitated by hard water.

Other names: Maleic hydrazide; MH-30 (Uniroyal); Retard (Ansul); De-Cut; De-Sprout; Regulox; Royal MH-30; Slo-Gro; Sprout-Stop; Stuntman; Suckerstuff; Vonaldehyde; Vondrax; KMH, Maintain 3; 1,2,3,6-tetrahydro-3,6-dioxo-pyridazine; 6-hydroxy-3-(2H)-pyridazinone

Reagents:

1. MH standard of known % purity
2. Sodium hydroxide, approx. 0.1N (freshly prepared)

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram MH into a 250 ml volumetric flask; dissolve in and make to volume with 0.1N sodium hydroxide solution. Mix thoroughly and pipette 5 ml into a 100 ml volumetric flask, make to volume with 0.1N sodium hydroxide solution, and mix thoroughly. (final conc 20 µg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram MH into a 250 ml volumetric flask, make to volume with 0.1N sodium hydroxide solution, and mix thoroughly. Pipette a 5 ml aliquot into a 100 ml volumetric flask and make to volume with 0.1N sodium hydroxide solution. (final conc 20 µg MH/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 330 nm with 0.1N sodium hydroxide solution in each cell. Scan both the standard and sample from 360 nm to 280 nm with 0.1N sodium hydroxide solution in the reference cell. Measure the absorbance of both standard and sample at 330 nm.

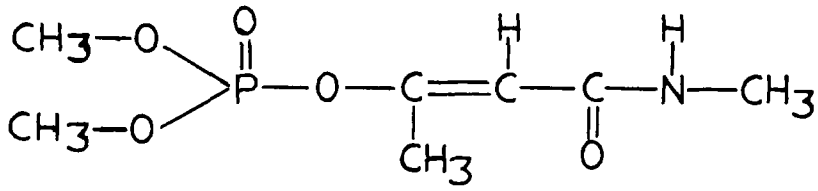
Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent MH as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

Determination of Monocrotophos by Infrared Spectroscopy

Monocrotophos is the common name for dimethyl phosphate of 3-hydroxy-N-methyl-cis-crotonamide, a registered insecticide having the chemical structure:



Molecular formula: $C_7H_{14}NO_5P$

Molecular weight: 223

Melting point: 54 to 55°C (technical material 25 to 30°C)

Physical state, color, and odor: colorless to white crystalline material with a mild ester odor. The technical product is a reddish brown semi-solid.

Solubility: miscible with water; soluble in acetone and ethanol; sparingly soluble in xylene but almost insoluble in diesel oils and kerosene

Stability: unstable in lower but stable in higher alcohols and glycols, stable in ketones; hydrolyzes slowly at pH 1 to 7, rapidly above pH 7; corrosive to black iron, drum steel, brass, SS 304, but does not attack glass, aluminum, or SS 316; incompatible with alkaline pesticides

Other names: Azodrin (Shell); Nuvacron (Ciba); Monocron; dimethyl-1-methyl-2-methyl-carbamoyl-vinyl phosphate; cis-3-(dimethoxyphosphinyloxy)-N-methylcrotonamide; O,O-dimethyl-O-(2 methylcarbamoyl-1-methyl-vinyl)-phosphate

Reagents:

1. Monocrotophos standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Anhydrous sodium sulfate, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.1 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps. These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.2 gram monocrotophos standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 20 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.2 gram monocrotophos into a glass-stoppered flask or screw-cap tube. Add 10 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close

tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 20 mg monocrotophos/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 945 cm^{-1} to 870 cm^{-1} (10.6 μ to 11.5 μ).

Determine the absorbance of standard and sample using the peak at 900 cm^{-1} (11.1 μ) and basepoint at 920 cm^{-1} (10.86 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent monocrotophos as follows:

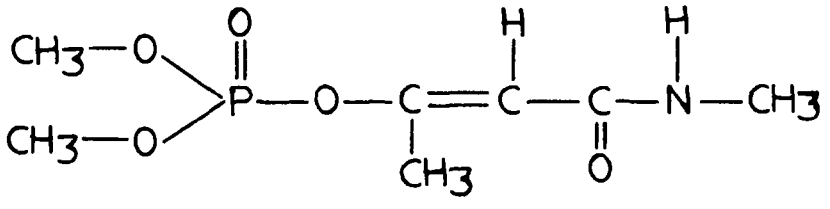
$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg monocrotophos/ml chloroform gives an absorbance of approx. 0.009 in a 0.1 mm cell.)

Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Determination of Monocrotophos by Gas-Liquid Chromatography (FID - Internal Standard)

Monocrotophos is the common name for dimethyl phosphate of 3-hydroxy-N-methyl-cis-crotonamide, a registered insecticide having the chemical structure:



Molecular formula: $C_7H_{14}NO_5P$

Molecular weight: 223

Melting point: 54 to 55°C (technical material 25 to 30°C)

Physical state, color, and odor: colorless to white crystalline material with a mild ester odor. The technical product is a reddish brown semi-solid.

Solubility: miscible with water; soluble in acetone and ethanol; sparingly soluble in xylene but almost insoluble in diesel oils and kerosene

Stability: unstable in lower but stable in higher alcohols and glycols, stable in ketones; hydrolyzes slowly at pH 1 to 7, rapidly above pH 7; corrosive to black iron, drum steel, brass, SS 304, but does not attack glass, aluminum, or SS 316; incompatible with alkaline pesticides

Other names: Azodrin (Shell); Nuvacron (Ciba); Monocron; dimethyl-1-methyl-2-methyl-carbamoyl-vinyl phosphate; cis-3-(dimethoxyphosphinyloxy)-N-methylcrotonamide; O,O-dimethyl-O-(2 methylcarbamoyl-1-methyl-vinyl)-phosphate

Reagents:

1. Monocrotophos standard of known % purity
2. Methyl parathion standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.75 gram methyl parathion into a 50 ml volumetric flask, dissolve in, and make to volume with acetone. (conc 15 mg methyl parathion/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 5' x 1/8" stainless steel column packed with 3% SE-30 on 100/120 Varaport 30 (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	175°C
Injection temperature:	225°C
Detector temperature:	240°C
Carrier gas:	Nitrogen
Carrier gas flow rate:	50 ml/min
Hydrogen flow rate:	30 ml/min
Air flow rate:	300 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram monocrotophos standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 10 mg monocrotophos and 15 mg methyl parathion/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram monocrotophos into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the monocrotophos. For coarse or granular materials, shake mechanically for 10-15 minutes or shake by hand intermittently for 25-30 minutes. (final conc 10 mg monocrotophos and 15 mg methyl parathion/ml)

Determination:

Inject 2-3 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is monocrotophos, then methyl parathion.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of monocrotophos and methyl parathion from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

IS = internal standard = methyl parathion

$$RF = \frac{(\text{wt. IS})(\%\text{ purity IS})(\text{pk. ht. or area monocrotophos})}{(\text{wt. monocrotophos})(\%\text{ purity monocrotophos})(\text{pk. ht. or area IS})}$$

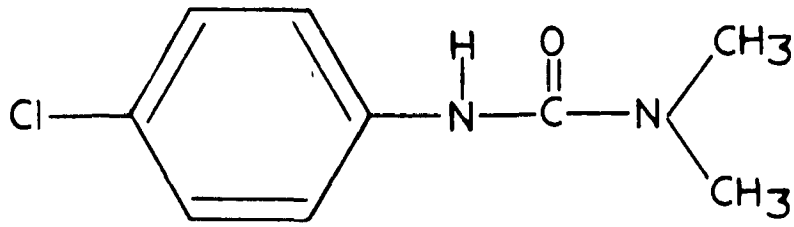
Determine the percent monocrotophos for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. IS})(\%\text{ purity IS})(\text{pk. ht. or area monocrotophos})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area IS})(RF)} \quad (4\text{-}1)$$

Method submitted by Division of Regulatory Services, Kentucky Agricultural Experiment Station, University of Kentucky, Lexington, Kentucky 40506.

Determination of Monuron by Alkaline Hydrolysis and Titration

Monuron is the common name for 3-(p-chlorophenyl)-1,1-dimethyl-urea, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{11}ClN_2O$

Molecular weight: 198.6

Melting point: 174-175°C

Physical state, color, and odor: odorless, white crystalline solid

Solubility: 230 ppm in water at 25°C; sparingly soluble in petroleum oils and in polar organic solvents; 5.2% in acetone at 27°C

Stability: stable toward moisture and oxidation at RT but is decomposed at 185-200°C; rate of hydrolysis at RT or neutrality is negligible but is increased at elevated temp. or more acid or alkaline conditions; non-corrosive and non-flammable

Other names: Telvar (DuPont), chlorfenidim (USSR), Monurex

Principle of the Method:

The monuron is hydrolyzed to p-chloroaniline, carbon dioxide (as carbonate), and dimethylamine. The dimethylamine is distilled and titrated. Volatile, moderately strong bases, or substances that hydrolyze to give them, interfere.

Reagents:

1. Potassium hydroxide, 20% solution
2. Hydrochloric acid, 0.1N standard solution
3. Sodium hydroxide, 0.1N standard solution
4. Ethyl alcohol, ACS
5. Glycerol, ACS

Equipment:

1. Distilling apparatus consisting of a 500 ml round-bottom flask with a thermometer well in the side and a 24/40 standard taper (ST) joint at the top. The flask is connected to the bottom of a vertical condenser which has its top connected to the top of a second vertical condenser by a horizontal tube with a right angle 24/40 ST joint on each end. The bottom of the second condenser is connected by 24/40 ST joint to the top of a delivery tube which has a narrow plain end extending almost to the bottom of a receiving beaker.
2. 500 ml size heating mantle with variable transformer control
3. Thermometer to 200°C
4. Potentiometric titrimeter
5. Usual laboratory glassware

Procedure:

Weigh a portion of sample equivalent to 0.4-0.5 gram monuron into the reaction flask, dissolve in 25 ml ethyl alcohol, and add 100 ml glycerol and 100 ml 20% potassium hydroxide solution. Attach immediately to the first condenser.

Pipette 50 ml of the 0.1N standard hydrochloric acid into the receiving beaker. Reflux at a moderate rate for 2-1/2 hours with water flowing through both condensers. Remove the water from the first condenser and distill until the temperature at the thermometer well reaches 175°C -- usually about 50 minutes. (The temperature rises rapidly at the end.)

Titration:

Remove the delivery tube and receiving beaker and rinse the delivery tube into the beaker. Titrate the excess standard acid with the 0.1N standard sodium hydroxide potentiometrically, using a glass electrode and a calomel electrode. The inflection point, which occurs at about pH 7.6, is taken as the endpoint.

With less accuracy, bromthymol blue may be used as an internal indicator.

Calculation:

Calculate the percentage of monuron as follows:

$$\% = \frac{(ml)(N)(0.1986)(100)}{(g \text{ sample})}$$

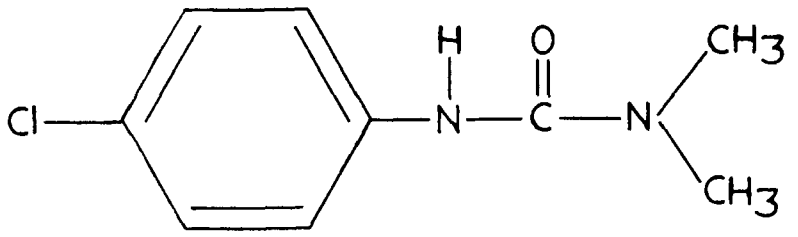
where: 0.1986 is the milliequivalent weight of monuron

(1 ml 0.1N HCl = 0.01986 g monuron)

This method is based on Lowen and Baker, Anal. Chem. 24, 1475 (1952).

Determination of Monuron by Ultraviolet Spectroscopy

Monuron is the common name for 3-(p-chlorophenyl)-1,1-dimethyl-urea, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{11}ClN_2O$

Molecular weight: 198.6

Melting point: 174-175°C

Physical state, color, and odor: odorless, white crystalline solid

Solubility: 230 ppm in water at 25°C; sparingly soluble in petroleum oils and in polar organic solvents; 5.2% in acetone at 27°C

Stability: stable toward moisture and oxidation at RT but is decomposed at 185-200°C; rate of hydrolysis at RT or neutrality is negligible but is increased at elevated temp. or more acid or alkaline conditions; non-corrosive and non-flammable

Other names: Telvar (DuPont), chlorfenidim (USSR), Monurex

Reagents:

1. Monuron standard of known % purity
2. Methanol, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm silica cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram monuron standard into a 100 ml volumetric flask, add 100 ml methanol by pipette, and mix thoroughly. Pipette 10 ml into a second 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette 5 ml into a third 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. (final conc 5 µg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram monuron into a 250 ml glass-stoppered or screw-cap flask, add 100 ml methanol by pipette, and shake on a mechanical shaker for 30 minutes. Allow to settle; centrifuge or filter if necessary, taking precautions to prevent evaporation. Pipette 10 ml into a 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette 5 ml of this solution into another 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. (final conc 5 µg monuron/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen at 0 and 100% transmission at 245 nm with

methanol in each cell. Scan both the standard and sample from 300 nm to 200 nm with methanol in the reference cell.

Measure the absorbance of standard and sample at 245 nm.

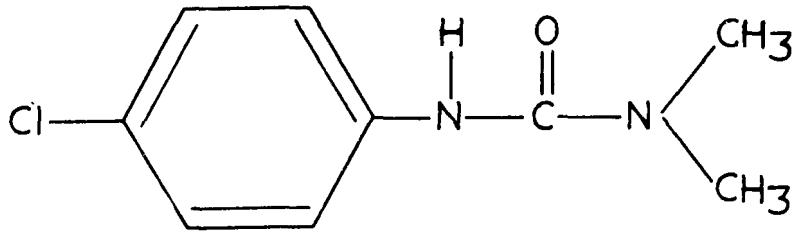
Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent monuron as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

Determination of Monuron by Infrared Spectroscopy

Monuron is the common name for 3-(p-chlorophenyl)-1,1-dimethyl-urea, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{11}ClN_2O$

Molecular weight: 198.6

Melting point: 174-175°C

Physical state, color, and odor: odorless, white crystalline solid

Solubility: 230 ppm in water at 25°C; sparingly soluble in petroleum oils and in polar organic solvents; 5.2% in acetone at 27°C

Stability: stable toward moisture and oxidation at RT but is decomposed at 185-200°C; rate of hydrolysis at RT or neutrality is negligible but is increased at elevated temp. or more acid or alkaline conditions; non-corrosive and non-flammable

Other names: Telvar (DuPont), chlorfenidim (USSR), Monurex

Reagents:

1. Monuron standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm KBr or NaCl cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram monuron standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.5 gram monuron into a glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precautions to prevent evaporation. (final conc 10 mg monuron/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings, scan both the standard and sample from 1400 cm^{-1} to 1300 cm^{-1} (7.1 μ to 7.7 μ).

Determine the absorbance of standard and sample using the peak at 1360 cm^{-1} (7.35 μ) and baseline from 1380 cm^{-1} to 1325 cm^{-1} (7.25 μ to 7.55 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent monuron as follows:

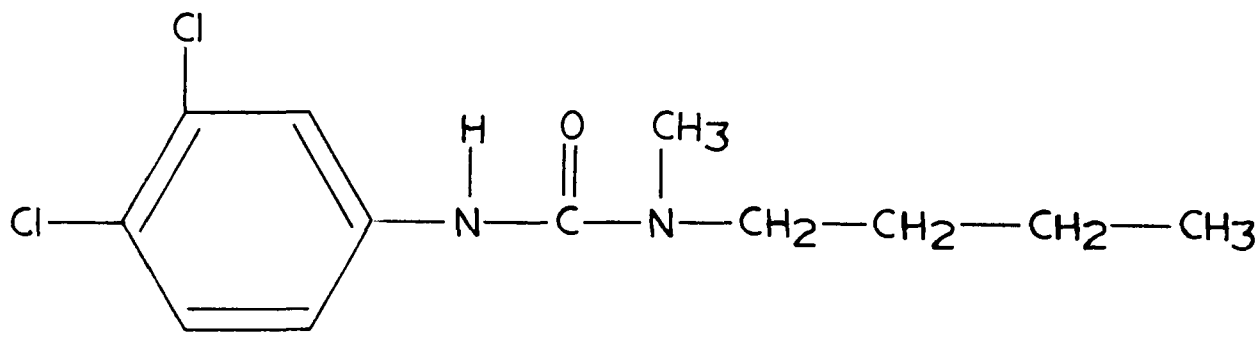
$$\% = \frac{\text{(abs. sample)(conc. std in mg/ml)(\% purity std)}}{\text{(abs. std)(conc. sample in mg/ml)}}$$

September 1975

Neburon EPA-1
(Tentative)

Determination of Neburon by Infrared Spectroscopy

Neburon is the accepted common name for 1-n-butyl-3-(3,4-dichlorophenyl)-1-methylurea, a registered herbicide having the chemical structure:



Molecular formula: $C_{12}H_{16}Cl_2N_2O$

Molecular weight: 275.18

Melting point: 102 to 103°C

Physical state, color, and odor: odorless, white crystalline solid

Solubility: 4.8 ppm in water at 24°C; very low in common hydrocarbon solvents

Stability: stable toward oxidation and moisture under normal storage conditions

Other names: Kloben (DuPont), Neburex, neburea (So. Africa)

Reagents:

1. Neburon standard of known % purity
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm KBr or NaCl cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.08 gram neburon standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml carbon disulfide by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 8 mg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.4 gram neburon into a glass-stoppered flask or screw-cap bottle. Add 50 ml carbon disulfide by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter, taking precaution to prevent evaporation. (final conc 8 mg neburon/ml)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1430 cm^{-1} to 1175 cm^{-1} (7.0 μ to 8.5 μ).

Determine the absorbance of the standard and sample using the peak at 1289 cm^{-1} (7.76 μ) and basepoint 1319 cm^{-1} (7.58 μ).

Calculation:

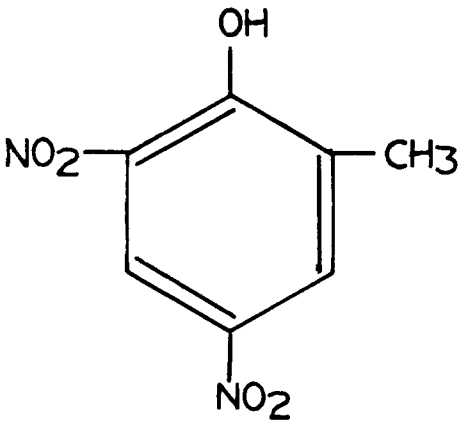
From the above absorbances and using the standard and sample solution concentrations, calculate the percent neburon as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Method contributed by Eva Santos, EPA Region IX, San Francisco, California.

Determination of Nitrophenols in Formulations by Stannous Chloride Reduction

Nitrophenols are those compounds having one or more nitro groups on a phenol. These compounds may be registered as acaricides, fungicides, herbicides, or insecticides. The chemical structure is similar to that of 4,6-dinitro-o-cresol which is:



4,6-dinitro-o-cresol has the common name DNOC and the following characteristics:

Molecular formula: $C_7H_6N_2O_5$

Molecular weight: 198.1

Melting point: 86°C

Physical state, color, and odor: yellowish, odorless, crystals

Solubility: 130 ppm in water at 15°C; soluble in most organic solvents and in acetic acid; alkali salts are water-soluble; technical grade is 95-98% pure and has a mp 83 to 85°C

Stability: explosive, therefore it is usually moistened with up to 10% water to reduce the hazard; corrosive to mild steel in the presence of moisture

Principle of the Method:

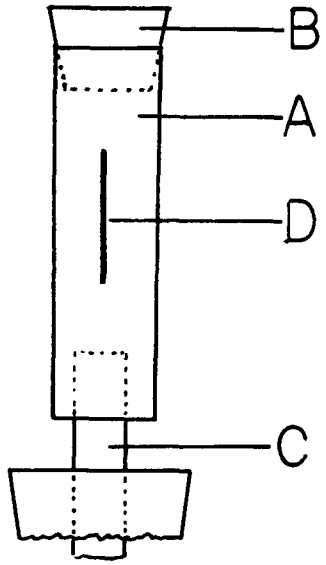
A volume of stannous chloride solution in excess of that needed by a weighed portion of sample is titrated with standard potassium dichromate solution without reacting it with the sample. A second identical portion is reacted with the sample and the excess titrated. The difference in titrations represents the amount of potassium dichromate equivalent to the sample. Other oxidizing compounds, reducible by stannous chloride, are titrated with standard sodium thiosulfate and are subtracted as milliequivalents from the dichromate milliequivalents of sample. The net milliequivalents are equal to the nitro phenolic compound in the sample.

Reagents:

1. Potassium dichromate, 0.3N standard solution - weigh 14.71 grams pure potassium dichromate (previously dried 2 hr at 100°C) into a one liter volumetric flask, dissolve in, and make to volume with distilled water.
2. Stannous chloride solution - weigh 17 grams stannous chloride dihydrate into a 500 ml volumetric flask, dissolve in, and make to volume with 18-19% hydrochloric acid (1+1 by weight). The strength of this solution is approximately equivalent to the dichromate solution but weakens gradually upon oxidation.
3. Glacial acetic acid, reagent grade
4. Concentrated hydrochloric acid
5. Potassium iodide, 15% solution in water
6. Starch indicator solution
7. Sodium thiosulfate, 0.1N (or 0.3N) standard solution

Equipment:

1. 300 ml Erlenmeyer flask with rubber stopper fitted with a Bunsen valve (described below)



The Bunsen valve is a short 2-4" length of rubber tubing (A) stoppered at one end (B) and fitted over a piece of glass tubing (C) at the other end. A 1/2-3/4" slit (D) is made with a razor blade along the length of the tubing. This slit allows internal pressure to be relieved by allowing gases to escape, but is sealed as outside pressure pushes in since the sides of the slit are pressed together.

2. Water bath, 95—100°C
3. Usual laboratory glassware and titration apparatus

Procedure: (written for dinitrocresol)

Weigh a portion of sample equivalent to 1.3-1.7 grams dinitrocresol into a 250 ml volumetric flask, dissolve in, and make to volume with distilled water.

Pipet a 10 ml aliquot of sample solution into a 250 ml Erlenmeyer flask, add 5 ml glacial acetic acid, 8 ml concentrated hydrochloric acid, and, by pipet, 25.0 ml stannous chloride solution. Close flask with stopper fitted with a Bunsen valve and heat on a water bath at 95—100°C for 30 minutes. Cool by immersing in cold water and dilute to about 200 ml with distilled water. Add 3 ml of 15% potassium iodide solution and 1 ml starch indicator solution. Titrate with 0.3N potassium dichromate solution with constant agitation to a blue end point. (If the end point is passed,

the slight excess of dichromate may be back-titrated with sodium thiosulfate.)

Determine the dichromate equivalent of 25.0 ml stannous chloride by repeating the above procedure, omitting the sample. Heating is not necessary, but would more closely match the sample determination conditions. The difference in the two dichromate titrations is equal to the dinitrocresol in the sample aliquot and any other oxidizing compounds, reducible by stannous chloride.

To determine the amount of other oxidizing compounds: take a 10 ml aliquot of sample solution, add 3 ml 15% potassium iodide solution, 5 ml glacial acetic acid, 1 ml starch indicator, 200 ml water, and titrate with 0.1N sodium thiosulfate solution to the disappearance of the blue color.

Calculations:

The ml dichromate used for 25 ml $SnCl_2$ (blank) minus the ml dichromate used for 25 ml $SnCl_2$ plus 10 ml sample solution (sample) multiplied by the normality of the dichromate (N) equals the milliequivalents (meqs.) of dinitrocresol (DNOC) and other oxidizing compounds (Ox cmpds.).

(Blank - sample)(N) = meqs. DNOC + Ox cmpds.

The ml thiosulfate multiplied by the normality equals the milliequivalents of other oxidizing compounds which is subtracted from the above to give the milliequivalents of DNOC in 10 ml of sample aliquot.

$$\% \text{ dinitrocresol in sample} = \frac{(\text{meqs. of DNOC in 10 ml})(100)}{(\text{grams sample})(10/250)}$$

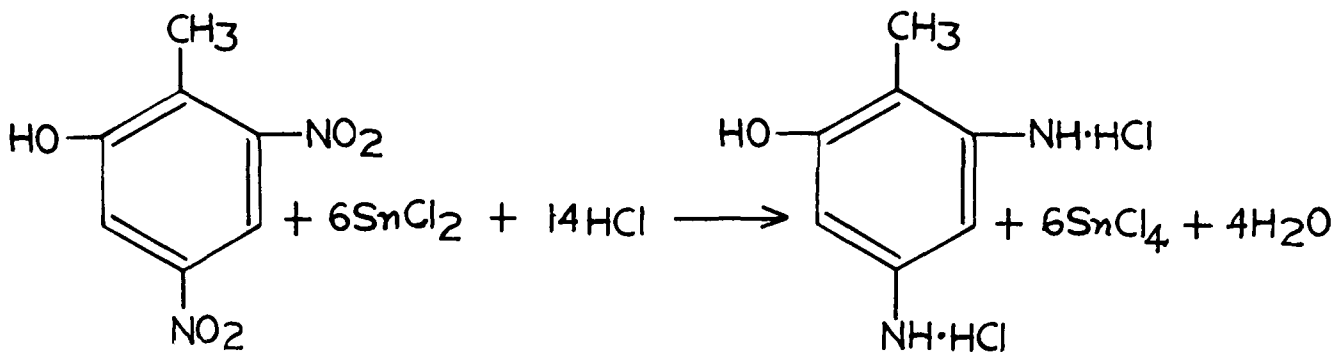
Chemical Reactions:

Dichromate equivalent of stannous chloride:

$$6SnCl_2 + 2K_2Cr_2O_7 + 28HCl \longrightarrow 6SnCl_4 + 4KCl + 4CrCl_3 + 14H_2O$$

$$K_2Cr_2O_7 + 6KI + 14HCl \longrightarrow 8KCl + 2CrCl_3 + 3I_2 + 7H_2O$$

Sample reaction with stannous chloride:



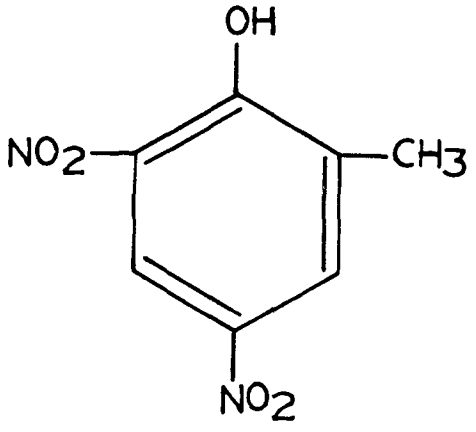
Oxidizing compounds with sodium thiosulfate:

$$\text{(oxidizing compounds)} + KI \xrightarrow{HCl} I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

Determination of Nitrophenols in Formulations by Total Nitrogen

Nitrophenols are those compounds having one or more nitro groups on a phenol. These compounds may be registered as acaricides, fungicides, herbicides, or insecticides. The chemical structure is similar to that of 4,6-dinitro-o-cresol which is:



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Stability: explosive, therefore it is usually moistened with up to 10% water to reduce the hazard; corrosive to mild steel in the presence of moisture

Principle of the Method:

These compounds may be in dusts, wettable powders, emulsifiable concentrates, oil sprays, or as 98-100% free acid flakes. If there are no interfering nitrogen-containing constituents present, they may be determined directly from total nitrogen; otherwise, an extraction clean-up procedure is necessary.

Since the nitrogen is present in the nitro (oxidized) form, it must be converted to the amino (reduced) form before being determined by the regular Kjeldahl procedure. This is done by reacting the sample with acetic acid-zinc dust and salicylic acid-sodium thiosulfate. These are the agents which reduce the nitro ($-NO_2$) to amino ($-NH_2$) so that it may be reduced to ammonium sulfate by the sulfuric acid regular Kjeldahl procedure.

Reagents:

1. Acetone
2. Concentrated hydrochloric acid
3. 50% ethyl alcohol-water (1+1)
4. Potassium hydroxide solution (1+1)
5. Ethyl ether
6. Petroleum ether
7. Acetic acid, glacial
8. Zinc dust
9. Sulfuric acid (1+4)
10. Sodium thiosulfate
11. Concentrated sulfuric acid, reagent grade

12. Salicylic acid, reagent grade

13. Zinc dust, reagent grade

14. Mercuric oxide, red, reagent grade

    (Commercial packages called "Kel-pacs" are available containing various oxidizing catalysts and various amounts of potassium sulfate in small oxidizable plastic packets. One packet can be dropped into the flask, saving the weighing and transfer of the HgO and K_2SO_4.)

15. Potassium sulfate, reagent grade (see above)

16. Sodium or potassium sulfide, reagent grade

17. Granulated zinc, reagent grade

18. Kjeldahl sodium hydroxide solution (450 grams NaOH, free from nitrates, in one liter of water)

19. Phenolphthalein indicator solution

20. Sulfuric acid, 0.1N standard solution

    (An alternative procedure is to use 50 ml of a saturated boric acid solution that simply holds the ammonia which is titrated with standard acid. The procedure eliminates the need for standard alkali solution.)

21. Sodium hydroxide, 0.1N standard solution (see above)

22. Mixed methyl red indicator solution - dissolve 1.25 grams methyl red and 0.825 gram methylene blue in one liter of 90% ethyl alcohol. The color change is from purple in acid to green in basic solution.

Equipment:

1. Filtration equipment

2. Steam bath

3. 800 ml Kjeldahl flask

4. Kjeldahl digestion and distillation apparatus

5. Titration apparatus

6. Usual laboratory glassware

Procedure:

Extraction-cleanup procedure:

If it is known that no interfering nitrogen-containing constituents are present, omit the following extraction cleanup procedure and begin directly with the nitrogen determination.

Weigh an amount of sample equivalent to 0.025-0.30 gram of nitrogen into a 200 ml volumetric flask. Add approximately 100 ml acetone and sufficient concentrated hydrochloric acid to make distinctly acid. Make to volume and shake intermittently over several hours. (If the amount of dust or powder is large, correct for its volume by adding the same weight to 200 ml acetone in an identical volumetric flask and note the increase above the line--adjust the sample flask to the same amount.)

Filter if necessary and pipette 100.0 ml of the clear liquid into a beaker or flask. Evaporate on a steam bath to remove the acetone. Add 50 ml of 50% ethyl alcohol and make alkaline to phenolphthalein with aqueous potassium hydroxide solution (1+1). Digest on a steam bath 10-15 minutes and cool. If oils are present, extract with petroleum ether. Filter and wash filter paper thoroughly with 50% alcohol. Evaporate most of the filtrate on a steam bath to remove the alcohol. Cool, transfer to a separatory funnel with water, and acidify with hydrochloric acid. Extract with ethyl ether three times, using each time a volume of ether equal to the volume of aqueous solution in the separatory funnel. Combine the ether extracts into a second separatory funnel and wash once with water acidified with HCl.

Reduction of NO_2 Group:

Transfer the ether into an 800 ml Kjeldahl flask and evaporate on a steam bath to just dryness. Dissolve the residue in 5 ml acetic acid, add 1 gram zinc dust, mix, and heat on a steam bath for 15 minutes. Add 1 ml sulfuric acid (1+4) and let stand overnight at room temperature. In the morning, add another 1 ml sulfuric acid (1+4) and heat on a steam bath for 15 minutes. Cool, add 35 ml concentrated sulfuric acid containing 2 grams salicylic acid, allow to stand a few minutes, add 5 grams sodium thiosulfate, and heat over a low flame until most of the sulfur dioxide is expelled.

Digestion:

Add 0.7 gram mercuric oxide and 10 grams potassium sulfate (or one Kel-pac) and continue boiling until the liquid in the flask has been colorless for one hour. If the contents of the flask tend to become solid before this point is reached, add 10 ml more of sulfuric acid. To avoid decomposition of ammonium sulfate and subsequent loss of ammonia, do not allow the flame to reach any part of the flask not in contact with liquid. The flask may be lifted from the digestion rack and the acid swirled around the inside of the flask to wash undigested particles back into the acid. When digestion is complete, cool; add 200 ml-300 ml water, making sure that the digestion mixture is completely dissolved.

Distillation:

Measure 50.00 ml of standard 0.1N sulfuric acid into a 500 ml Erlenmeyer wide-mouth flask, add several drops of mixed methyl red indicator solution, and place under the condenser of the distilling apparatus, making sure that the condenser tube extends beneath the surface of the acid in the flask. A glass tube attached by inert tubing to the condenser outlet tube is very convenient when later

removing the receiving flask. If the indicator changes from acidic (purple) to basic (green), the determination must be repeated using less sample or more acid in the receiving flask.

Add 25 ml sodium or potassium sulfide solution and mix thoroughly; then add several pieces of granulated zinc.

(When using mercury as a catalyst, it must be precipitated with K or Na sulfide before the distillation process since it forms a complex substance with ammonia which is not readily decomposed by alkali.)

(Zinc in an alkaline solution slowly reacts to form a zincate and hydrogen: $Zn + 2NaOH \longrightarrow Na\ ZnO_2 + H_2\uparrow$ This slow evolution of hydrogen keeps the solution stirred, thereby preventing superheating.

Pour about 110 ml of the Kjeldahl sodium hydroxide solution (or if extra acid was added, use 25 ml more alkali for each 10 ml acid added) slowly down the inclined neck of the flask so that it layers under the acid solution without mixing. A few drops of phenolphthalein may be added to be sure sufficient alkali is added to neutralize all the acid, remembering that a considerable excess of alkali will destroy the pink color.

Connect the flask to the condenser by means of a Kjeldahl connecting bulb, ignite the burner, and quickly mix the contents of the flask thoroughly with a rotary motion. It is advisable to begin the distillation with a small flame until the solution begins to boil, then increase the heat until the solution boils briskly. Distill 150-200 ml of the liquid (the first 150 ml usually contains all of the ammonia) into the receiving flask. Move the flask so that the tip of the delivery tube is above the level of the liquid and distill another 10 ml or so to wash the inside of the tube. Shut off heat, wash the outside of the delivery tube, and remove flask from apparatus.

Titration and Calculation:

Titrate the excess standard acid with standard 0.1N sodium hydroxide using mixed methyl red indicator. Reagents for this determination should be acid-free or a reagent blank should be run. Calculate the percent nitrogen as follows:

Using a blank:

$$\% = \frac{(\text{ml NaOH for blank} - \text{ml NaOH for sample})(\text{N of NaOH})(.01401)(100)}{(\text{grams of sample})^*}$$

Not using a blank:

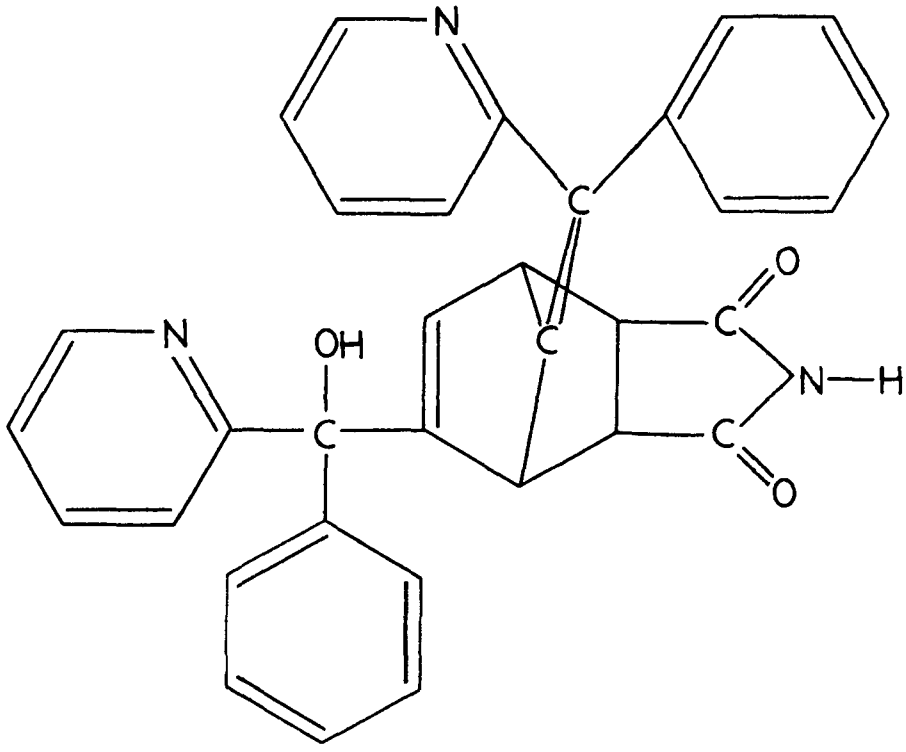
$$\% = \frac{[(\text{ml } H_2SO_4)(\text{N of } H_2SO_4) - (\text{ml NaOH})(\text{N of NaOH})](.01401)(100)}{(\text{grams of sample})^*}$$

$$\% \text{ Nitrophenolic compound} = \frac{\% \text{ nitrogen in sample}}{\% \text{ nitrogen in nitrophenolic compound}}$$

* If extraction-cleanup procedure was used, a dilution factor of 100/200 must be added here.

Determination of Norbormide in Baits by Ultraviolet Spectroscopy

Norbormide is the accepted common name for 5-(alpha-hydroxy-alpha-2-pyridylbenzyl)-7-(alpha-2-pyridylbenzylidene)-5-norbornene-2,3-dicarboximide, a registered rodenticide having the chemical structure:



Molecular formula: $C_{33}H_{25}N_3O_3$

Molecular weight: 511.6

Melting point: 180 to 190°C (190 to 198° on crystals from methylene chloride + ether)

Physical state and color: white to off-white crystalline powder (mixture of isomers)

Solubility: 60 ppm in water at RT; at 30°C solubility in 100 ml is 1.4 mg in ethanol, 15 mg in chloroform, 0.1 mg in ether, 2.9 mg in 0.1N HCl; soluble in dilute acids

Stability: stable at RT when dry, and to boiling water; hydrolyzed by alkali; non-corrosive

Other names: Shoxin, Raticate (McNeil Laboratories)

Reagents:

1. Norbormide standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular
4. Decolorizing carbon (Norit A or equivalent)

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm silica cells
2. Mechanical shaker
3. Filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram norbormide standard into a 100 ml volumetric flask, dissolve, make to volume with chloroform, and mix thoroughly. Pipette 2 ml into a second 100 ml volumetric flask and make to volume with chloroform. (final conc 20 µg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.02 gram norbormide into a 250-300 ml glass-stoppered flask, add 2 grams anhydrous sodium sulfate and 2 grams decolorizing carbon (Norit A or equivalent), pipette in 100 ml chloroform, and shake on a mechanical shaker for one hour. Filter a portion of the chloroform extract through a coarse, soft, rapid filter paper, taking precautions against solvent loss by evaporation. Pipette 10 ml of clear filtrate (discard the first few ml coming through the paper) into a 100 ml volumetric flask and make to volume with chloroform. (final conc 20 µg norbormide/ml)

UV Determination:

Using the optimum quantitative settings for the particular UV instrument being used, adjust the 0 and 100% settings at 253 nm with chloroform in both cells. Scan both standard and sample from 300 nm to 200 nm.

Calculation:

Measure the absorbance of standard and sample at 253 nm and calculate the percent norbormide as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

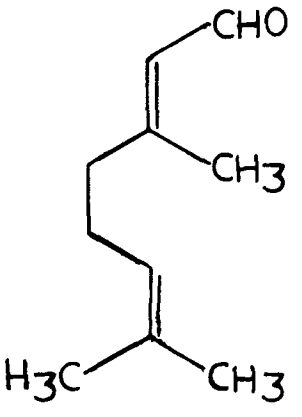
or using dilution factors, as follows:

$$\% = \frac{(\text{abs. sample})(\text{wt. std})(\text{purity std})(1/100)(2/100)(100)}{(\text{abs. std})(\text{wt. sample})(1/100)(10/100)}$$

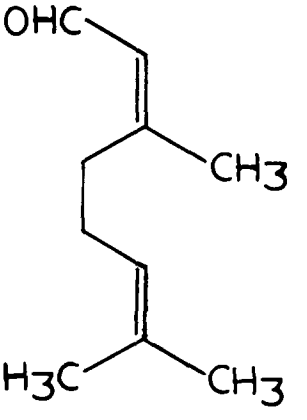
Determination of Oil of Lemongrass by Gas-Liquid Chromatography (TCD)

Oil of Lemongrass is a registered animal repellent consisting of 75-85% citral as the active constituent. Citral is 3,7-dimethyl-2,6-octadienal which occurs in two geometric isomers with chemical structures as follows:

geranial (citral a)



neral (citral b)



Molecular formula: $C_{10}H_{16}O$

Molecular weight: 152.23

geranial is a light oily liquid with a strong lemon odor; b.p.$_{2.6}$ 92-93°C; d_4^{20} 0.8888; n_D^{20} 1.48982; practically insoluble in water; miscible with alcohol, ether, benzyl benzoate, diethyl phthalate, glycerol, propylene glycol, mineral oil, essential oils

neral is a light oily liquid; lemon odor not as intense but sweeter than geranial; b.p.$_{2.6}$ 91-92°; d_4^{20} 0.8869; n_D^{20} 1.48690; solubilities same as geranial

Stability: unstable to alkalis and strong acids; will cause discoloration of white soaps and alkaline cosmetics

Other names: Lemongrass oil, oil of verbena (Indian)

Note - oil of lemongrass is also used in the synthesis of vitamin A; as a flavor in fortifying lemon oil; in perfumery for citrus effect in lemon and verbena scents, in cologne odors, in perfumes for colored soaps.

This method is based on the thermal conductivity detection of both isomers of citral using a 20% SE-30 column. See note at end of method for alternative procedures.

Reagents:

1. Oil of Lemongrass standard of known citral content
2. Acetone, pesticide or spectro grade

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 5' x 1/4" O.D. aluminum column packed with 20% SE-30 on 60/80 mesh Chromosorb W AW DMCS (or equivalent column)(SS or glass is preferred to Al)
3. Precision liquid syringe: 25 or 50 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	150°C
Injection temperature:	250°C
Detector temperature:	250°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas flow rate:	100 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.6 gram oil of lemongrass standard into a 10 ml volumetric flask and make to volume with acetone. (conc 60 µg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.6 gram oil of lemongrass into a 10 ml volumetric flask and make to volume with acetone. (conc 60 µg oil lemongrass/ml)

For the analysis of aerosols some care must be used in removing the freons. The chilled sample should be allowed to warm to room temperature and then heated gently to about 40-50°C just until the freons are removed. This will minimize loss of any volatile constituents from the oil of lemongrass.

Determination:

Using a precision liquid syringe, alternately inject three 20-30 µl portions each of standard and sample solutions, allowing sufficient time between injections for all sample constituents to clear the column.

Calculation:

Measure and combine the area of both citral peaks (citral a and citral b) for both the standard and sample. Using the average of several injections, calculate the % oil lemongrass as follows:

$$\% = \frac{(\text{pk. area sample})(\text{wt. standard injected})(\% \text{ purity standard})}{(\text{pk. area standard})(\text{wt. sample injected})}$$

(If sample was an aerosol, multiply above result by the % nonvolatile.)

The above method is basically that developed by Margaret Frost and Mario V. Conti, EPA, Region IX, San Francisco, Calif. A few changes were made and some additional information obtained at EPA's Beltsville Chemistry Laboratories was added in this write-up; therefore, any suggestions, data, or criticisms are most welcome.

Note on alternative procedures:

Frost and Conti have also successfully used a 10% Carbowax 20 M column and a 10% QF-1 column both at 155° using a thermal conductivity detector.

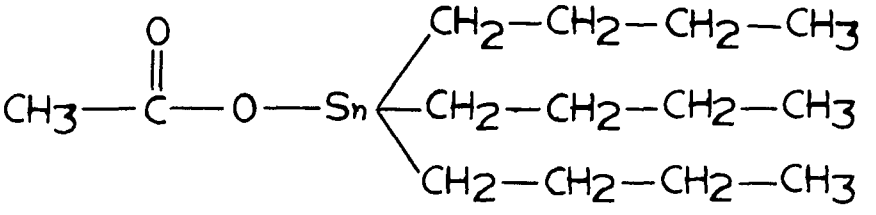
Ronald F. Thomas, EPA, Beltsville, Md., has used a 1/8" x 5' pyrex 10% Carbowax 20 M 60/80 Chromosorb W AW column at 105°C with a flame ionization detector and nitrogen for carrier gas.

Determination of Tin in Organotin Compounds by Oxidation, Reduction, and Titration

Several tin-based organic compounds are registered fungicides, bactericides, algicides, and molluscicides. These compounds are of two main types:

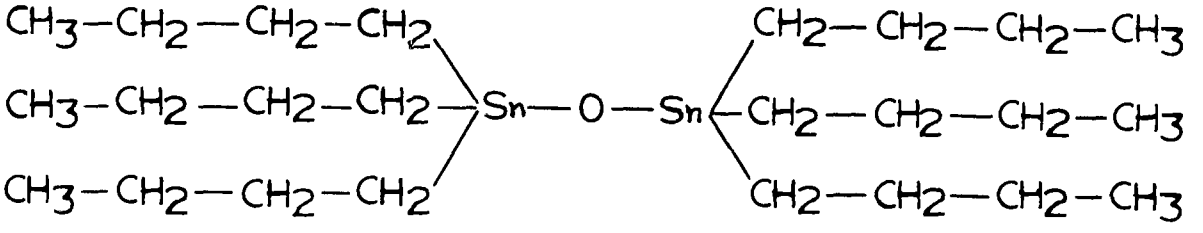
(a) tributyltin or triphenyltin compounds:

example: tributyltin acetate



(b) bis (tributyltin) compounds:

example: bis (tributyltin) oxide



In general, these compounds are practically insoluble in water but are miscible with organic solvents. Some are solids and some are liquids. The stability of these compounds varies but most are stable when dry and stored in dark, closed containers. Most are compatible with common pesticides, but not with liquids or oil emulsions.

Principle of the Method:

The organotin compound is digested with sulfuric and nitric acids, reduced with nickel and iron, and titrated with potassium iodate and starch as elemental tin. This is then calculated to the specific organotin compound.

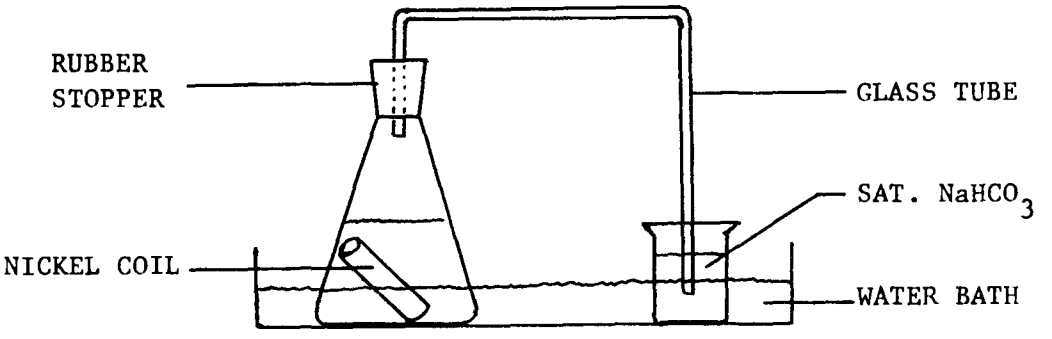
Reagents:

1. Tin standard, pure foil
2. Sulfuric acid, concentrated, ACS
3. Nitric acid, concentrated, ACS
4. Distilled water, boiled and cooled to remove oxygen
5. Hydrochloric acid, (1+2) in water
6. Nickel coil - roll a 6" x 3" x 0.15 (or 0.25)" sheet of pure nickel into a 3" long roll. Clean before each use by boiling in (1+2) hydrochloric acid.
7. Iron powder
8. Sodium bicarbonate, saturated solution
9. Dry ice
10. Starch indicator solution, 1% prepared fresh
11. Potassium iodide, 10% solution
12. Potassium iodate, 0.1N standard solution - Prepare and standardize as described under procedure.

Equipment:

1. Kjeldahl flask and digestion set-up
2. Hot plate

3. 500 ml Erlenmeyer with a rubber stopper into which a 7 mm piece of glass tubing is fitted; the glass tubing is bent to extend from just below the stopper on the inside, up, over, and down on the outside to a level just above the bottom of the flask. (The drawing below shows the shape of the tubing and how it is extended into a beaker of saturated sodium carbonate during the cooling operation.)



4. Water bath (or ice bath)
5. Titration apparatus
6. Usual laboratory glassware

Procedure:

Preparation of 0.1N Potassium Iodate Solution:

Weigh 3.567 grams potassium iodate and 10 grams potassium iodide, place in a one-liter volumetric flask, add one pellet of potassium hydroxide, dissolve in, and make to volume with oxygen-free water.

Place 0.25 gram pure tin foil (accurately weighed) into a 500 ml Erlenmeyer flask and dissolve in 100 ml concentrated hydrochloric acid. Add 180 ml oxygen-free water and 10 ml concentrated sulfuric acid.

Proceed following the same reduction and titration procedure as for sample. Calculate the normality as shown under calculations.

Preparation of Sample:

Weigh a portion of sample equivalent to about 0.2 gram tin into a 500 ml (or 800 ml) Kjeldahl flask, add 10 ml concentrated sulfuric acid, and, cautiously, 20 ml concentrated nitric acid. Place flask on an asbestos mat with a 2" hole and heat with a small flame at first until any vigorous reaction subsides. Increase the heat and digest until white fumes of sulfuric acid are evolved. If the solution darkens or chars, add more concentrated nitric acid until the solution remains colorless or a pale yellow. Cool, add 25 ml water, and heat again to white fumes to expel any oxides of nitrogen. Cool, add 80 ml water, and transfer to a 500 ml Erlenmeyer flask. Rinse the Kjeldahl flask with 100 ml water and add to the 500 ml Erlenmeyer flask. Add 100 ml concentrated hydrochloric acid and proceed under reduction.

Reduction:

Treat both the standard tin solution and the digested sample solution as follows:

Add a nickel coil (previously washed) and 5 grams iron powder. Place the rubber stopper fitted with the glass tubing (as described under equipment) tightly into the flask, heat to boiling on a hot plate, and boil gently for about 20 minutes - the iron powder should dissolve completely.

Remove from the hot plate and immediately immerse the outlet end of the glass tubing in saturated sodium bicarbonate solution contained in a beaker. Cool to room temperature in a water bath (or ice bath).

Titration:

Remove the stopper, quickly add a few pieces of dry ice, 5 ml 10% potassium iodide solution, and a few ml starch indicator. Titrate with 0.1N standard potassium iodate solution to a permanent blue endpoint.

Calculation:

Calculate the normality of the potassium iodate solution as follows:

$$N = \frac{(\text{grams tin standard})}{(\text{ml } KIO_3)(.05935)}$$

milliequivalent weight of tin = 0.05935

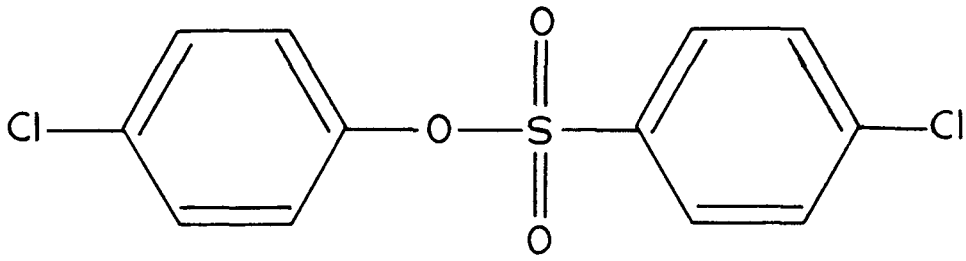
Calculate the percent tin and organotin compound in the sample as follows:

$$\% \text{ tin} = \frac{(\text{ml } KIO_3)(\text{N } KIO_3)(0.05935)(100)}{(\text{grams sample})}$$

% Organotin compound = % tin x factor (e.g., 2.511 for Bis(tributyltin)oxide)

Determination of Ovex by Infrared Spectroscopy

Ovex is the accepted common name for p-chlorophenyl-p-chlorobenzenesulfonate, a registered acaricide having the chemical structure:



Molecular formula: $C_{12}H_8Cl_2O_3S$

Molecular weight: 303.2

Melting point: 86.5°C (pure); about 80°C (tech.)

Physical state and color: white crystalline solid (pure), white to tan flaky solid (technical - about 80 to 90%)

Solubility: practically insoluble in water; moderately soluble in alcohol; readily soluble in acetone, dichloroethane, carbon tetrachloride, and aromatic solvents

Stability: chemically stable; hydrolyzed by caustic alkalis; compatible with all commonly used spray materials. (Sometimes imparts an unpleasant taste to fruits because of chlorophenol which forms on hydrolysis.)

Other names: Ovotran (Dow Chemical), chlorfension (ISO), ovatran (Argentina), difenson (Denmark), chlorfenizon (France), ephirsulphonate (USSR), CPCBS, Corotran, Estonmite, Niagaratran, ovochlor, Sappiran, trichlorfension

This method is primarily for dusts and wettable powders; however, there is a suggested procedure at the end for emulsifiable concentrates.

Reagents:

1. Ovex standard of known % purity
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.08 gram ovex standard into a small glass-stoppered flask or screw-cap tube, add 10 ml carbon disulfide by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 8 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.4 gram ovex into a glass-stoppered flask or screw-cap tube. Add 50 ml carbon disulfide and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 8 mg ovex/ml)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan the standard and sample from 800 cm^{-1} to 740 cm^{-1} (12.5 μ to 13.5 μ).

Determine the absorbance of standard and sample using the peak at 770.4 cm^{-1} (12.98 μ) and baseline from 794 cm^{-1} to 755 cm^{-1} (12.6 μ to 13.25 μ).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent ovex as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

The above method is essentially that method (No. 632.0 Nov. 1963) used by the Pesticide Regulation Division, USDA, now Technical Services Division, Office of Pesticide Programs, EPA.

A modification of the extraction procedure and a refinement of the scanning, analytical peak, and baseline wavelengths has been submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services.

Beltsville Chemical Laboratory suggests the following sample preparation procedure for emulsifiable concentrates:

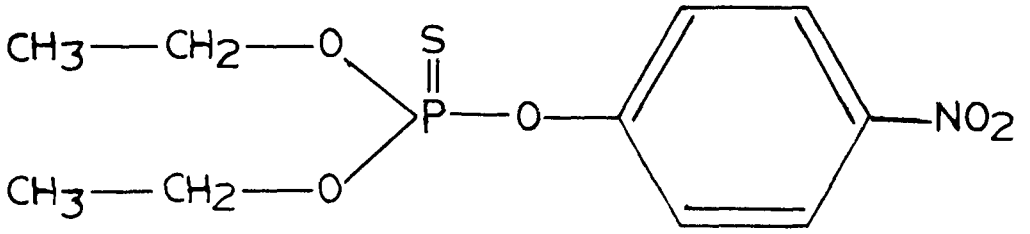
> Weigh a portion of sample equivalent to 0.4 gram ovex into a small glass-stoppered flask or screw-cap tube, add 50 ml carbon disulfide by pipette, and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for 10-15 minutes. Allow to settle. If the carbon disulfide solution is not clear, add more sodium sulfate and shake again. When the carbon disulfide solution is sufficiently clear and dry, proceed with the IR determination. Interfering substances may or may not be present as shown by a normal or distorted IR curve.

December 1975

Parathion EPA-1
(Tentative)

Determination of Parathion by High Pressure Liquid Chromatography

Parathion is the official name for O,O-diethyl-O-p-nitrophenyl phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_{10}H_{14}NO_5PS$

Molecular weight: 291.3

Melting/boiling point: m.p. 6.0°C, b.p. 157 to 162°C at 6 mm Hg

Physical state, color, and odor: pale yellow liquid; the technical product is a brown liquid with a garlic-like odor

Solubility: 24 ppm in water at 25°C; slightly soluble in petroleum oils; miscible with most organic solvents

Stability: rapidly hydrolyzed in alkaline media (at pH 5 to 6, 1% in 62 days at 25°C); isomerizes on heating to the OS-diethyl isomer

Other names: ACC 3422, Thiophos (American Cyanamid); E-605, Folidol Bladan (Bayer); Niran (Monsanto); Fosferno (Plant Protection Ltd.); thiophos (USSR); Alkron, Alleron, Aphamite, Corothion, Ethyl Parathion, Etilon, Fosfono, Orthophos, Panthion, Paramar, Paraphos, Parathene, Parawet, Phoskil, Rhodiatox, Soprathion, Strathion

Reagents:

1. Parathion standard of known % purity
2. Methanol, ACS

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm. If a variable wavelength UV detector is available, other wavelengths may be useful to increase sensitivity or eliminate interference. 235 nm has been found useful for parathion.
2. Suitable column such as:
   a. DuPont ODS Permaphase, 1 meter x 2.1 mm ID
   b. Perkin-Elmer ODS Sil-X II-RP, 1/2 meter x 2.6 mm ID
3. High pressure liquid syringe or sample injection loop
4. Usual laboratory glassware

Operating Conditions:

Mobile phase:	20% methanol + 80% water
Column temperature:	50-55°C
Chart speed:	5 min/inch or equivalent
Flow rate:	0.5 to 1.5 ml/min (Perkin-Elmer 1/2 meter column)
Pressure:	700 psi (DuPont 1 meter column)
Attenuation:	Adjusted

Conditions may have to be varied by the analyst for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.06 gram parathion standard into a small glass-stoppered flask or vial, add 20 ml methanol by pipette, dissolve, and mix well. (final conc 3 μg/μl)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.3 gram parathion into a glass-stoppered flask or vial, add 100 ml methanol by pipette, and shake thoroughly to dissolve the parathion. With granules or dusts, shake for 30 minutes on a mechanical shaker or shake by hand intermittently for one hour. Allow any solid matter to settle; filter or centrifuge if necessary. (final conc 3 μg parathion/μl)

Determination:

Using a high pressure liquid syringe or sample injection loop, alternately inject three 5 μl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent parathion as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

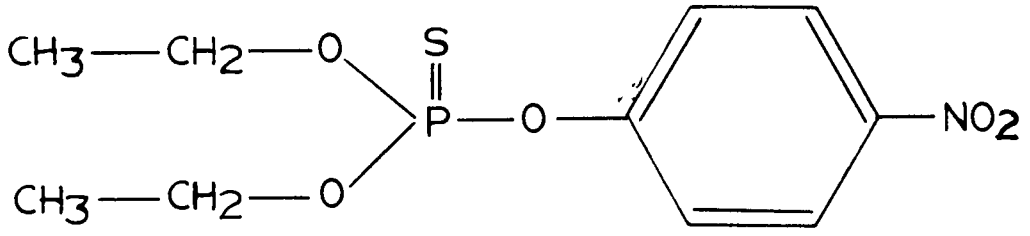
Method submitted by Elmer H. Hayes, EPA, Beltsville, Md.

December 1975

Parathion EPA-2
(Tentative)

Determination of Parathion by Gas-Liquid Chromatography (FID - Internal Standard)

Parathion is the official name for O,O-diethyl-O-p-nitrophenyl phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_{10}H_{14}NO_5PS$

Molecular weight: 291.3

Melting/boiling point: m.p. 6.0°C, b.p. 157 to 162°C at 6 mm Hg

Physical state, color, and odor: pale yellow liquid; the technical product is a brown liquid with a garlic-like odor

Solubility: 24 ppm in water at 25°C; slightly soluble in petroleum oils; miscible with most organic solvents

Stability: rapidly hydrolyzed in alkaline media (at pH 5 to 6, 1% in 62 days at 25°C); isomerizes on heating to the OS-diethyl isomer

Other names: ACC 3422, Thiophos (American Cyanamid); E-605, Folidol Bladan (Bayer); Niran (Monsanto); Fosferno (Plant Protection Ltd.); thiophos (USSR); Alkron, Alleron, Aphamite, Corothion, Ethyl Parathion, Etilon, Fosfono, Orthophos, Panthion, Paramar, Paraphos, Parathene, Parawet, Phoskil, Rhodiatox, Soprathion, Strathion

Reagents:

1. Parathion standard of known % purity
2. Alachlor standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.2 gram alachlor into a 100 ml volumetric flask and make to volume with acetone. (conc 2 mg alachlor/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm I.D. glass column packed with 3% OV-17 on 60/80 Gas Chrom Q (or equivalent column)*
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	190°C
Injection temperature:	240°C
Detector temperature:	240°C
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi (adjusted for specific GC)
Hydrogen pressure:	20 psi (adjusted for specific GC)
Air pressure:	30 psi (adjusted for specific GC)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram parathion standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 25 ml of the internal standard solution and shake to dissolve. (final conc 2 mg parathion and 2 mg alachlor/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.05 gram parathion into a small glass-stoppered flask or screw-cap bottle. Add by pipette 25 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the parathion. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 2 mg parathion and 2 mg alachlor/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is alachlor, then parathion.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of parathion and alachlor from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. alachlor})(\%\text{ purity alachlor})(\text{pk. ht. or area parathion})}{(\text{wt. parathion})(\%\text{ purity parathion})(\text{pk. ht. or area alachlor})}$$

Determine the percent parathion for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. alachlor})(\%\text{ purity alachlor})(\text{pk. ht. or area parathion})\cancel{(100)}}{(\text{wt. sample})(\text{pk. ht. or area alachlor})(RF)} \quad (4\text{-}1)$$

*The following columns also seem satisfactory:

(1) 4' x 2 mm I.D. glass, packed with 5% SE-30 on 80/100 mesh Chromosorb W HP at 170°C

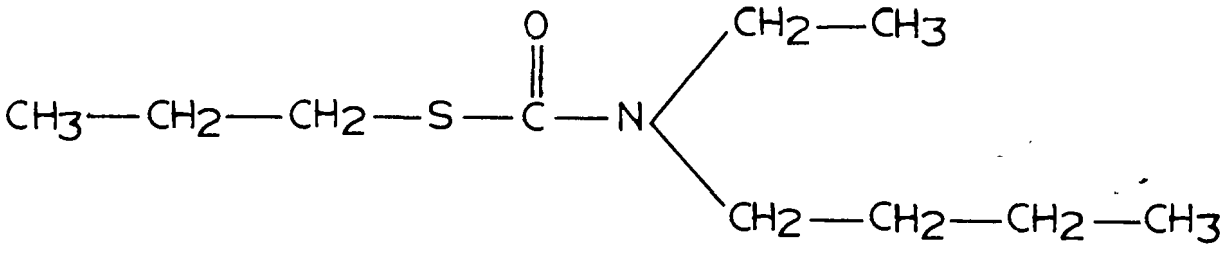
(2) 4' x 2 mm I.D. glass, packed with 5% OV-210 on 80/100 mesh Chromosorb W HP at 180°C

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Note! This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Chemistry Lab. Any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated.

Determination of Pebulate by Gas-Liquid Chromatography (TCD)

Pebulate is the common name for S-propyl butylethylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_{21}NOS$

Molecular weight: 203.4

Boiling point: 142°C at 21 mm

Physical state, color, and odor: clear yellow liquid with an amine-like odor

Solubility: 60 ppm in water at 20°C; miscible with acetone, benzene, ethanol, isopropanol, kerosene, toluene, xylene

Stability: stable; non-corrosive

Other names: Tillam (Stauffer), R-2061

Reagents:

1. Pebulate standard of known % purity
2. Chloroform, pesticide or spectro grade

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 6' x 1/4" O.D. aluminum, packed with 20% Dow Silicone High Vacuum Grease on 60/80 Chromosorb G AW (or equivalent column - SS or glass would be better)
3. Precision liquid syringe: 10 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	160°C
Injection temperature:	185°C
Detector temperature:	185°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas flow rate:	adjusted for specific GC

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.5 gram pebulate standard into a 10 ml volumetric flask; dissolve and make to volume with chloroform. (conc 50 mg/ml)

Preparation of Sample:

For technical material and liquid formulations, weigh a portion of sample equivalent to 0.5 gram pebulate into a 10 ml volumetric flask, make to volume with chloroform, and mix thoroughly. (final conc 50 mg pebulate/ml)

For dry formulations, weigh a portion of sample equivalent to 2.5 grams pebulate into a 125 ml screw-cap flask, add by pipette 50 ml chloroform, and shake for one hour. Allow to settle; filter or centrifuge if necessary, taking precautions to prevent evaporation. (final conc 50 mg pebulate/ml)

Determination:

Using a precision liquid syringe, alternately inject three 5 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent pebulate as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

This method is based on EPA's Exp. Method No. 50, which was based on information from Stauffer Chemical Co., Richmond Research Center. Some of the data has been supplied by EPA's Beltsville Chemistry Laboratory. Any comments, criticisms, suggestions, data, etc. concerning this method are welcome.

Note! When operating conditions are such that the retention time of pebulate is 13.8 minutes, the retention times of known impurities are:

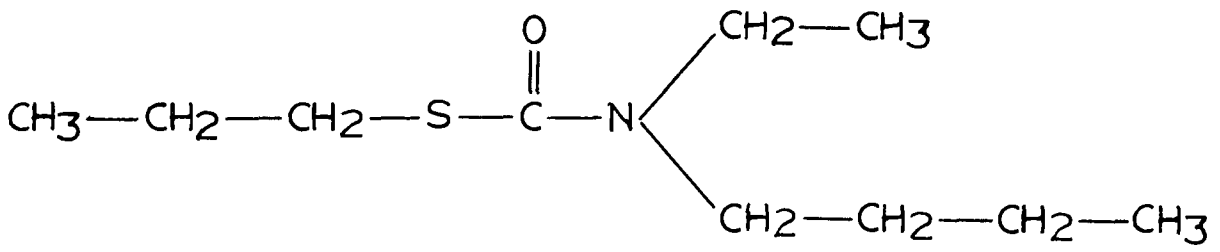
Iso-tillam (iso-pebulate)		9.5 min.
N,N'-ethylbutyl n-propyl carbamate		6.8 "
di-n-propyl dithiocarbamate		5.7 "
di-n-propyl disulfide		3.1 "
isopropyl propyl disulfide		2.5 "
ethyl butylamine	less than -	1.0 "
n-propyl mercaptan	less than -	1.0 "
phosgene	less than -	1.0 "

December 1975

Pebulate EPA-2
(Tentative)

Determination of Pebulate by Gas-Liquid Chromatography (FID - Internal Standard)

Pebulate is the common name for S-propyl butylethylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_{21}NOS$

Molecular weight: 203.4

Boiling point: 142°C at 21 mm

Physical state, color, and odor: clear yellow liquid with an amine-like odor

Solubility: 60 ppm in water at 20°C; miscible with acetone, benzene, ethanol, isopropanol, kerosene, toluene, xylene

Stability: stable; non-corrosive

Other names: Tillam (Stauffer), R-2061

Reagents:

1. Pebulate standard of known % purity
2. Cycloate standard of known % purity

3. Carbon disulfide, pesticide or spectro grade
4. Chloroform, pesticide or spectro grade
5. Methanol, pesticide or spectro grade
6. Internal Standard solution - weigh 0.2 gram cycloate into a 50 ml volumetric flask, dissolve in, and make to volume with a solvent mixture consisting of 80% carbon disulfide + 15% chloroform + 5% methanol. (conc 4 mg cycloate/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 4 mm glass column packed with 3% OV-1 on 60/80 mesh Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	150°C
Injection temperature:	225°C
Detector temperature:	250°C
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi (adjusted for specific GC)
Hydrogen pressure:	34 psi (adjusted for specific GC)
Air pressure:	28 psi (adjusted for specific GC)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.08 gram pebulate standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 4 mg pebulate and 4 mg cycloate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.08 gram pebulate into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the pebulate. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 4 mg pebulate and 4 mg cycloate/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is pebulate, then cycloate.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of pebulate and cycloate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{\text{(wt. cycloate)(\% purity cycloate)(pk. ht. or area pebulate)}}{\text{(wt. pebulate)(\% purity pebulate)(pk. ht. or area cycloate)}}$$

Determine the percent pebulate for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{\text{(wt. cycloate)(\% purity cycloate)(pk. ht. or area pebulate)}\cancel{(100)}}{\text{(wt. sample)(pk. ht. or area cycloate)(RF)}}\ (100)$$

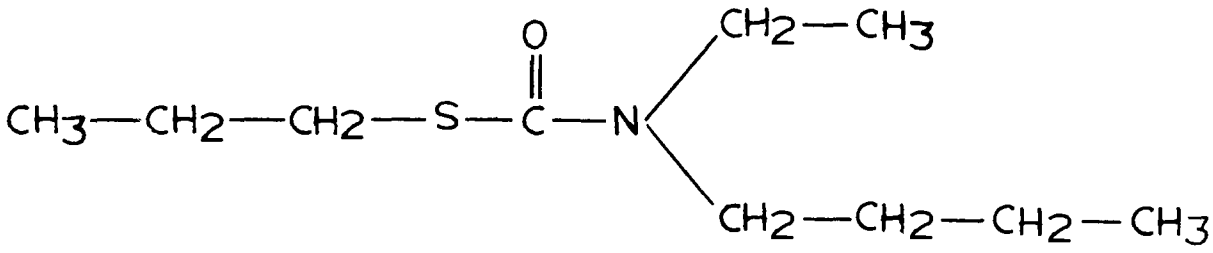
Method submitted by Division of Regulatory Services, Kentucky Agricultural Experiment Station, University of Kentucky, Lexington, Kentucky 40506.

December 1975

Pebulate EPA-3
(Tentative)

Determination of Pebulate by Gas-Liquid Chromatography (FID - Internal Standard)

Pebulate is the common name for S-propyl butylethylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_{21}NOS$

Molecular weight: 203.4

Boiling point: 142°C at 21 mm

Physical state, color, and odor: clear yellow liquid with an amine-like odor

Solubility: 60 ppm in water at 20°C; miscible with acetone, benzene, ethanol, isopropanol, kerosene, toluene, xylene

Stability: stable; non-corrosive

Other names: Tillam (Stauffer), R-2061

Reagents:

1. Pebulate standard of known % purity
2. S-Ethyl dipropylthiocarbamate (EPTC) standard of known % purity

3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.1 gram EPTC into a 50 ml volumetric flask; dissolve in and make to volume with acetone. (conc 2 mg EPTC/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm glass column packed with 5% SE-30 on 80/100 mesh Chromosorb W HP (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	130°C
Injection temperature:	180°C
Detector temperature:	180°C
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi (adjusted for specific GC)
Hydrogen pressure:	20 psi (adjusted for specific GC)
Air pressure:	30 psi (adjusted for specific GC)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.06 gram pebulate standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 3 mg pebulate and 2 mg EPTC/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.06 gram pebulate into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the pebulate. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 3 mg pebulate and 2 mg EPTC/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is EPTC, then pebulate.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of pebulate and EPTC from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. EPTC})(\%\text{ purity EPTC})(\text{pk. ht. or area pebulate})}{(\text{wt. pebulate})(\%\text{ purity pebulate})(\text{pk. ht. or area EPTC})}$$

Determine the percent pebulate for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. EPTC})(\%\text{ purity EPTC})(\text{pk. ht. or area pebulate})(100)}{(\text{wt. sample})(\text{pk. ht. or area EPTC})(RF)} \quad (4-1)$$

Method submitted by the Commonwealth of Virginia, Division of Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Note! This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Chemistry Laboratory. Any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated.

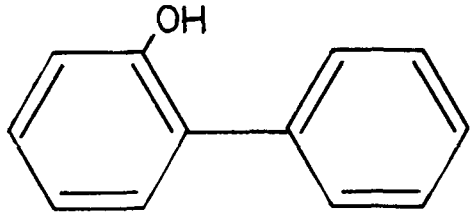
Definition, Structure, and Technical Data

This group of compounds consists of various aliphatic, aromatic, and chlorine substituted phenols.

These compounds are registered as germicides and/or fungicides. Many are used in the form of alkali salts or amine salts.

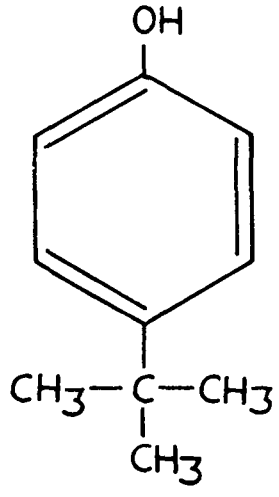
The following physical and chemical data are for the free phenols.

o-phenylphenol $C_{12}H_{10}O$ mol. wt. 170.20



white flaky crystals; mild characteristic odor; mp 55.5-57.5°C: bp 280-284°C; practically insoluble in water, soluble in alkali hydroxide solutions and most organic solvents. Other names: Dowcide 1, o-hydrodiphenyl, orthoxenol

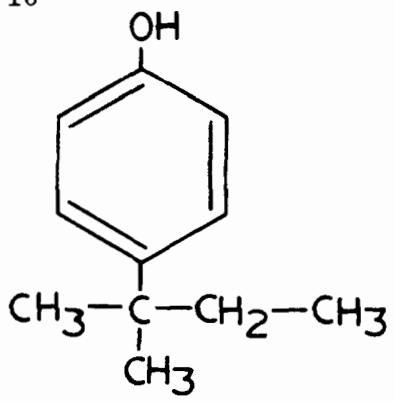
p-tert-butylphenol $C_{10}H_{14}O$ mol. wt. 150.21



white crystalline solid; distinctive odor; mp 98-100°C; bp 237-239°C; practically insoluble in cold water, soluble in alcohol, ether.

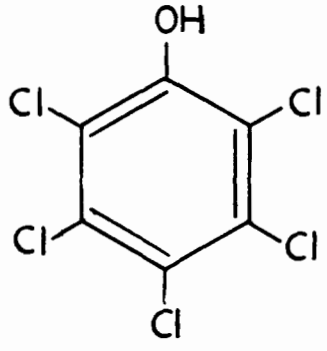
Other names: Butylphen

p-tert-amylphenol $C_{11}H_{16}O$ mol. wt. 164.24



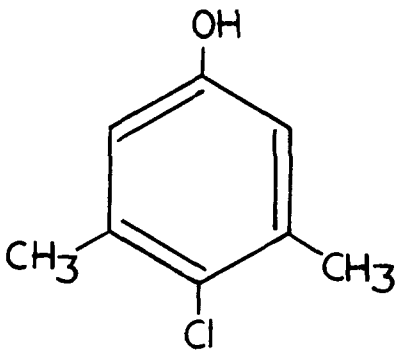
white crystals (irritating to skin); mp 94-95°C; bp 262.5°C; practically insoluble in water, soluble in alcohol, ether, benzene, chloroform. Other names: p-tert-pentylphenol, Pentaphen

pentachlorophenol C_6Cl_5OH mol. wt. 266.35



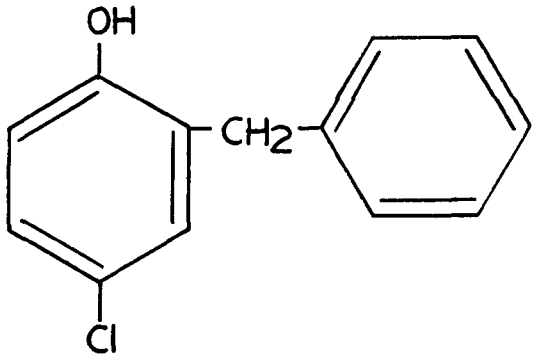
white powder or crystals; very pungent odor when hot; mp 190-191°C; bp about 309-310°C with decomposition; almost insoluble in water, soluble in dilute alkali, alcohol, acetone, ether, pine oil, benzene; slightly soluble in cold petroleum ether. Other names: PCP, Penta, Santophen 20

4-chloro-3,5-xylenol C_8H_9ClO mol. wt. 156.61



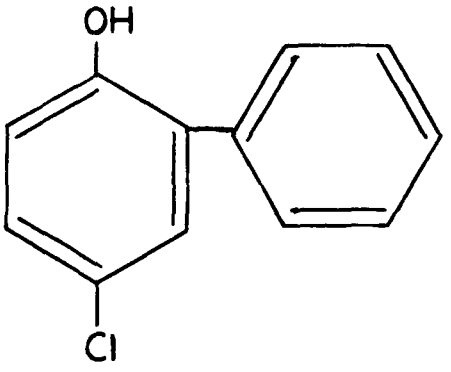
crystals with phenolic odor; mp 115.5°C; bp 246°C: volatile with steam; one gram dissolves in 3 liters of water at 20°C; more stable in hot water; soluble in 1 part of 95% alcohol; soluble in ether, benzene, terpenes, fixed oils, and solutions of alkali hydroxides. Other names: p-chloro-m-xylenol, Benzytol, 4-chloro-3,5-dimethylphenol, 2-chloro-5-hydroxy-1,3-dimethylbenzene

o-benzyl-p-chlorophenol $C_{13}H_{11}ClO$ mol. wt. 218.69

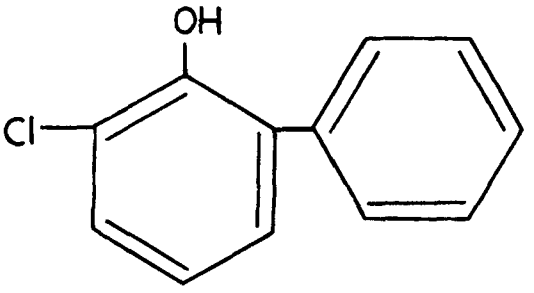


white to light tan or pink flakes; slight phenolic odor; mp 48.5°C; insoluble in water; highly soluble in alcohol and other organic solvents; dispersible in aqueous media with the aid of soaps or synthetic dispersing agents; non-corrosive to most metals. Other names: Santophen 1, Septiphene, Clorophene, 2-benzyl-4-chlorophenol

4-chloro-2-phenylphenol



6-chloro-2-phenylphenol



$C_{12}H_9ClO$ mol. wt. 204.65

clear colorless to straw-colored viscous liquid
with faint characteristic odor

boiling range 5-95% 146-158.7°C (5 mm)

readily soluble in most organic liquids

composition 80% 4-chloro-2-phenylphenol
20% 6-chloro-2-phenylphenol

Other phenols and chlorinated phenols not listed here are also used as germicides or fungicides and may be found in various commercial formulations, such as:

4-Chloro-2-cyclopentylphenol
2,2'-Methylenebis (4-chlorophenol)
2,2'-Methylenebis (3,4,6-trichlorophenol)

Determination of o-Phenylphenol in Disinfectant Formulations by Ultraviolet Spectroscopy

For definition, structure, and technical data on o-phenylphenol, see Phenols and Chlorophenols EPA-1.

This method is intended primarily for alcohol solutions of about 0.1% o-phenylphenol (tert-amylphenol interferes very little). Data and information on the use of this method for other phenols and chlorophenols will be appreciated by the editorial committee.

Reagents:

1. o-Phenylphenol standard of known % purity
2. Sodium hydroxide, 1N aqueous solution
3. Ethanol, ACS
4. Hexane, purified. Extract 250 ml n-hexane with two 20 ml portions of 1N sodium hydroxide solution and one 20 ml portion of water; discard the extracts.
5. Sulfuric acid, 1+4 solution

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Rotary evaporator
3. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.04 gram o-phenylphenol standard into a 100 ml volumetric flask, add 5 ml 1N sodium hydroxide solution, dissolve and dilute

to volume with water. Mix thoroughly and pipette 2 ml into a 50 ml volumetric flask. Add 5 ml 1N sodium hydroxide solution, 25 ml ethanol, dilute to volume with water, and mix thoroughly. (final conc 16 µg o-phenylphenol/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.008 gram o-phenylphenol into a 125 ml Erlenmeyer flask, add 1 drop of 1N sodium hydroxide, and evaporate to dryness on a rotary evaporator. Dissolve the residue in about 40 ml water and 20 ml hexane, transfer quantitatively to a 250 ml separatory funnel, add 5 ml 1N sodium hydroxide solution, shake, and allow the layers to separate.

Transfer the aqueous layer to a second 250 ml separatory funnel. Wash the hexane layer in the first separatory funnel with two 20 ml portions of water and add the washings to the second separatory funnel. Acidify with 3 ml of 1+4 sulfuric acid solution and extract with 50 ml hexane. Repeat with 25 ml hexane and combine the hexane extracts in a 125 ml separatory funnel. Extract the combined hexane layers with 20 ml 1N sodium hydroxide solution; transfer the alkaline aqueous extract into a 100 ml volumetric flask. Extract the hexane with 20 ml water and add to the 100 ml volumetric flask. Dilute to volume with water and mix thoroughly.

Pipette 10 ml of this solution into a 50 ml volumetric flask, add 3 ml 1N sodium hydroxide solution and 25 ml ethanol, dilute to volume with water, and mix thoroughly. (final conc 16 µg o-phenylphenol/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 312 nm with 0.1N sodium hydroxide solution in each cell. Scan both the standard and sample from 360 nm to 260 nm with 0.1N sodium hydroxide solution in the reference cell. Measure the absorbance of both standard and sample at 312 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent o-phenylphenol as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu\text{g/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu\text{g/ml})}$$

Determination of Chlorophenols by the Total Chloride Lime Fusion Method

For definition, structure, and technical data on chlorophenols, see Phenols and Chlorophenols EPA-1.

Principle of the Method:

The method was developed primarily for pentachlorophenol in oil solutions; however, it may be used for other chlorinated phenols. It is not applicable to samples containing other halogens unless these halogens can be determined and appropriate corrections made. This method is based on destroying organic material by heating and absorbing the liberated hydrochloric acid in calcium hydroxide. The hydroxide is neutralized with nitric acid and the chloride determined potentiometrically. Organic matter should be limited to 2 grams and the chlorinated phenol to 35 mg in terms of chlorine.

Reagents:

1. Fusion mixture - 9 parts calcium hydroxide powder plus 1 part potassium nitrate powder, thoroughly mixed. (see note below)
2. Nitric acid, concentrated, ACS
3. Silver nitrate, 0.1N standardized solution

Note: All reagents should be virtually chloride-free. ACS specifications should meet this requirement; however, for greatest accuracy a blank on all reagents should be run using the same amounts and method as for the sample.

4. Phenolphthalein indicator solution

Equipment:

1. Potentiometric titrimeter equipped with a glass reference electrode and a silver electrode
2. Iron crucible, 100 ml capacity, with cover
3. Meker burner, adjustable from minimum air to maximum air
4. Tripod stand and metal triangle (to hold crucible)
5. Ice bath
6. Magnetic stirrer
7. Usual laboratory glassware

Determination:

Place 100 grams of the calcium hydroxide-potassium nitrate mixture in a 100 ml iron crucible, tap gently to settle the contents, and form a small depression with the round bottom of a test tube. From a weighing burette add a weight of sample equivalent to 0.035 gram chlorine. (Solid samples may be mixed with a little fusion mixture and placed in the depression.)

Place 20 grams of the fusion mixture over the sample in the crucible and tap gently on a hard surface to settle and evenly distribute the fusion mixture. It is essential that the fusion mixture be uniformly packed (settled) so that no air pockets are present and thorough and even heating results.

The crucible with cover (to suppress burning of volatile materials on the surface of the fusion mixture) should be placed in a metal triangle on a ring stand so that the bottom is one-half inch above the top of a Meker burner. With the air supply almost completely shut off

and using a very luminous flame, the crucible is heated for about 15 minutes, allowing the flame to completely engulf the crucible all around. Gradually increase the flame temperature (increase the air) to maximum over the next ten minutes until the bottom of the crucible is red hot. Heat at full heat for at least 30 minutes. Samples should be free of unburned carbon; however, a small amount usually presents no errors. Surface should be free of large cracks.

Cool the crucible until it can be handled, then empty the contents into a 600 ml beaker, scraping any adhering fusion mixture into the beaker. Cautiously add about 100 ml water to the beaker and rinse the crucible with small portions of water into the beaker. Place the beaker in an ice bath in a glass dish on a magnetic stirrer. Put a glass or teflon-coated stirring bar and a few drops of phenolphthalein in the beaker and cover with a watchglass. While stirring, cautiously and slowly pour sufficient conc. nitric acid (50 to 60 ml) slowly down the side of the beaker to neutralize the sodium carbonate (keep the beaker covered as much as possible with the watchglass). Cool, and determine the chloride content potentiometrically, titrating with 0.1N silver nitrate solution. A blank should be run on each new batch of fusion mixture and with each change of reagent. Corrections in calculation should be made (usually about 0.05-0.06 ml silver nitrate solution subtracted from the ml silver nitrate used for the sample titration).

Calculations:

Calculate the percent chlorine and chlorinated phenol as follows:

$$\% \text{ chlorine} = \frac{(\text{net ml } AgNO_3)(N\ AgNO_3)(0.03545)(100)}{(\text{gram sample})}$$

(0.03545 = milliequivalent weight of chlorine)

% Chlorinated phenol = % chlorine X factor Cl to chlorinated phenol

Determination of o-Phenylphenol and Sodium Salt of o-Phenylphenol by Bromination and Titration

For definition, structure, and technical data on o-phenylphenol, see Phenols and Chlorophenols EPA-1.

Principle of the Method:

Sodium o-phenylphenol formulations are dissolved in water and filtered. o-Phenylphenol in oil formulations is distilled from acid solution, made alkaline, and evaporated to remove volatile organic interfering substances. A known portion of prepared sample is reacted with excess bromate-bromide solution and the excess determined iodometrically using standard sodium thiosulfate. The o-phenylphenol is calculated from the net difference in sodium thiosulfate used by a blank and by the sample.

Reagents:

1. Sodium hydroxide solution, 10% aqueous solution
2. Hydrochloric acid, concentrated, ACS
3. Bromate-bromide 0.1N solution - dissolve 2.78 grams of potassium bromate and 15 grams potassium bromide in water and make to one liter. This solution need not be standardized if a blank using the same quantity as the sample is run each time.
4. Potassium iodide, 40% aqueous solution
5. Sodium thiosulfate, 0.1N standardized solution
6. Starch indicator solution - 1 gram soluble starch boiled 2 minutes in 100 ml water

Equipment:

1. One liter distilling flask with condenser
2. Filtration apparatus
3. Hot plate
4. Air stream
5. 500 ml iodine flask
6. Titration apparatus
7. Usual laboratory glassware

Procedure:

Preparation of Sample:

(a) o-Phenylphenol in oil solutions - weigh a portion of sample equivalent to 0.04 gram o-phenylphenol into a one liter distilling flask, add 10 ml of 10% sodium hydroxide solution, and dilute to about 600 ml. Add 20 ml concentrated hydrochloric acid and a few boiling chips, and distill about 400 ml into a 1000 ml Erlenmeyer flask. Interrupt the distillation, add about 400 ml water to the distilling flask, and distill an additional 300 ml into the same 1000 ml Erlenmeyer flask. Add 15 ml of 10% sodium hydroxide solution to the distillate and boil down to about 50 ml using a stream of air against the surface of the liquid to prevent frothing. Transfer quantitatively to a 500 ml iodine flask.

(b) Sodium salt of o-phenylphenol - weigh a portion of sample equivalent to 1 gram sodium salt of o-phenylphenol into a 200 ml volumetric flask; dissolve in and make to volume with water. Filter, discarding the first 50 ml, pipette a 10 ml portion of the clear filtrate into a 500 ml iodine flask, and add 50 ml water.

Titration:

Pipette 25 ml 0.1N bromate-bromide solution into the iodine flask, add 15 ml concentrated hydrochloric acid, stopper, and allow to stand 15 minutes in a dark place with occasional shaking. Remove the stopper just sufficiently to quickly add 5 ml of 40% potassium iodine solution, taking care that no bromine vapor escapes. Restopper at once. Shake thoroughly. Remove the stopper, rinsing it and the well of the flask with water so that the washings flow into the flask. Wash down the inside walls of the flask with 5-10 ml water.

Titrate the liberated iodine with 0.1N standard thiosulfate solution using starch indicator near the endpoint.

Run a blank in the same way using the same quantity of reagents beginning with 50 ml of water in an iodine flask.

Calculations:

Subtract the ml used for the sample titration from the ml used for the blank titration to obtain the net ml equivalent to the o-phenylphenol in the sample.

Calculate the o-phenylphenol in oil solution as under sample preparation (a) as follows:

$$\% = \frac{(\text{net ml } Na_2S_2O_3)(\text{N } Na_2S_2O_3)(0.04255)(100)}{(\text{grams sample})}$$

0.04255 = milliequivalent weight of o-phenylphenol

Calculate the sodium salt of o-phenylphenol as under sample preparation (b) as follows:

$$\% = \frac{(\text{net ml } Na_2S_2O_3)(\text{N } Na_2S_2O_3)(0.04805)(100)}{(\text{grams sample})(10/200)}$$

0.04805 = milliequivalent weight of the sodium salt of o-phenylphenol

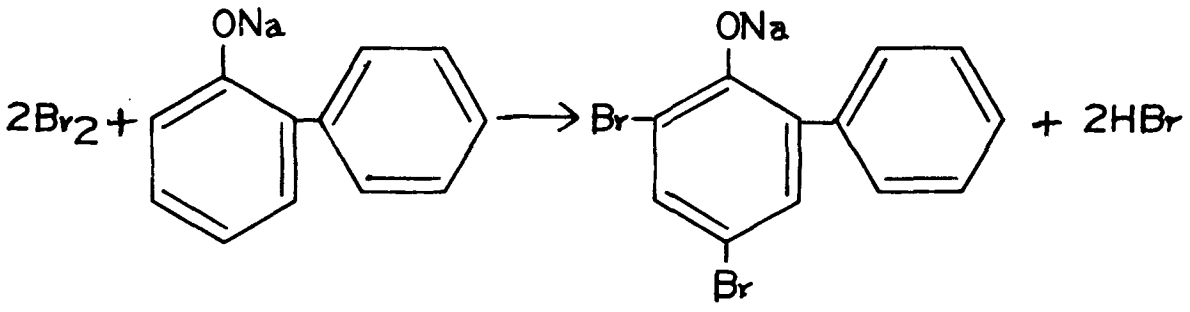
10/200 = dilution factor in sample preparation

Reactions:

1. Release of bromine from bromate-bromide solution:

$$KBrO_3 + 6KBr + 6HCl \longrightarrow 3Br_2 + KBr + 6KCl + 3H_2O$$

2. Bromination of the o-phenylphenol:



3. Release of iodine from excess bromine:

$$(excess)Br_2 + 2KI \longrightarrow I_2 + 2KBr$$

4. Titration of iodine with sodium thiosulfate:

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

Determination of Pentachlorophenol by High Pressure Liquid Chromatography

For definition, structure, and technical data on pentachlorophenol, see Phenols and Chlorophenols EPA-1.

Reagents:

1. Pentachlorophenol standard of known % purity
2. Benzyl benzoate standard of known % purity
3. Ethanol, ACS
4. Internal standard solution - weigh 5 grams benzyl benzoate into a 50 ml volumetric flask; dissolve in and make to volume with ethanol. (conc 100 mg/ml)

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm. If a variable wavelength UV detector is available, other wavelengths may be useful to increase sensitivity or eliminate interference.
2. Column: 0.5 meter x 2.1 mm ID packed with DuPont ODS Permaphase (or equivalent column)
3. High pressure liquid syringe or sample injection loop
4. Usual laboratory glassware

Operating Conditions:

Mobile phase:	30% methanol + 70% water
Column temperature:	60°C
Chart speed:	12 inches/minute
Flow rate:	1.0 ml/minute

Pressure: 800-1000 psi

Detector: UV at 254 nm

Attenuation: adjusted

Conditions may have to be varied by the analyst for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram pentachlorophenol standard into a 100 ml volumetric flask, add 5 ml of the internal standard solution by pipette, make to volume with ethanol, and mix thoroughly. (conc 0.5 mg pentachlorophenol and 5 mg benzyl benzoate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.05 g pentachlorophenol into a 100 ml volumetric flask, add 5 ml internal standard solution by pipette, make to volume with ethanol, and mix thoroughly. (conc 0.5 mg pentachlorophenol and 5 mg benzyl benzoate/ml)

Determination:

Inject 5 µl of standard solution and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is pentachlorophenol, then benzyl benzoate. Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of pentachlorophenol and benzyl benzoate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

IS = internal standard = benzyl benzoate

PCP = pentachlorophenol

$$RF = \frac{(\text{wt. IS})(\%\text{ purity IS})(\text{pk. ht. or area PCP})}{(\text{wt. PCP})(\%\text{ purity PCP})(\text{pk. ht. or area IS})}$$

Determine the percent PCP for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. IS})(\%\text{ purity IS})(\text{pk. ht. or area PCP})(100)}{(\text{wt. sample})(\text{pk. ht. or area IS})(RF)}$$

Method submitted by Elmer H. Hayes, EPA, Beltsville, Md.

Determination of Phenols and Chlorophenols by Gas-Liquid Chromatography (FID)

For definition, structure, and technical data on these compounds, see Phenols and Chlorophenols EPA-1.

This method has been found suitable for o-phenylphenol, p-tert-amyl-phenol, and o-benzyl-p-chlorophenol; however, with modification it should be suitable for several other phenol and chlorophenol compounds.

Reagents:

1. Phenol or chlorophenol standard of known % purity
2. Acetone, ACS
3. Ethyl ether, ACS
4. Sulfuric acid, ACS, 1+9 solution

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 1/4" glass column packed with 5% XE-60 on 60/80 Chromosorb W DMCS (or equivalent column)
3. Precision liquid syringe: 10 µl
4. 125 ml separatory funnels
5. Usual laboratory glassware

Operating Conditions for FID:

Column temperature: See under determination

Injection temperature: 250°C

Detector temperature: 250°C

Carrier gas: Nitrogen

Carrier gas pressure: 60 psi, adjusted for particular GC

Hydrogen pressure: 20 psi, adjusted for particular GC

Air pressure: 30 psi, adjusted for particular GC

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.04 gram o-phenylphenol or p-tert-amylphenol, or 0.08 gram o-benzyl-p-chlorophenol into a 25 ml volumetric flask, dissolve in, and make to volume with acetone. Mix well. (conc 1.6 mg/ml each of o-phenylphenol and p-tert-amylphenol and 3.2 mg/ml of o-benzyl-p-chlorophenol)

(Other phenols may require slightly different concentrations.)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.04 gram o-phenylphenol or p-tert-amylphenol, or 0.08 gram o-benzyl-p-chlorophenol into a 125 ml separatory funnel. Make slightly acidic with 1+9 sulfuric acid; then add 10 ml in excess. Extract three times with 25-50 ml portions of ethyl ether, collecting the extracts in a second separatory funnel. Wash once with a few ml of 1+9 sulfuric acid. Drain the ether extracts into a beaker, rinsing the separatory funnel with a few ml ether twice and adding the washings to the beaker. Allow the ether to evaporate (overnight) at room temperature using no heat or air jet. Dissolve the residue in a

small amount of acetone, quantitatively transfer to a 25 ml volumetric flask, and make to volume with acetone. (Samples in aerosols usually do not require extraction and can be weighed directly into a volumetric flask and made to volume.)

(If only one phenol is present, concentration after the above procedure should be 1.6 mg/ml each for o-phenylphenol and p-tert-amylphenol and 3.2 mg/ml for o-benzyl-p-chlorophenol.)

Determination:

A column temperature of 180°C is sufficient for o-phenylphenol and p-tert-amylphenol, eluting in that order. However, a 220°C temperature is needed for o-benzyl-p-chlorophenol to prevent an excessively long retention time.

Using a precision liquid syringe, alternately inject three 5 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

When several phenols or chlorophenols are present in the same sample, a standard approximating the sample composition should be made. In this case the column temperature may have to be programmed from about 150°C to 250°C.

Calculation:

From the average peak height or peak area calculate the percent phenol or chlorophenol compound as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Elmer H. Hayes, EPA, OPP, TSD, Beltsville, Md.

Determination of 4-Chloro-3,5-Xylenol by Gas-Liquid Chromatography (TCD and/or FID)

For definition, structure, and technical data on 4-chloro-3,5-xylenol, see Phenols and Chlorophenols EPA-1.

Reagents:

1. 4-chloro-3,5-xylenol standard of known % purity
2. Acetone, ACS
3. Petroleum ether, ACS
4. Ethyl ether, ACS
5. Sodium hydroxide, 1N aqueous solution
6. Sulfuric acid, 1+4 solution

Equipment:

1. Gas-Liquid Chromatograph with thermal conductivity detector (TCD) or flame ionization detector (FID)
2. Column for TCD: 5' x 1/4" O.D. glass column packed with 20% SE-30 on 60/80 Chromosorb, AW, DMCS (or equivalent column)
3. Column for FID: 6' x 1/4" O.D. glass column packed with 3% OV-1 on 80/100 Gas Chrom Q (or equivalent column)
4. Precision liquid syringe: 10 µl or 50 µl
5. Usual laboratory glassware

Procedure using Thermal Conductivity Detector:

Operating Conditions for TCD:

Column temperature: 210°C

Injection temperature: 240°C

Detector temperature: 270°C

Carrier gas: Helium

Flow rate: 100 ml/min

Operating conditions for filament current, column temperature, or gas flow should be adjusted by the analyst to obtain optimum response and reproducibility.

Preparation of Standard:

Weigh 0.2 grams 4-chloro-3,5-xylenol standard into a small glass-stoppered flask or screw-cap bottle, add by pipette 10 ml acetone, and shake to dissolve. (conc 20 mg/ml)

Preparation of Sample:

(a) For technical material, weigh a portion of sample equivalent to 0.2 gram 4-chloro-3,5-xylenol into a small glass-stoppered flask or screw-cap bottle, add by pipette 10 ml acetone, and shake to dissolve. (conc 20 mg/ml)

(b) For low % formulations in oils, weigh a portion of sample equivalent to 0.2 gram 4-chloro-3,5-xylenol into a 250 ml separatory funnel. Add about 100 ml petroleum ether and extract three times with 25 ml 1N sodium hydroxide solution. Combine the extracts into a second 250 ml separatory funnel, acidify with 1+4 sulfuric acid solution, and add 5 ml in excess. Extract twice with 75 ml ethyl ether. Filter the ether extracts through a cotton plug into a 300 ml flask and evaporate almost to dryness on a steam bath, allowing the last traces of ether to evaporate spontaneously from the warm flask. Dissolve the residue, transfer quantitatively to a 10 ml volumetric flask, and make to volume with acetone. Mix well. (conc 20 mg/ml)

Determination:

Using a precision liquid syringe, alternately inject three 30-40 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent 4-chloro-3,5-xylenol as follows:

$$\% = \frac{\text{(pk. ht. or area sample)(wt. std injected)(\% purity of std)}}{\text{(pk. ht. or area standard)(wt. sample injected)}}$$

Procedure for Flame Ionization Detector:

Operating Conditions for FID:

Column temperature:	145°C
Injection temperature:	225°C
Detector temperature:	220°C
Carrier gas:	Nitrogen (30 ml/min)
Carrier gas pressure:	60 psi, adjusted for particular GC
Hydrogen pressure:	20 psi, adjusted for particular GC
Air pressure:	30 psi, adjusted for particular GC

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Preparation of Standard:

Same as for TCD except use a 100 ml volumetric flask instead of a 10 ml volumetric flask. (conc 2 mg/ml)

Preparation of Sample:

Same as for TCD except use a 100 ml volumetric flask instead of a 10 ml volumetric flask. (conc 2 mg/ml)

Determination:

Using a precision liquid syringe, alternately inject three 2-4 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent 4-chloro-3,5-xylenol as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Eva Santos and Dean Hill, EPA Region IX, San Francisco, California.

Determination of Phenols and Chlorophenols by Gas-Liquid Chromatography (TCD-IS-BSA derivatization)

For definition, structure, and technical data on these compounds, see Phenols and Chlorophenols EPA-1.

Principle of the Method:

Trimethyl silyl derivatives of phenols and chlorophenols yield sharp, symmetrical peaks ideal for quantitative measurement. These peaks are also stronger and thus increase the sensitivitv of the analysis. The BSA reagent produces no interference.

The precision of this method is very good -- the same sample analyzed several times was found to give almost identical results. Also, the stability of the BSA derivative gave no detectable change over six days. Germicide formulations containing such compounds as soaps, triethanolamines, oils, and other active and inert ingredients seemed to present no problems and the results obtained were satisfactory.

A portion of prepared sample solution in chloroform is evaporated to dryness, treated with BSA reagent, has a portion of internal standard solution added, and is chromatographed with good results.

Reagents:

1. Phenol or chlorophenol standards of known % purity (see table of components and internal standards)
2. Internal standards, technical (or better) (see table of components and internal standards)
3. Chloroform, ACS

4. N,O-bis(trimethylsilyl)acetamide (BSA)
5. Sodium hydroxide, 1N solution
6. Sulfuric acid, 10% solution
7. Ethyl ether, ACS

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 4' x 1/4" O.D. glass packed with 4% SE-30 80/100 mesh Diatoport S (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Rotary evaporator
5. Steam bath with gentle stream of air
6. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	165°C
Injection temperature:	215°C
Detector temperature:	230°C
Filament current:	200 ma
Carrier gas:	Helium 25 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standards:

Weigh 0.25 gram of the phenol or chlorophenol standard into a 25 ml volumetric flask; dissolve in and make to volume with chloroform. (conc 10 mg/ml)

Preparation of Samples:

(a) For samples containing an appreciable amount of alcohol, weigh a portion of sample equivalent to 0.5 gram phenol or chlorophenol into a standard taper Erlenmeyer flask, make alkaline with 1N sodium hydroxide solution, and evaporate the water and alcohol to about 3-4 ml. Transfer quantitatively with 50 ml water into a 250 ml separatory funnel, neutralize with 10% sulfuric acid solution, and add 10 ml in excess. Extract two times with 50 ml of ethyl ether. Combine the ether extracts and wash with 10 ml water. Filter and dry the ether extracts by passing thru a plug of cotton and anhydrous sodium sulfate into a 250 ml standard taper Erlenmeyer flask and evaporate on a rotary evaporator (the ether may also be evaporated with a stream of dry air). Quantitatively transfer to a 50 ml volumetric flask and make to volume with chloroform. Mix thoroughly.

(b) For samples containing slight amounts (3%) of alcohol, weigh a portion of sample equivalent to 0.5 gram phenol or chlorophenol directly into the 250 ml separatory funnel and proceed as above beginning "neutralize with 10% sulfuric acid . . ."

Preparation of Internal Standard Solutions:

Prepare chloroform solutions of the internal standard solutions as follows:

(1) n-tetradecane, 1 gram in 50 ml, conc 20 mg/ml

(2) lindane, 4 grams in 50 ml, conc 80 mg/ml

(3) n-hexadecane, 0.5 gram in 50 ml, conc 10 mg/ml

(4) benzylbenzoate, 0.625 gram in 50 ml, conc 12.5 mg/ml

(5) di-2-ethylhexylphthalate(A), 0.5 gram in 50 ml, conc 10 mg/ml

(6) di-2-ethylhexylphthalate(B), 2 grams in 50 ml, conc 40 mg/ml

These concentrations are suggested for a 1:1 peak height ratio with 20 mg of phenol or chlorophenol.

Determination:

Pipette a 2 ml aliquot of the standard and sample solutions into separate 15 ml screw-cap vials and evaporate the chloroform to near dryness with a gentle stream of dry air. Add 1 ml BSA reagent, close tightly, shake to dissolve the residue, and allow to stand 10 minutes with occasional shaking. Add 1 ml of the appropriate internal standard as listed in the table below and mix well.

2 ml phenol compound (20 mg)	1 ml internal standard (mg as listed)
p-tert-butylphenol	n-tetradecane 20 mg
p-tert-amylphenol	n-tetradecane 20 mg
o-phenylphenol	lindane 80 mg
4-chloro-2-cyclopentylphenol	n-hexane 10 mg
o-benzyl-p-chlorophenol	benzyl benzoate 12.5 mg
4 or 6-chloro-2-phenylphenol	benzyl benzoate 12.5 mg
2,2'-methylenebis(3,4,6-trichlorophenol)	di-2-ethylhexylphthalate(A) 10 mg 10 mg
2,2'-methylenebis(4-chlorophenol)	di-2-ethylhexylphthalate(B) 40 mg 40 mg

Adjust the GC parameters and the size of the injection (3-4 µl) so that an injection of ether solution shows complete separation of the internal standard and the derivatized phenol compound within 10 minutes and so that there is no interference by other peaks. The height of both peaks should be between 1/2 to 3/4 full scale.

Make at least three injections of the standard solution. The ratio of the peak height of the derivatized standard to the peak height of the internal standard should be within 3% of the ratio of the previous injection. This will indicate that the instrument has reached equilibrium and that the operator has standardized his injection technique.

Proceed, making at least three injections of each solution, allowing time for any accompanying peak in the sample to elute before making the next injection.

Calculation:

Measure the peak heights of the internal standard and the derivatized standard phenol. Determine the RF value for each injection and average.

$$RF = \frac{\text{(wt. internal std.)(peak ht. of derivatized phenol)}}{\text{(wt. phenol std.)(\% purity phenol std.)(peak ht. internal std.)}}$$

Measure the peak heights of the internal standard and the derivatized sample phenol and calculate the average. Determine the percent phenol as follows:

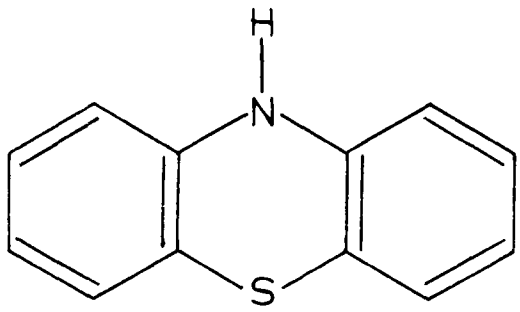
$$\% = \frac{\text{(wt. internal std.)(peak ht. of derivatized phenol)}\cancel{(100)}}{\text{(wt. sample)(peak height of internal standard)(RF)}} \quad (4\text{-}1)$$

December 1975

Phenothiazine EPA-1
(Tentative)

Determination of Phenothiazine by Infrared Spectroscopy

Phenothiazine is a registered oral insecticide and anthelmintic having the chemical structure:



Molecular formula: $C_{12}H_9NS$

Molecular weight: 199.3

Melting point: 185°C, sublimes 130°C (1 mm); b.p. 371°C

Physical state, color, odor, and taste: tasteless, crystalline solid with a slight odor; almost colorless when freshly sublimed, darkens to deep olive-green on exposure to light

Solubility: insoluble in water, chloroform; slightly soluble in alcohol, ether; soluble in acetone, benzene

Stability: oxidized in the presence of air and light to phenothiazone and thionol

Other names: thiodiphenylamine

Reagents:

1. Phenothiazine standard of known % purity
2. Benzene, pesticide or spectro grade
3. Carbon disulfide, pesticide or spectro grade
4. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm NaCl or KBr cells
2. Soxhlet extraction apparatus
3. Steam bath
4. Compressed air source
5. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.15 gram phenothiazine standard into a small glass-stoppered flask or screw-cap tube, add by pipette 25 ml carbon disulfide, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 6 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 1.5 grams phenothiazine into a Soxhlet thimble, plug with cotton or glass wool, and extract with benzene 3-4 hours. Cool, transfer to a 250 ml volumetric flask, and make to volume with benzene. Evaporate a 25 ml aliquot to just dryness using a gentle stream of air and a steam bath. Add 5 ml carbon disulfide and again evaporate to dryness to remove residual benzene. Dissolve residue, transfer to a 25 ml volumetric flask, and make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate to absorb any water and to clarify the solution. (final conc 6 mg phenothiazine/ml)

IR Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample solutions from 1430 cm^{-1} to 1250 cm^{-1} (7.0 μ to 8.0 μ). For a qualitative comparison, run a full scan.

Determine the absorbance of standard and sample using the minimum absorbance at 1333 cm^{-1} (7.5 μ) and the maximum absorbance at 1299 cm^{-1} (7.7 μ).

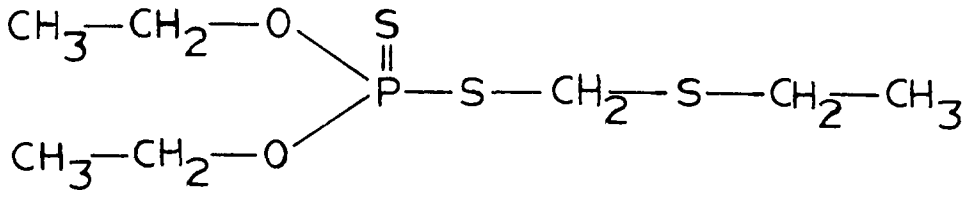
Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent phenothiazine as follows:

$$\% = \frac{\text{(abs. sample)(conc. std in mg/ml)(\% purity std)}}{\text{(abs. std)(conc. sample in mg/ml)}}$$

Determination of Phorate by Infrared Spectroscopy

Phorate is the acceptable common name for O,O-diethyl S-(ethylthiomethyl) phosphorodithioate, a registered insecticide having the chemical structure:



Molecular formula: $C_7H_{17}O_2PS_3$

Molecular weight: 260.4

Melting and boiling point: mp -42.9°C (pure material)
bp 118-120°C at 0.8 mm Hg

Physical state and color: clear mobile liquid

Solubility: 50 ppm in water at RT; miscible with alcohols, esters, ethers, carbon tetrachloride, dioxane, xylene, and vegetable oils

Stability: stable at room temperature but is hydrolyzed in the presence of moisture and by alkalis; incompatible with alkaline pesticides

Other names: Thimet (American Cyanamid Co.); timet (common name in USSR), Rampart

Reagents:

1. Phorate standard of known % purity
2. Acetonitrile, pesticide or spectro grade
3. Carbon disulfide, pesticide or spectro grade
4. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Water bath
5. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.1 gram phorate standard into a 10 ml volumetric flask, make to volume with chloroform, and mix well. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.5 gram phorate into a glass-stoppered flask or screw-cap bottle. Add 50 ml acetonitrile by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. Evaporate a 10 ml aliquot on a water bath at 40°C with a stream of dry air blowing across the surface; remove immediately after the last trace of acetonitrile has evaporated. Dissolve in a small amount of carbon disulfide, transfer to a 10 ml volumetric flask, make to volume, and mix well. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 10 mg phorate/ml)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative settings for the particular IR instrument being used, scan both the standard and sample from 730 cm^{-1} to 592 cm^{-1} (13.7 μ to 16.9 μ).

Determine the absorbance of standard and sample using the peak at 654 cm^{-1} (15.3 μ) and baseline from 709 cm^{-1} to 599 cm^{-1} (14.1 μ to 16.7 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent of phorate as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg phorate/ml carbon disulfide gives an absorbance of approx. 0.03 in a 0.2 mm cell.)

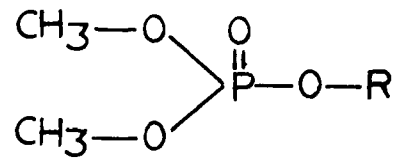
Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Determination of Total Phosphorus in Pastes and Organophosphate Formulations (Acid Digestion and Gravimetric Procedure)

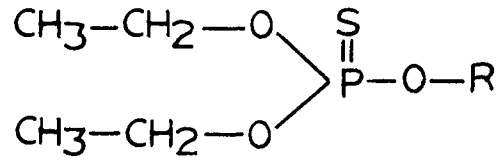
Inorganic phosphorus has been used as an insecticide and rodenticide in pastes made by grinding yellow phosphorus in the presence of water and mixing with flour; sometimes glycerin is added.

Organophosphorus compounds of several types have been and are used as pesticides. These compounds are anticholinesterase chemicals and may involve danger for the applicator. Examples of the leading series are as follows (where R represents an organic radical):

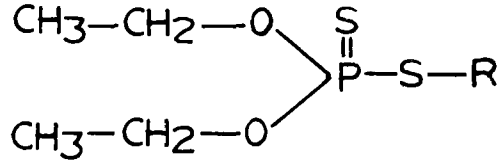
Phosphate: (dicrotophos)



Phosphorothioate: (parathion)



Phosphorodithioate: (phorate)



There are many analytical methods of different types available for organophosphorus compounds; however, there are times when a total phosphorus determination is the only immediate means of analysis: e.g., new compounds, combinations difficult to separate, analytical standard not available, etc. For data on these compounds, check other methods, reference book, or company sale literature and data sheets.

Phosphorus exists in three allotropic forms as follows:

(1) White phosphorus (also called yellow phosphorus):

Molecular (atomic) formula: P

Molecular (atomic) weight: 30.975

Melting/boiling point: mp 44.1°C, bp 280°C (volatile, sublimes in vacuo at ordinary temperature when exposed to light)

Physical state and color: white or yellow, soft waxy solid or transparent crystals

Solubility: insoluble in water and alcohol; moderately soluble in chloroform and benzene; very soluble in carbon disulfide

Stability: at RT it exhibits phosphorescence (slow, luminous oxidation) in air; it ignites spontaneously in moist air at about 30°C; stored and shipped beneath water to avoid ignition. It is very poisonous and causes severe burns.

(2) Red phosphorus: violet-red, amorphous powder, obtained from white phosphorus by heating in the presence of a catalyst; nonpoisonous and much less reactive than the white form; ignites in air at about 260°C; insoluble in organic solvents.

(3) Black phosphorus: black, lustrous crystals resembling graphite; obtained by heating white phosphorus under high pressure; does not catch fire spontaneously; insoluble in organic solvents.

Principle of Method:

Organic matter is destroyed and the phosphorus is oxidized to phosphoric acid by a wet acid digestion. The phosphorus is precipitated as

ammonium phosphomolybdate, filtered, washed free from impurities, redissolved, and then precipitated as magnesium ammonium pyrophosphate, which is filtered, washed, and ignited to magnesium pyrophosphate. From the amount of magnesium pyrophosphate present, the percent phosphorus or organophosphorus compound may be calculated.

Reagents:

1. Fuming nitric acid, ACS
2. Concentrated sulfuric acid, ACS
3. Concentrated nitric acid, ACS
4. Ammonium nitrate solution - dissolve 100 grams of phosphate-free ammonium nitrate, ACS in water and make to 1 liter.
5. Concentrated ammonium hydroxide, ACS
6. Ammonium molybdate solution - dissolve 100 grams molybdic acid, ACS in dilute ammonium hydroxide (144 ml conc. ammonium hydroxide + 271 ml water); pour this solution slowly and with constant stirring into dilute nitric acid (489 ml concentrated nitric + 1148 ml water). Keep the mixture in a warm place for several days or until a portion heated to 65°C deposits no yellow precipitate of ammonium phosphomolybdate. An alternative procedure is to heat to 65°C for 1-2 hours and allow to cool and stand overnight. Decant the solution from any sediment into a clean glass bottle with a glass stopper or a teflon-lined cap.
7. Ammonium hydroxide 1 + 1
8. Hydrochloric acid, dilute
9. Magnesia Mixture - dissolve 55 grams of crystallized magnesium chloride hexahydrate ACS in water; add 140 grams ammonium chloride ACS and 130.5 ml ammonium hydroxide, and dilute to 1 liter. This solution may form a precipitate if stored for a long time.

Equipment:

1. Kjeldahl flasks, 500 ml or 800 ml
2. Meker burner
3. Asbestos board with 1.5"-2.0" hole
4. Digestion rack or ring stand and flask support
5. Fume hood
6. Glass beads, small
7. Dropper
8. Filter paper, Whatman No. 7 (special for ammonium phosphomolybdate precipitate)
9. Platinum Gooch crucible
10. Asbestos, acid and alkali washed (preferably pre-ignited at 900°-1000°C before washing)
11. Muffle furnace
12. Usual laboratory glassware

Procedure:

Preparation of Sample - Phosphorus Pastes:

Weigh quickly an amount of well mixed sample equivalent to 0.02 gram phosphorus in a 500-800 ml Kjeldahl flask and immediately add 15 ml of water to prevent oxidation by air.

In phosphorus pastes, the phosphorus has a tendency to settle to the bottom; therefore, it is very important to thoroughly mix the entire sample before taking a portion for analysis.

A portion of the sample may conveniently be weighed in a No. 11 gelatin capsule and transferred to the digestion flask.

Preparation of Sample - Organophosphate Formulations:

Transfer a weight of sample or an aliquot from a chloroform extract equivalent to about 0.02 gram of phosphorus into a 500 ml or 800 ml Kjeldahl flask.

This method is applicable to aerosols, liquid formulations, emulsifiable concentrates, and chloroform extracts of granules, dusts, and wettable powders. For the analysis of organophosphates in granules, dusts, or wettable powders, it is recommended that the sample be extracted with chloroform. This will simplify digestion and avoid detection of inorganic phosphates when the organophosphates only are of interest.

Samples may be extracted on a Soxhlet or shaken out with solvent as follows: a portion of sample not to exceed 50 grams may be shaken for 2 hours on a shaking machine with 200 ml of chloroform in a 300 ml screw-cap bottle. After settling or filtering, an aliquot of the chloroform solution is taken for analysis.

For large aliquots of chloroform extracts or large samples containing petroleum hydrocarbons, add 25 ml of water before adding the sulfuric and nitric acids. Evaporate as much as possible of the organic solvent on a steam bath before digesting over a flame.

Digestion:

For Phosphorus Pastes - place flask on a digestion rack equipped with an asbestos board having an opening of 1.5-2 inches diameter. Add 20 ml fuming nitric acid, a few ml at a time, mixing gently but thoroughly after each addition of acid. A vigorous reaction will take place. When this action has subsided, heat on a steam bath until the dense nitric oxide fumes have been expelled. (Use of nitric acid alone in the initial stages of digestion is desirable since sulfuric acid will char hydrocarbons and increase the digestion time and difficulty.) Add 6 small glass beads and 10 ml sulfuric acid, and continue the digestion as below, beginning "Continue the addition - - - - - -."

For Organophosphorus Compounds - add 5 ml concentrated sulfuric acid and mix by swirling; cautiously add concentrated nitric acid, a few drops at a time, until any vigorous reaction is complete; then add 5 ml in excess. Add 6 small glass beads and place flask on a digestion rack equipped with an asbestos board having an opening of 1.5"-2.0". Heat gently at first over a free flame until the dense nitric oxide fumes have been expelled. Add a few drops of nitric acid and heat more vigorously.

Continue the addition of nitric acid and heating until all organic matter is destroyed, as evidenced by a colorless or light yellow solution that no longer turns dark. White fumes of sulfur trioxide will begin to show, and addition of a drop of nitric acid will cause a sputtering and dense brown fumes. Boil a few minutes to expel any nitric oxide fumes. Cool, add 10 ml of water, and heat to SO_3 fumes. Recool; add another 10 ml of water. If brown fumes appear, again heat to SO_3 fumes.

Allow to cool, add about 25 ml water, and recool. Transfer quantitatively to a 600 ml beaker, filtering if not clear. Add 50 ml of ammonium nitrate solution (or 5 grams solid ammonium nitrate if volume of solution is over 150 ml). Dilute to about 200 ml.

Precipitation as Ammonium Molybdate:

Add ammonium hydroxide to slight alkalinity and then make distinctly acid with nitric acid. Heat to 65°C and add 70 ml of ammonium molybdate solution. Stir and digest at 65°C for 30 minutes or longer if necessary to obtain a clear supernatant liquid. Determine if the phosphorus has been completely precipitated by adding more molybdate reagent to the supernatant liquid as soon as it has cleared.

Filter and wash five times by decantation with the ammonium nitrate solution. The ammonium phosphomolybdate precipitate may be left in the beaker and washed by decantation or it may be all transferred to the filter paper and washed there. Test the filtrate with more ammonium molybdate solution to make certain that enough has been used to precipitate all of the phosphorus.

Precipitation as Magnesium Ammonium Phosphate:

Dissolve the precipitate on the filter with ammonium hydroxide (1 + 1) into the beaker in which the precipitate was formed. Wash the filter with hot water and rinse off the outside of the filter funnel stem. Add sufficient ammonium hydroxide to dissolve all the precipitate and dilute to about 100 ml with water. Neutralize with hydrochloric acid. Phenolphthalein may be used as an internal indicator. If the solution is made too acidic, a yellow precipitate will begin to form. If this happens, add ammonium hydroxide until precipitate redissolves. Cool and add 20 ml magnesia mixture very slowly (one drop per second) with constant stirring. Allow to stand 15 minutes, add 15 ml concentrated ammonium hydroxide, and allow to stand overnight or two hours in an ice bath.

Filtration and Ignition:

Filter through a prepared and tared platinum Gooch crucible, previously ignited for 30 minutes in a muffle furnace at a temperature of 900-1000°C. Wash with ammonium hydroxide (1 + 9) until free from chlorides as shown by testing a portion of the acidified filtrate with silver nitrate. Dry and ignite for 30 minutes at 900-1000°C until the residue is white. Cool and weigh as magnesium pyrophosphate.

Calculation:

From the weight of magnesium pyrophosphate, $Mg_2P_2O_7$, calculate the percent phosphorus in the sample as follows:

$$\% \text{ phosphorus} = \frac{(\text{grams } Mg_2P_2O_7)(0.2783)(100)}{(\text{grams sample})}$$

0.2783 = factor $Mg_2P_2O_7$ to phosphorus

Calculate the percent organophosphate from the percent phosphorus as follows:

$$\% \text{ organophosphate} = \frac{\% \text{ phosphorus}}{\% \text{ phosphorus in the organophosphate}}$$

$$\% \text{ organophosphate} = \% \text{ P} \times \text{factor P to compound}$$

Reactions involved in this method:

$$\text{Organophosphate} \xrightarrow[\triangle]{HNO_3 + H_2SO_4} H_3PO_4 + \text{Oxidation product}$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow (NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12H_2O$$

$$(NH_4)_3PO_4.12MoO_3 + 24NH_4OH \longrightarrow (NH_4)_3PO_4 + 12(NH_4)_2MoO_4 + 12H_2O$$

$$(NH_4)_3PO_4 + MgCl_2 + NH_4OH \longrightarrow MgNH_4PO_4 + 2NH_4Cl + NH_4OH$$

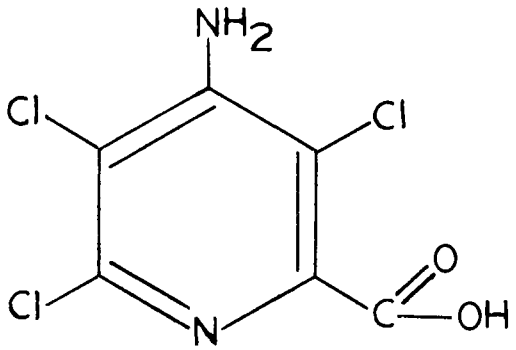
$$2MgNH_4PO_4 \xrightarrow[\triangle]{} Mg_2P_2O_7 + 2NH_3 + H_2O$$

July 1975

Picloram EPA-1
(Tentative)

Determination of Picloram by High Pressure Liquid Chromatography

Picloram is the common name for 4-amino-3,5,6-trichloropicolinic acid, a registered herbicide having the chemical structure:



Molecular formula: $C_6H_3Cl_3N_2O_2$

Molecular weight: 241.5

Physical state, color, and odor: white powder, chlorine-like odor

Melting point: decomposes before melting

Solubility: 430 ppm in water at 25°C; low in most organic solvents, 1.98 g/100 ml in acetone, 0.55 g/100 ml isopropanol, less than 50 ppm in carbon disulfide; potassium salt 40% in water

Stability: decomposes approximately 215°C; subject to photo-decomposition

Other names: Tordon (Dow Chem. Co.), Borolin

Reagents:

1. Picloram standard of known % purity
2. Methanol, pesticide or spectro grade

Equipment:

1. High pressure liquid chromatograph
2. High pressure liquid syringe or sample injection loop
3. Liquid chromatographic column, 2.1 mm I.D. x 1 meter packed with an anion exchange material such as DuPont's Permaphase AXX - a quaternary amine bonded to the support by Si-O-Si linkages
4. Usual laboratory glassware

Operating conditions for DuPont Model 830 LC:

Mobile phase: 90% water (containing 0.2 gram H_3PO_4 per liter - approx. 0.003M) + 10% methanol

Column temperature: 65°C

Column pressure: 900 PSI

Flow rate: 8 ml/min

Chart speed: 10 min/inch

Detector: UV at 254 nm

Attenuation: 4×10^{-2}

Conditions may have to be varied by the analyst for other instruments, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram picloram standard into a small glass-stoppered flask or vial, add 10 ml methanol by pipette, dissolve, and mix well (final conc 10 mg/ml).

Preparation of Sample:

Weigh an amount of sample equivalent to 0.1 gram picloram into a small glass-stoppered flask or vial, add 10 ml methanol by pipette, and shake thoroughly to dissolve the picloram. Allow any solid matter to settle; filter or centrifuge if necessary (final conc 10 mg/ml).

Determination:

Alternately inject three 10 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

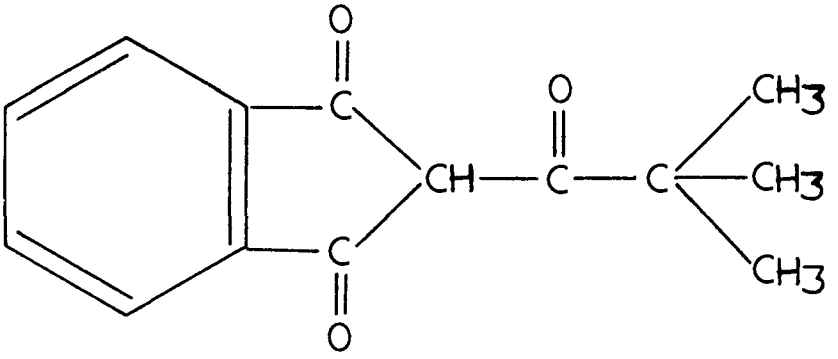
From the average peak height or peak area calculate the percent picloram as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method developed by Elmer H. Hayes, EPA, Beltsville, Md.

Determination of Pindone in Baits and Concentrates by Ultraviolet Spectroscopy (Ether Extraction)

Pindone is the common name for 2-pivalyl-1,3-indandione, a registered rodenticide and insecticide having the chemical structure:



Molecular formula: $C_{14}H_{14}O_3$

Molecular weight: 230.3

Melting point: 108.5 to 110.5°C

Physical state and color: yellow crystalline solid

Solubility: 18 ppm in water at 25°C; soluble in most organic solvents; soluble in aqueous alkali or ammonia to form bright yellow salts

Stability: stable under normal conditions

Other names: Pivalyl Valone, Pival, Pivalyn (Kilgore Chem. Co.); pivaldione (France), pival (Portugal, Turkey)

This method may be used for analyzing both bait materials and concentrates containing about 0.025% and 0.5% active ingredient.

The method does not distinguish between pindone (2-pivalyl-1,3-indandione) and PMP (2-isovaleryl-1,3-indandione), both of which have UV absorption maxima at 283, 312, and 324 nm. However, they may be identified by extraction from the formulation with ether (ethyl or petroleum), evaporation of the solvent, recrystallization from pentane, and determination of the melting point. Pindone melts at 110-111°C and PMP melts at 67-68°C.

Sodium or calcium salts cannot be determined by the ether extraction method (EPA-1) but can be determined by the pyrophosphate extraction method (EPA-2).

Reagents:

1. Pindone standard of known % purity
2. Sodium pyrophosphate, 1% solution - dissolve 5 grams $Na_4P_2O_7.10H_2O$ in 500 ml water.
3. Ethyl ether, ACS
4. Petroleum ether - extract 200 ml petroleum ether three times with 20 ml of 1% sodium pyrophosphate solution.

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Soxhlet extraction apparatus
3. Mechanical shaker
4. Centrifuge with 16 x 150 mm glass-stoppered tubes
5. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.08 gram pindone standard into a 100 ml volumetric flask, dissolve in, and make to volume with 1% sodium pyrophosphate solution. Mix thoroughly, pipette 10 ml into a 100 ml volumetric flask, make to volume with pyrophosphate solution, and mix thoroughly. Pipette 5 ml into a second 100 ml volumetric flask, make to volume with pyrophosphate solution, and mix well. (final conc 4 µg pindone/ml)

Preparation of Sample:

For 0.025% Baits - weigh 16 grams ground sample (0.004 g pindone) into a Soxhlet thimble, plug with cotton or glass wool, and extract with ethyl ether on a Soxhlet apparatus for about four hours. Cool, transfer the extract to a 200 ml volumetric flask, and make to volume with ethyl ether. Mix thoroughly.

For 0.5% Concentrates - weigh 0.8 gram ground sample (0.004 g pindone) into a 500 ml glass-stoppered flask, add 200 ml ethyl ether by pipette, and shake on a mechanical shaker for 30 minutes. Centrifuge a portion of the extract to clarify if necessary, taking care to avoid evaporation of ether.

Pipette 2 ml of the clear ether solution into a 16 x 150 mm glass-stoppered centrifuge tube. Add 10 ml of 1% sodium pyrophosphate solution by pipette, shake vigorously for two minutes, and centrifuge at high speed until the aqueous layer is clear. Draw off the ether layer and any remaining emulsion using an aspirator with a glass tube drawn into a fine tip. Add 2 ml ethyl ether, shake, centrifuge, and draw off the ether. Repeat twice more with 2 ml portions of petroleum ether. If the aqueous layer is not clear, centrifuge for a few minutes with the stopper off to remove any residual ether. (final conc 4 µg pindone/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen for 0 and 100% at 283 nm with 1% pyrophosphate solution in each cell. Scan both standard and sample from 350 nm to 200 nm with the pyrophosphate solution in the reference cell.

Calculation:

Measure the absorbance of standard and sample at 283 nm and calculate the percent pindone as follows:

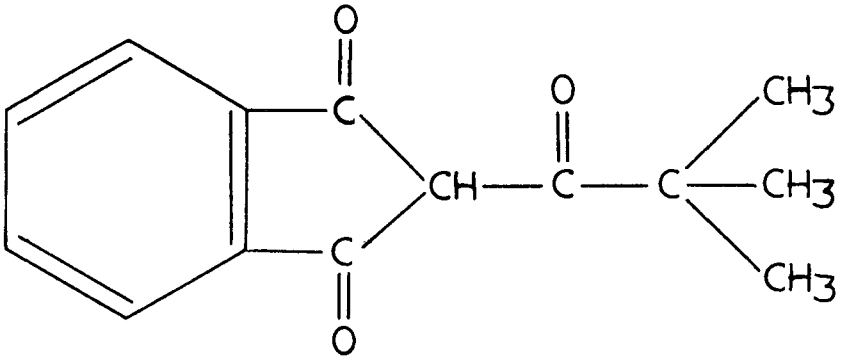
$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

or using dilution factors, as follows:

$$\% = \frac{(\text{abs. sample})(\text{wt. std})(\text{purity std})(1/100)(10/100)(5/100)(100)}{(\text{abs. std})(1/200)(2/10)}$$

Determination of Pindone in Baits and Concentrates by Ultraviolet Spectroscopy (Pyrophosphate Extraction)

Pindone is the common name for 2-pivalyl-1,3-indandione, a registered rodenticide and insecticide having the chemical structure:



Molecular formula: $C_{14}H_{14}O_3$

Molecular weight: 230.3

Melting point: 108.5 to 110.5°C

Physical state and color: yellow crystalline solid

Solubility: 18 ppm in water at 25°C; soluble in most organic solvents; soluble in aqueous alkali or ammonia to form bright yellow salts

Stability: stable under normal conditions

Other names: Pivalyl Valone, Pival, Pivalyn (Kilgore Chem. Co.), pivaldione (France), pival (Portugal, Turkey)

This method may be used for analyzing both bait materials and concentrates containing about 0.025% and 0.5% active ingredient.

The method does not distinguish between pindone (2-pivalyl-1,3-indandione) and PMP (2-isovaleryl-1,3-indandione), both of which have UV absorption maxima at 283, 312, and 324 nm. However, they may be identified by extraction from the formulation with ether (ethyl or petroleum), evaporation of the solvent, recrystallization from pentane, and determination of the melting point. Pindone melts at 110-111°C and PMP melts at 67-68°C.

Sodium or calcium salts cannot be determined by the ether extraction method (EPA-1) but can be determined by the pyrophosphate extraction method (EPA-2).

Reagents:

1. Pindone standard of known % purity
2. Sodium pyrophosphate, 1% solution - dissolve 5 grams $Na_4P_2O_7.10H_2O$ in 500 ml water.
3. Ethyl ether-petroleum ether (20-80) - extract 200 ml petroleum ether three times with 20 ml portions of pyrophosphate solution and add 50 ml ethyl ether.
4. Hydrochloric acid, 2.5N solution

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Centrifuge with 100 ml glass-stoppered centrifuge tubes
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.08 gram pindone standard into a 100 ml volumetric flask, dissolve in, and make to volume with 1% sodium pyrophosphate solution. Mix thoroughly and pipette 10 ml into a 100 ml volumetric flask, make to volume with pyrophosphate solution, and mix thoroughly. Pipette 5 ml into a second 100 ml volumetric flask, make to volume with pyrophosphate solution, and mix well. (final conc 4 µg pindone/ml)

Preparation of Sample:

Weigh an amount of finely ground sample equivalent to 0.001 gram pindone (4 grams of 0.025% Bait or 0.2 gram 0.5% Concentrate) into a 250 ml glass-stoppered flask, add by pipette 100 ml 1% sodium pyrophosphate solution, and shake on a mechanical shaker for one hour. Transfer 40-50 ml to a glass-stoppered centrifuge tube and centrifuge for at least 5 minutes. Pipette 20 ml of this solution into a glass-stoppered 100 ml centrifuge tube, add 5 ml 2.5N hydrochloric acid and 50 ml (by pipette) of the mixed ether solution, and shake for five minutes. If an emulsion forms, centrifuge to break the emulsion. Pipette 10 ml of the ether layer to a clean centrifuge tube and add 10 ml pyrophosphate solution by pipette. Shake for 2 minutes and remove the ether layer using an aspirator with a glass tube drawn to a fine tip. If the aqueous layer is not clear, centrifuge for a few minutes with the stopper off to remove any residual ether. (final conc 4 µg pindone/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen for 0 and 100% at 283 nm with 1% pyrophosphate solution in each cell. Scan both standard and sample from 350 nm to 200 nm with the pyrophosphate solution in the reference cell.

Calculation:

Measure the absorbance of standard and sample at 283 nm and calculate the percent pindone as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

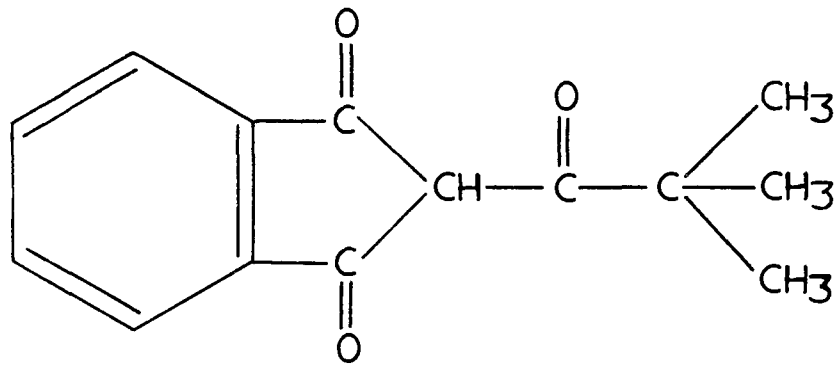
or using dilution factors, as follows:

$$\% = \frac{(\text{abs. sample})(\text{wt. std})(\text{purity std})(1/100)(10/100)(5/100)(100)}{(\text{abs. std})(\text{wt. sample})(1/100)(20/50)(10/10)}$$

% Sodium pindone = % pindone X 1.096

Determination of Pindone in Water-Soluble Formulations by Ultraviolet Spectroscopy (Pyrophosphate Extraction)

Pindone is the common name for 2-pivalyl-1,3-indandione, a registered rodenticide and insecticide having the chemical structure:



Molecular formula: $C_{14}H_{14}O_3$

Molecular weight: 230.3

Melting point: 108.5 to 110.5°C

Physical state and color: yellow crystalline solid

Solubility: 18 ppm in water at 25°C; soluble in most organic solvents; soluble in aqueous alkali or ammonia to form bright yellow salts

Stability: stable under normal conditions

Other names: Pivalyl Valone, Pival, Pivalyn (Kilgore Chem. Co.); pivaldione (France), pival (Portugal, Turkey)

Pindone (2-pivalyl-1,3-indandione) and PMP (2-isovaleryl-1,3-indandione) are often formulated as water-soluble powders containing the sodium salts of these two materials, along with sodium benzoate,

sodium ethylenediamine tetraacetate (EDTA), and sugar. Sodium benzoate and the sodium EDTA interfere moderately at the strongest absorption maxima near 283 nm, decreasing to about 275 nm and then increasing again; however, a determination can be made at the secondary maxima near 311 and 323 nm.

A solution of pindone containing 10 µg/ml in 1% pyrophosphate has an approximate absorbance of 0.394 at 324 nm; a solution of PMP containing 7.5 µg/ml in 1% pyrophosphate has an approximate absorbance of 0.398 at 323 nm. If there is no interference and the absorbances are read at 283 nm, the concentrations of the standards and/or sample solutions should each be about one-third as great.

This method does not distinguish between pindone and PMP; however, they may be identified by extracting an acidified aqueous solution of the formulation with ether (ethyl or petroleum), evaporating the solvent, recrystallizing from pentane, and determining the melting point. Pindone melts at 110-111°C and PMP melts at 67-68°C.

The presence of sodium benzoate or sodium EDTA may be confirmed by the procedure at the end of this method.

Reagents:

1. Pindone standard of known % purity
2. Sodium pyrophosphate, 1% solution - dissolve 10 grams $Na_4P_2O_7.10H_2O$ in one liter of water.

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram pindone standard into a 100 ml volumetric flask; dissolve and make to volume with 1% sodium pyrophosphate solution. Mix thoroughly and pipette 5 ml into a 50 ml volumetric flask, and make to volume with pyrophosphate solution; mix well, pipette 5 ml into a second 50 ml volumetric flask, and make to volume with pyrophosphate solution. (final conc 10 µg pindone/ml)

If absorbances are to be read at 283 nm, pipette 2 ml instead of 5 ml into the second 50 ml volumetric flask. (final conc 4 µg pindone/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.004 gram pindone into a 100 ml volumetric flask; dissolve and make to volume with 1% sodium pyrophosphate solution. Mix thoroughly, pipette 25 ml into a second 100 ml volumetric flask, and make to volume with the 1% pyrophosphate solution. (final conc 10 µg pindone/ml)

If the absorbances are to be read at 283 nm, pipette 10 ml instead of 25 ml into the second 100 ml volumetric flask. (final conc 4 µg pindone/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen for 0 and 100% at 324 nm (or at 283 nm if no sodium benzoate or sodium EDTA interference is present) with 1% pyrophosphate solution in each cell. Scan both the standard and sample from 350 nm to 250 nm with pyrophosphate solution in the reference cell.

Calculation:

Measure the absorbance of standard and sample at 324 nm or 283 nm, and calculate the percent pindone as follows:

% pindone at 324 nm:

$$\% = \frac{(\text{abs. sample})(\text{wt. std})(\text{purity std})(1/100)(5/50)(5/50)}{(\text{abs. std})(\text{wt. sample})(1/100)(25/100)}$$

% pindone at 283 nm:

$$\% = \frac{(\text{abs. sample})(\text{wt. std})(\text{purity std})(1/100)(5/50)(2/50)}{(\text{abs. std})(\text{wt. sample})(1/100)(10/100)}$$

Procedure for Confirming the Presence of Sodium Benzoate and Sodium EDTA:

Sodium benzoate and sodium EDTA may be identified by the following procedure: Make an aqueous extract of the sample, acidify with hydrochloric acid, and filter. Save both filtrate and residue. Use the filtrate for EDTA and the residue for benzoate as follows:

For EDTA - place one drop of nickel sulfate solution (0.01% in water) and one drop concentrated ammonium hydroxide into each of two depressions on a spot plate. To one add a drop of water and to another a drop of the sample extract filtrate. Add a drop of dimethylglyoxime solution (saturated - approx. 0.1 g in 50 ml water) to each. The blank becomes pink immediately, but if the solution contains a sequestering agent--EDTA--it remains colorless or becomes only very faintly pink.

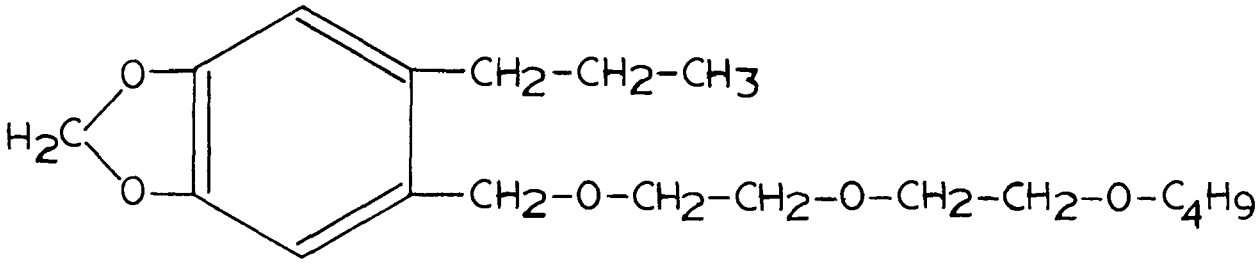
For Benzoate - wash the residue with hot water to remove the benzoic acid (pindone and PMP are practically insoluble in water). Make alkaline with a few drops of ammonium hydroxide, heat gently to expel excess ammonia by evaporation, dissolve residue in a few ml water (filter if necessary), and add a few drops of aqueous 0.5% ferric chloride solution. A salmon-color precipitate of ferric benzoate indicates presence of benzoic acid. An alternative procedure is to evaporate the acidified filtrate and determine the melting point. Benzoic acid melts at 122°C.

Detection of Piperonyl Butoxide in Pesticides - Qualitative Test

Piperonyl butoxide, technical is the official name for the commercial product consisting of 80% (butyl carbityl)(6-propylpiperonyl) ether and 20% related compounds.

Piperonyl butoxide is a registered pesticide ingredient and, although itself without marked insecticidal properties, enhances the toxicity, paralytic effect, and persistent contact toxicity of the pyrethrins and related compounds. It is also used with rotenone and tetramethrin.

The chemical structure is:



Molecular formula: $C_{19}H_{30}O_5$

Molecular weight: 338.5

Boiling point: 180°C at 1 mm Hg

Physical state, color, and odor: odorless, pale yellow oily liquid

Solubility: soluble in most organic solvents including petroleum oils and dichlorodifluoromethane; insoluble in water

Stability: stable to light; resistant to hydrolysis; non-corrosive

Other names: Butacide (FMC), NIA 5273 (Niagara), FMC 5273, α-[2-(2-n-butoxyethoxy)-ethoxy]-4,5-methylenedioxy-2-propyltoluene

Reagents:

1. Tannic acid
2. Acetic acid, glacial
3. Phosphoric acid, 85%
4. Color development reagent - dissolve completely 0.05 gram tannic acid in 15 ml glacial acetic acid, add 35 ml 85% phosphoric acid, and mix thoroughly. Prepare fresh daily and keep in tightly stoppered bottle since the solution is hygroscopic.

   Stock solutions of tannic acid in acetic acid (solution A) and phosphoric acid (solution B) may be kept separately and mixed 1.5 ml A + 3.5 ml B just before use.

Equipment:

1. 18 x 150 mm test tube
2. Boiling water bath
3. Usual laboratory glassware

Preparation of Sample:

The sample to be tested should contain 1-2 mg per ml of solution.

Oil solutions may be diluted with ether or an odorless base oil such as Deo Base.

Powders should be extracted with ethyl ether by shaking in a flask on a shaking machine and evaporated or diluted to the desired concentration.

Qualitative Determination:

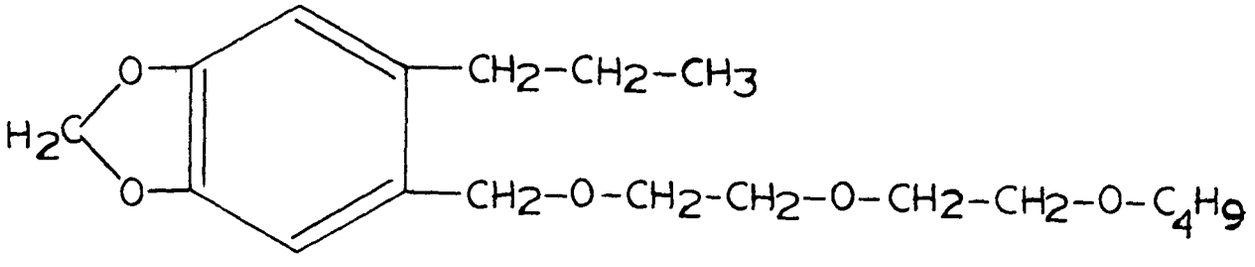
Place 0.1 ml of sample solution and 5 ml of color reagent in an 18 x 150 mm test tube. Shake the tube vigorously for 30 seconds and place in a bath of boiling water for 5 minutes. A blue color indicates the presence of piperonyl butoxide.

Determination of Piperonyl Butoxide by Gas-Liquid Chromatography (FID - Internal Standard)

Piperonyl butoxide, technical is the official name for the commercial product consisting of 80% (butyl carbityl)(6-propylpiperonyl) ether and 20% related compounds.

Piperonyl butoxide is a registered pesticide ingredient and, although itself without marked insecticidal properties, enhances the toxicity, paralytic effect, and persistent contact toxicity of the pyrethrins and related compounds. It is also used with rotenone and tetramethrin.

The chemical structure is:



Molecular formula: $C_{19}H_{30}O_5$

Molecular weight: 338.5

Boiling point: 180°C at 1 mm Hg

Physical state, color, and odor: odorless, pale yellow oily liquid

Solubility: soluble in most organic solvents including petroleum oils and dichlorodifluoromethane; insoluble in water

Stability: stable to light; resistant to hydrolysis; non-corrosive

Other names: Butacide (FMC), NIA 5273 (Niagara), FMC 5273, α-[2-(2-n-butoxyethoxy)-ethoxy]-4,5-methylenedioxy-2-propyltoluene

Reagents:

1. Piperonyl butoxide of known % purity
2. Dioctyl phthalate
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.18 gram dioctyl phthalate into a 100 ml volumetric flask; dissolve in and make to volume with acetone. (conc 1.8 mg dioctyl phthalate/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 4 mm glass column packed with 3% OV-1 on 60/80 mesh Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	230°C
Injection temperature:	260°C
Detector temperature:	270°C
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi (adjusted for specific GC)
Hydrogen pressure:	20 psi (30 ml/min)
Air pressure:	30 psi (300 ml/min)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.03 gram piperonyl butoxide standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 25 ml of the internal standard solution and shake to dissolve. (final conc 1.2 mg piperonyl butoxide and 1.8 mg dioctyl phthalate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.03 gram piperonyl butoxide into a small glass-stoppered flask or screw-cap bottle. Add by pipette 25 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the piperonyl butoxide. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 1.2 mg piperonyl butoxide and 1.8 mg dioctyl phthalate/ml)

Determination:

Inject 2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is piperonyl butoxide, then dioctyl phthalate.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of piperonyl butoxide and dioctyl phthalate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

I.S. = Internal Standard = dioctyl phthalate

$$RF = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area piperonyl butoxide})}{(\text{wt. piperonyl butoxide})(\%\text{ purity piperonyl butoxide})(\text{pk. ht. or area I.S.})}$$

Determine the percent piperonyl butoxide for each injection of the sample-internal standard solution as follows and calculate the average:

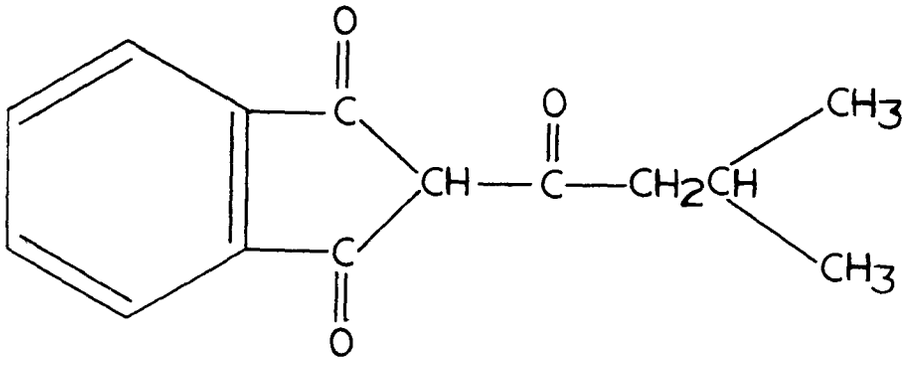
$$\% = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area piperonyl butoxide})(100)}{(\text{wt. sample})(\text{pk. ht. or area I.S.})(RF)}$$

(11-1)

Method submitted by Division of Regulatory Services, Kentucky Agricultural Experiment Station, University of Kentucky, Lexington, Kentucky 40506.

Determination of PMP in Baits and Concentrates by Ultraviolet Spectroscopy (Ether Extraction)

PMP is 2-isovaleryl-1,3-indandione, a registered rodenticide having the chemical structure:



Molecular formula: $C_{14}H_{14}O_3$

Molecular weight: 230.3

Melting point: 67 to 68°C

Physical state and color: yellow crystalline solid

Solubility: practically insoluble in water; soluble in most organic solvents; soluble in aqueous alkali or ammonia to form bright yellow salts

Stability: stable under normal conditions

Other names: Valone (Kilgore Chem. Co.)

This method may be used for analyzing both bait materials and concentrates containing about 0.025% and 0.5% active ingredient.

The method does not distinguish between pindone (2-pivalyl-1,3-indandione) and PMP (2-isovaleryl-1,3-indandione), both of which have UV absorption maxima at 283, 312, and 324 nm. However, they may be identified by extraction from the formulation with ether (ethyl or petroleum), evaporation of the solvent, recrystallization from pentane, and determination of the melting point. Pindone melts at 110-111°C and PMP melts at 67-68°C.

Sodium or calcium salts cannot be determined by the ether extraction method (EPA-1) but can be determined by the pyrophosphate extraction method (EPA-2).

Reagents:

1. PMP standard of known % purity
2. Sodium pyrophosphate, 1% solution - dissolve 5 grams $Na_4P_2O_7.10H_2O$ in 500 ml water.
3. Ethyl ether, ACS
4. Petroleum ether - extract 200 ml petroleum ether three times with 20 ml of 1% sodium pyrophosphate solution.

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Soxhlet extraction apparatus
3. Mechanical shaker
4. Centrifuge with 16 x 150 mm glass-stoppered tubes
5. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.08 gram PMP standard into a 100 ml volumetric flask, dissolve in, and make to volume with 1% sodium pyrophosphate solution. Mix thoroughly, pipette 10 ml into a 100 ml volumetric flask, make to volume with pyrophosphate solution, and again mix thoroughly. Pipette 5 ml into a second 100 ml volumetric flask, make to volume with pyrophosphate solution, and mix well. (final conc 4 µg PMP/ml)

Preparation of Sample:

For 0.025% Baits - weigh 16 grams ground sample (0.004 g PMP) into a Soxhlet thimble, plug with cotton or glass wool, and extract with ethyl ether on a Soxhlet apparatus for about four hours. Cool, transfer the extract to a 200 ml volumetric flask, and make to volume with ethyl ether. Mix thoroughly.

For 0.5% Concentrates - weigh 0.8 gram ground sample (0.004 g PMP) into a 500 ml glass-stoppered flask, add 200 ml ethyl ether by pipette, and shake on a mechanical shaker for 30 minutes. Centrifuge a portion of the extract to clarify if necessary, taking care to avoid evaporation of ether.

Pipette 2 ml of the clear ether solution into a 16 x 150 mm glass-stoppered centrifuge tube. Add 10 ml of 1% sodium pyrophosphate solution by pipette, shake vigorously for two minutes, and centrifuge at high speed until the aqueous layer is clear. Draw off the ether layer and any remaining emulsion using an aspirator with a glass tube drawn into a fine tip. Add 2 ml ethyl ether, shake, centrifuge, and draw off the ether. Repeat twice more with 2 ml portions of petroleum ether. If the aqueous layer is not clear, centrifuge for a few minutes with the stopper off to remove any residual ether. (final conc 4 µg PMP/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen for 0 and 100% at 283 nm with 1% pyrophosphate solution in each cell. Scan both standard and sample from 350 nm to 200 nm with the pyrophosphate solution in the reference cell.

Calculation:

Measure the absorbance of standard and sample at 283 nm and calculate the percent PMP as follows:

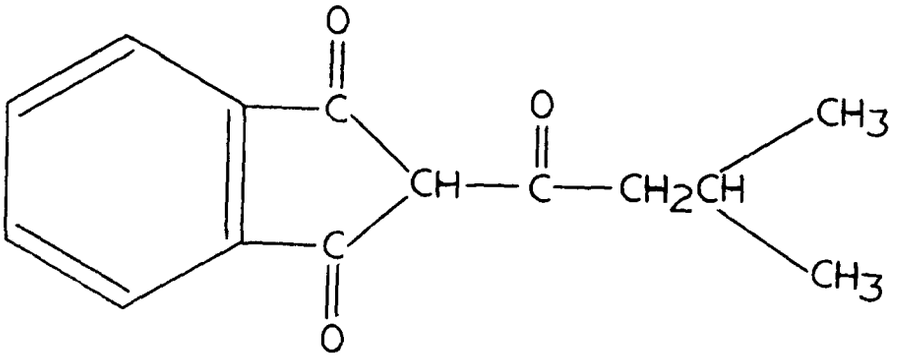
$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu\text{g/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu\text{g/ml})}$$

or using dilution factors, as follows:

$$\% = \frac{(\text{abs. sample})(\text{wt. std})(\text{purity std})(1/100)(10/100)(5/100)(100)}{(\text{abs. std})(1/200)(2/10)}$$

Determination of PMP in Baits and Concentrates by Ultraviolet Spectroscopy (Pyrophosphate Extraction)

PMP is 2-isovaleryl-1,3-indandione, a registered rodenticide having the chemical structure:



Molecular formula: $C_{14}H_{14}O_3$

Molecular weight: 230.3

Melting point: 67 to 68°C

Physical state and color: yellow crystalline solid

Solubility: practically insoluble in water; soluble in most organic solvents; soluble in aqueous alkali or ammonia to form bright yellow salts

Stability: stable under normal conditions

Other names: Valone (Kilgore Chem. Co.)

This method may be used for analyzing both bait materials and concentrates containing about 0.025% and 0.5% active ingredient.

The method does not distinguish between pindone (2-pivalyl-1,3-indandione) and PMP (2-isovaleryl-1,3-indandione), both of which have UV absorption maxima at 283, 312, and 324 nm. However, they may be identified by extraction from the formulation with ether (ethyl or petroleum), evaporation of the solvent, recrystallization from pentane, and determination of the melting point. Pindone melts at 110-111°C and PMP melts at 67-68°C.

Sodium or calcium salts cannot be determined by the ether extraction method (EPA-1) but can be determined by the pyrophosphate extraction method (EPA-2).

Reagents:

1. PMP standard of known % purity
2. Sodium pyrophosphate, 1% solution - dissolve 5 grams $Na_4P_2O_7.10H_2O$ in 500 ml water.
3. Ethyl ether-petroleum ether (20-80) - extract 200 ml petroleum ether three times with 20 ml portions of pyrophosphate solution and add 50 ml ethyl ether.
4. Hydrochloric acid, 2.5N solution

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Centrifuge with 100 ml glass-stoppered centrifuge tubes
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.08 gram PMP standard into a 100 ml volumetric flask, dissolve in, and make to volume with 1% sodium pyrophosphate solution. Mix thoroughly and pipette 10 ml into a 100 ml volumetric flask, make to volume with pyrophosphate solution, and again mix thoroughly. Pipette 5 ml into a second 100 ml volumetric flask, make to volume with pyrophosphate solution, and mix well. (final conc 4 µg PMP/ml)

Preparation of Sample:

Weigh an amount of finely ground sample equivalent to 0.001 gram PMP (4 grams of 0.025% Bait or 0.2 gram 0.5% Concentrate) into a 250 ml glass-stoppered flask, add by pipette 100 ml 1% sodium pyrophosphate solution, and shake on a mechanical shaker for one hour. Transfer 40-50 ml to a glass-stoppered centrifuge tube and centrifuge for at least 5 minutes. Pipette 20 ml of this solution into a glass-stoppered 100 ml centrifuge tube, add 5 ml 2.5N hydrochloric acid and 50 ml (by pipette) of the mixed ether solution, and shake for five minutes. If an emulsion forms, centrifuge to break the emulsion. Pipette 10 ml of the ether layer to a clean centrifuge tube and add 10 ml pyrophosphate solution by pipette. Shake for 2 minutes and remove the ether layer using an aspirator with a glass tube drawn to a fine tip. If the aqueous layer is not clear, centrifuge for a few minutes with the stopper off to remove any residual ether. (final conc 4 µg PMP/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen for 0 and 100% at 283 nm with 1% pyrophosphate solution in each cell. Scan both standard and sample from 350 nm to 200 nm with the pyrophosphate solution in the reference cell.

Calculation:

Measure the absorbance of standard and sample at 283 nm and calculate the percent PMP as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

% Calcium PMP = % PMP X 1.083

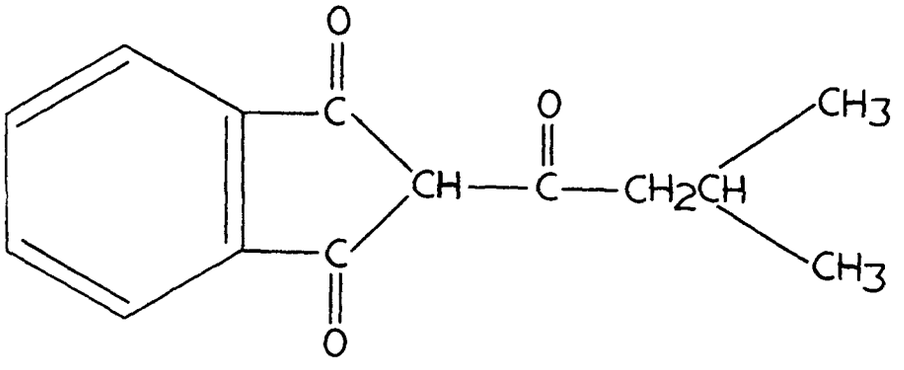
% Sodium PMP (anhydrous) = % PMP X 1.096

or using dilution factors, as follows:

$$\% = \frac{(\text{abs. sample})(\text{wt. std})(\text{purity std})(1/100)(10/100)(5/100)(100)}{(\text{abs. std})(\text{wt. sample})(1/100)(20/50)(10/10)}$$

Determination of PMP in Water-Soluble Formulations by Ultraviolet Spectroscopy (Pyrophosphate Extraction)

PMP is 2-isovaleryl-1,3-indandione, a registered rodenticide having the chemical structure:



Molecular formula: $C_{14}H_{14}O_3$

Molecular weight: 230.3

Melting point: 67 to 68°C

Physical state and color: yellow crystalline solid

Solubility: practically insoluble in water; soluble in most organic solvents; soluble in aqueous alkali or ammonia to form bright yellow salts

Stability: stable under normal conditions

Other names: Valone (Kilgore Chem. Co.)

Pindone (2-pivalyl-1,3-indandione) and PMP (2-isovaleryl-1,3-indandione) are often formulated as water-soluble powders containing the sodium salts of these two materials, along with sodium benzoate, sodium ethylenediamine tetraacetate (EDTA), and sugar. Sodium benzoate

and the sodium EDTA interfere moderately at the strongest absorption maxima near 283 nm, decreasing to about 275 nm and then increasing again; however, a determination can be made at the secondary maxima near 311 and 323 nm.

A solution of pindone containing 10 μg/ml in 1% pyrophosphate has an approximate absorbance of 0.394 at 324 nm; a solution of PMP containing 7.5 μg/ml in 1% pyrophosphate has an approximate absorbance of 0.398 at 323 nm. If there is no interference and the absorbances are read at 283 nm, the concentrations of the standards and/or sample solutions should each be about one-third as great.

This method does not distinguish between pindone and PMP; however, they may be identified by extracting an acidified aqueous solution of the formulation with ether (ethyl or petroleum), evaporating the solvent, recrystallizing from pentane, and determining the melting point. Pindone melts at 110-111°C and PMP melts at 67-68°C.

The presence of sodium benzoate or sodium EDTA may be confirmed by the procedure at the end of this method.

Reagents:

1. PMP standard of known % purity
2. Sodium pyrophosphate, 1% solution - dissolve 10 grams $Na_4P_2O_7.10H_2O$ in one liter of water.

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.075 gram PMP standard into a 100 ml volumetric flask; dissolve and make to volume with 1% sodium pyrophosphate solution. Mix thoroughly and pipette 5 ml into a 50 ml volumetric flask, and make to volume with pyrophosphate solution; mix well, pipette 5 ml into a second 50 ml volumetric flask, and make to volume with pyrophosphate solution. (final conc 7.5 µg PMP/ml)

If absorbances are to be read at 283 nm, pipette 2 ml instead of 5 ml into the second 50 ml volumetric flask. (final conc 3 µg PMP/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.003 gram PMP into a 100 ml volumetric flask; dissolve and make to volume with 1% sodium pyrophosphate solution. Mix thoroughly, pipette 25 ml into a second 100 ml volumetric flask, and make to volume with the 1% pyrophosphate solution. (final conc 7.5 µg PMP/ml)

If the absorbances are to be read at 283 nm, pipette 10 ml instead of 25 ml into the second 100 ml volumetric flask. (final conc 3 µg PMP/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen for 0 and 100% at 324 nm (or at 283 nm if no sodium benzoate or sodium EDTA interference is present) with 1% pyrophosphate solution in each cell. Scan both the standard and sample from 350 nm to 250 nm with pyrophosphate solution in the reference cell.

Calculation:

Measure the absorbance of standard and sample at 324 nm or 283 nm, and calculate the percent PMP as follows:

% PMP at 324 nm:

$$\% = \frac{(\text{abs. sample})(\text{wt. std})(\text{purity std})(1/100)(5/50)(5/50)}{(\text{abs. std})(\text{wt. sample})(1/100)(25/100)}$$

% PMP at 283 nm:

$$\% = \frac{(\text{abs. sample})(\text{wt. std})(\text{purity std})(1/100)(5/50)(2/50)}{(\text{abs. std})(\text{wt. sample})(1/100)(10/100)}$$

Procedure for Confirming the Presence of Sodium Benzoate and Sodium EDTA:

Sodium benzoate and sodium EDTA may be identified by the following procedure: Make an aqueous extract of the sample, acidify with hydrochloric acid, and filter. Save both filtrate and residue. Use the filtrate for EDTA and the residue for benzoate as follows:

For EDTA - place one drop of nickel sulfate solution (0.01% in water) and one drop concentrated ammonium hydroxide into each of two depressions on a spot plate. To one add a drop of water and to another a drop of the sample extract filtrate. Add a drop of dimethylglyoxime solution (saturated - approx. 0.1 g in 50 ml water) to each. The blank becomes pink immediately, but if the solution contains a sequestering agent--EDTA--it remains colorless or becomes only very faintly pink.

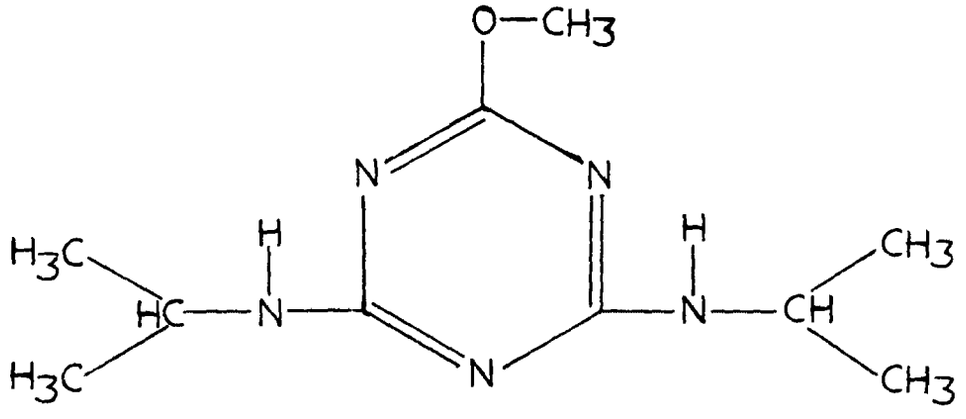
For Benzoate - wash the residue with hot water to remove the benzoic acid (pindone and PMP are practically insoluble in water). Make alkaline with a few drops of ammonium hydroxide, heat gently to expel excess ammonia by evaporation, dissolve residue in a few ml water (filter if necessary), and add a few drops of aqueous 0.5% ferric chloride solution. A salmon-color precipitate of ferric benzoate indicates presence of benzoic acid. An alternative procedure is to evaporate the acidified filtrate and determine the melting point. Benzoic acid melts at 122°C.

November 1975

Prometone EPA-1
(Tentative)

Determination of Prometone by Gas–Liquid Chromatography (TCD - Internal Standard)

Prometone is the accepted common name for 2,4-bis (isopropylamino)-6-methoxy-s-triazine, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_{19}N_5O$

Molecular weight: 225.3

Melting point: 91 to 92°C; the technical product is at least 97% pure and has a m.p. of 88-90°C

Physical state and color: white crystalline solid

Solubility: 750 ppm in water at 20°C; readily soluble in acetone, benzene, chloroform, methanol

Stability: stable under neutral or slightly acidic or alkaline conditions but is hydrolyzed by stronger acid or alkali; compatible with most other pesticides when used at normal rates; non-corrosive under normal use conditions

Other names: Primatol, Pramitol, G41435 (Ciba-Geigy); prometon (ISO), Gesafram, Outrack

Reagents:

1. Prometone standard of known % purity
2. Technical heptachlor
3. Chloroform, pesticide or spectro grade
4. Internal Standard solution - weigh 0.25 gram technical heptachlor into a 25 ml volumetric flask; dissolve in and make to volume with chloroform. (conc 10 mg heptachlor/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 6' x 1/4" OD glass column packed with 4% SE-30 on 80/100 mesh Diatoport S (or equivalent column - glass should be used because heptachlor degrades on metal column)
3. Precision liquid syringe: 5 or 10 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	175°C
Injection temperature:	225°C
Detector temperature:	250°C
Filament current:	225 ma
Carrier gas:	Helium
Carrier gas flow rate:	30 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.025 gram prometone standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 2.5 mg prometone and 10 mg heptachlor/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.025 gram prometone into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the prometone. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 2.5 mg prometone and 10 mg heptachlor/ml)

Determination:

Inject 2-4 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is prometone, then heptachlor.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of prometone and heptachlor from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. heptachlor})(\%\text{ purity heptachlor})(\text{pk. ht. or area prometone})}{(\text{wt. prometone})(\%\text{ purity prometone})(\text{pk. ht. or area heptachlor})}$$

Determine the percent prometone for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. heptachlor})(\%\text{ purity heptachlor})(\text{pk. ht. or area prometone})(100)}{(\text{wt. sample})(\text{pk. ht. or area heptachlor})(RF)}$$

(4-1)

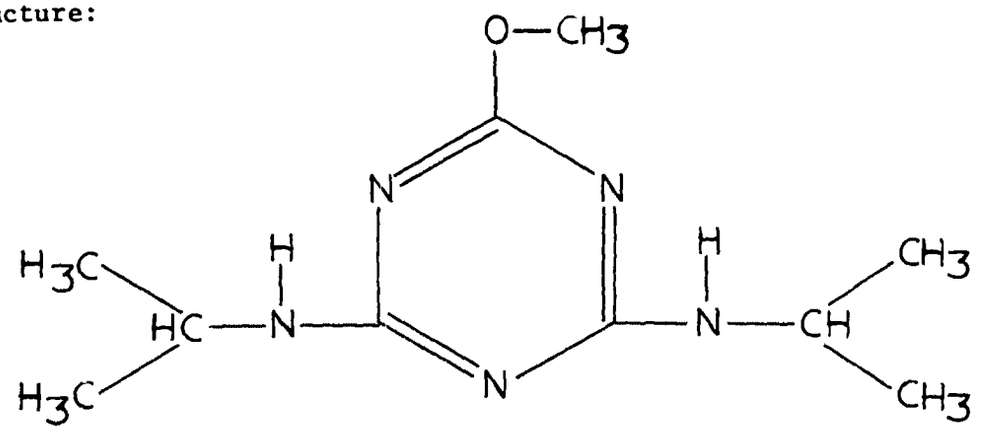
This method was developed by Stelios Gerazounis, EPA, Region II, New York, N. Y., and was collaborated (with slight modification) by Elmer Hayes, EPA, Beltsville Chemistry Laboratory, Beltsville, Md.

January 1976

Prometone EPA-2
(Tentative)

Determination of Prometone by Gas–Liquid Chromatography (FID - Internal Standard)

Prometone is the accepted common name for 2,4-bis (isopropylamino)-6-methoxy-s-triazine, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_{19}N_5O$

Molecular weight: 225.3

Melting point: 91 to 92°C; the technical product is at least 97% pure and has a m.p. of 88-90°C

Physical state and color: white crystalline solid

Solubility: 750 ppm in water at 20°C; readily soluble in acetone, benzene, chloroform, methanol

Stability: stable under neutral or slightly acidic or alkaline conditions but is hydrolyzed by stronger acid or alkali; compatible with most other pesticides when used at normal rates; non-corrosive under normal use conditions

Other names: Primatol, Pramitol, G 41435 (Ciba-Geigy); prometon (ISO) Gesafram, Outrack

Reagents:

1. Prometone standard of known % purity
2. Alachlor standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.5 gram alachlor into a 100 ml volumetric flask; dissolve in and make to volume with acetone. (conc 5 mg alachlor/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm glass column packed with 3% OV-17 on 80/100 Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	180°C
Injection temperature:	230°C
Detector temperature:	230°C
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi (adjusted for specific GC)
Hydrogen pressure:	20 psi (adjusted for specific GC)
Air pressure:	30 psi (adjusted for specific GC)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure: (see note after calculations)

Preparation of Standard:

Weigh 0.05 gram prometone standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 25 ml of the internal standard solution and shake to dissolve. (final conc 2 mg prometone and 5 mg alachlor/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.05 gram prometone into a small glass-stoppered flask or screw-cap bottle. Add by pipette 25 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the prometone. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 2 mg prometone and 5 mg alachlor/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is prometone, then alachlor.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of prometone and alachlor from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. alachlor})(\%\text{ purity alachlor})(\text{pk. ht. or area prometone})}{(\text{wt. prometone})(\%\text{ purity prometone})(\text{pk. ht. or area alachlor})}$$

Determine the percent for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. alachlor})(\%\text{ purity alachlor})(\text{pk. ht. or area prometone})(100)}{(\text{wt. sample})(\text{pk. ht. or area alachlor})(RF)} \quad (4\text{-}1)$$

Note: For an alternative procedure to the above method, the following changes can be made:

solvent: chloroform

sample concentration: 1.6 mg/ml

column: 4' x 2 mm ID glass, packed with 5% OV-210 on 80/100 Chromosorb W HP

column temperature: 160°

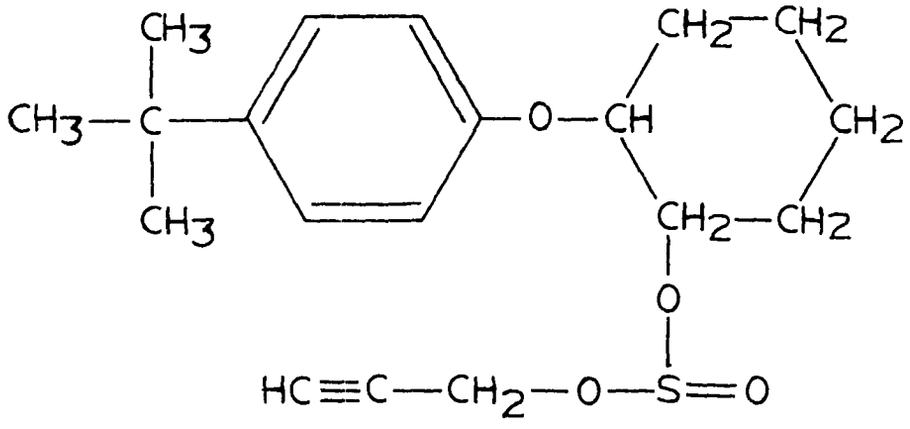
other parameters: adjusted as needed to give optimum results with the changed conditions

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Chemistry Lab. Any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated.

Determination of Propargite by Infrared Spectroscopy

Propargite is a common name for 2-(p-tert-butylphenoxy)cyclohexyl-2-propynyl sulfite, a registered acaricide having the chemical structure:



Molecular formula: $C_{19}H_{26}O_4S$

Molecular weight: 350

Melting or boiling point: (not available)

Physical state and color: light to dark amber viscous liquid of d^{25} 1.085-1.115; the technical product is at least 80%

Solubility: practically insoluble in water; soluble in most organic solvents

Stability: (not available)

Other names: Omite, D014 (Uniroyal); Comite

Reagents:

1. Propargite standard of known % purity
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording, with matched .5 mm NaCl or KBr cells
2. Mechanical shaker
3. Rotary evaporator or steam bath
4. Filtration apparatus or centrifuge
5. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram propargite standard into a 10 ml volumetric flask; dissolve in and make to volume with carbon disulfide. Add a small amount of granular anhydrous sodium sulfate to insure dryness. (conc 10 mg propargite/ml)

Preparation of Sample:

For dust, granules, and wettable powder, weigh a portion of sample equivalent to 1 gram propargite into a 250 ml glass-stoppered Erlenmeyer flask, add by pipette 100 ml carbon disulfide, stopper, and shake on a mechanical shaker for 1 hour. Allow to settle; filter or centrifuge if necessary. Add a small amount of granular anhydrous sodium sulfate to insure dryness. (conc 10 mg propargite/ml)

For liquid formulations and emulsifiable concentrates, weigh a portion of sample equivalent to 1 gram propargite into a 100 ml volumetric flask, make to volume with carbon disulfide, and mix thoroughly. (Interference from solvents in the sample can sometimes be removed by evaporation on a rotary evaporator under vacuum at about 60°C before making to volume.) Add a small amount of granular anhydrous sodium sulfate to insure dryness and clarify the solution. (conc 10 mg propargite/ml)

An alternative extraction procedure for liquid formulations and E.C.'s is to shake a 1 gram sample with 100 ml carbon disulfide and 25-50 ml water in a sealed bottle or flask for 2 hours on a shaker. Allow to stand for 15 minutes or longer to permit the carbon disulfide and water layers to separate. With a syringe, draw off 20-25 ml of carbon disulfide from the bottom of the bottle and transfer to small vial. Add anhydrous sodium sulfate to insure dryness and clarify the solution. (conc 10 mg propargite/ml)

IR Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 4000 cm^{-1} to 3125 cm^{-1} (2.5 μ to 3.2 μ).

Determine the absorbance of standard and sample using the peak at 3300 cm^{-1} (3.03 μ) and a baseline from 3356 cm^{-1} to 3247 cm^{-1} (2.98 μ to 3.08 μ).

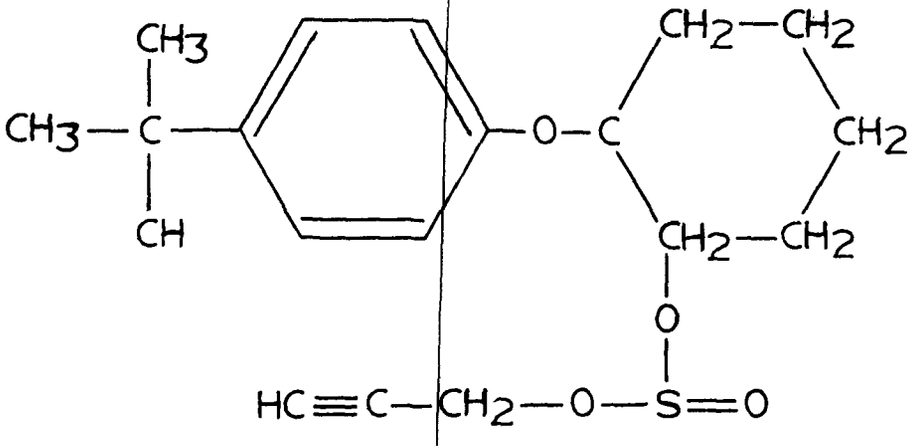
Calculation:

From the above absorbances, calculate the percent propargite as follows:

$$\% = \frac{\text{(abs. sample)(conc. std in mg/ml)(\% purity std)}}{\text{(abs. std)(conc. sample in mg/ml)}}$$

Determination of Propargite by Gas–Liquid Chromatography (TCD - Internal Standard)

Propargite is a common name for 2-(p-tert-butylphenoxy)cyclohexyl-2-propynyl sulfite, a registered acaricide having the chemical structure:



Molecular formula: $C_{19}H_{26}O_4S$

Molecular weight: 350

Melting or boiling point: (not available)

Physical state and color: light to dark amber viscous liquid of d^{25} 1.085-1.115; the technical product is at least 80%

Solubility: practically insoluble in water; soluble in most organic solvents

Stability: (not available)

Other names: Omite, D014 (Uniroyal); Comite

Reagents:

1. Propargite standard of known % purity
2. Dieldrin standard of known HEOD content
3. Chloroform, pesticide or spectro grade
4. Internal Standard solution - weigh 0.5 gram HEOD into a 25 ml volumetric flask; dissolve in and make to volume with chloroform. (conc 20 mg HEOD/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 4' x 1/4" OD glass, packed with 3% XE-60 on 60/80 mesh Chromosorb G DMCS (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	220°C
Injection temperature:	250°C
Detector temperature:	250°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas pressure:	40 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.2 gram propargite standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 20 mg propargite and 20 mg HEOD/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.2 gram propargite into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the propargite. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 20 mg propargite and 20 mg HEOD/ml)

Determination:

Inject 5 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is HEOD, then propargite.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of propargite and HEOD from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. HEOD})(\%\ \text{purity HEOD})(\text{pk. ht. or area propargite})}{(\text{wt. propargite})(\%\ \text{purity propargite})(\text{pk. ht. or area HEOD})}$$

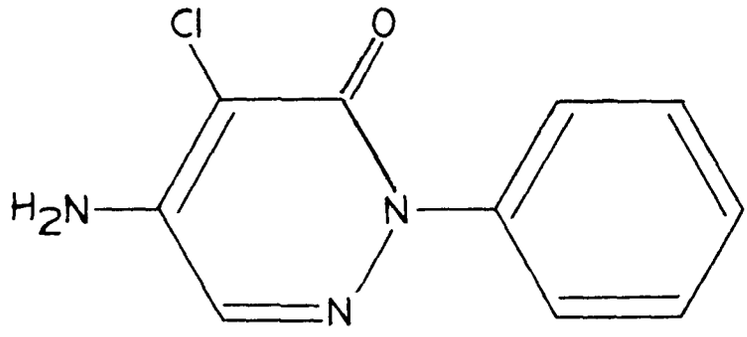
Determine the percent propargite for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. HEOD})(\%\ \text{purity HEOD})(\text{pk. ht. or area propargite})(100)}{(\text{wt. sample})(\text{pk. ht. or area HEOD})(RF)}$$ (4-1)

Method submitted by Stelios Gerazounis, EPA, Region II, New York, N. Y.

Determination of Pyrazon in Wettable Powder by Infrared Spectroscopy

Pyrazon is the accepted common name for 5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_8ClN_3O$

Molecular weight: 221.6

Melting point: 207°C with decomposition

Physical state, color, and odor: yellowish-tan to brown powder, odorless when pure

Solubility: 400 ppm in water at 20°C, 2.8% in acetone, 3.4% in methanol, 0.07% in benzene and in ether, 0.21% in chloroform, 0.6% in ethyl acetate

Stability: stable; non-corrosive; decomposes at mp

Other names: Pyramin (Badische Anilin-& Soda-Fabrik AG, West Germany)
PCA, H119

Reagents:

1. Pyrazon standard of known % purity
2. Acetonitrile, pesticide or spectro grade
3. Sodium Sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm KBr or NaCl cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.08 gram pyrazon standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml acetonitrile by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 8 mg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.4 gram pyrazon into a glass-stoppered flask or screw-cap bottle. Add 50 ml acetonitrile by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter, taking precaution to prevent evaporation. (final conc 8 mg pyrazon/ml)

Determination:

With acetonitrile in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 910 cm^{-1} to 770 cm^{-1} (11.0 μ to 13.0 μ).

Determine the absorbance of the standard and sample using the peak at 826 cm^{-1} (12.10 μ) and baseline from 844 cm^{-1} to 797 cm^{-1} (11.85 μ to 12.55 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent pyrazon as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

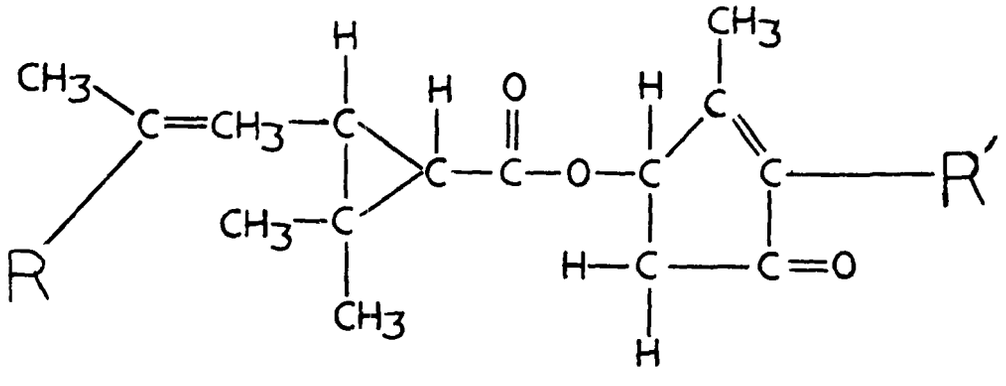
Method contributed by Eva Santos, EPA Region IX, San Francisco, California.

Description, Structure, Technical Data

The name pyrethrin refers to a registered insecticide consisting of pyrethrin I and pyrethrin II.

Pyrethrins is the trivial name given to the botanical insecticide obtained from Chrysanthemum cinerariaefolium. The flowers are the source of the active principles which are pyrethrin I and II, cinerin I and II, and jasmolin I and II. The pyrethrin content of flowers and extracts is as follows: dried flowers 1-3%, crude extract or oleoresin 30-35%, and the most refined grade (dewaxed and decolored) about 60%.

The chemical structure of these compounds is as follows:



	R	R'
pyrethrin I ($C_{21}H_{28}O_3$)	$-CH_3$	$-CH_2-CH=CH-CH=CH_2$
pyrethrin II ($C_{22}H_{28}O_5$)	$-CO-O-CH_3$	$-CH_2-CH=CH-CH=CH_2$
cinerin I ($C_{20}H_{28}O_3$)	$-CH_3$	$-CH_2-CH=CH-CH_3$
cinerin II ($C_{21}H_{28}O_5$)	$-CO-O-CH_3$	$-CH_2-CH=CH-CH_3$
jasmolin I ($C_{21}H_{30}O_3$)	$-CH_3$	$-CH_2-CH=CH-CH_2-CH_3$
jasmolin II ($C_{22}H_{30}O_5$)	$-CO-O-CH_3$	$-CH_2-CH=CH-CH_2-CH_3$

Pyrethrin I, cinerin I, and jasmolin I are esters of chrysanthemum monocarboxylic acid and three different ketonic alcohols; pyrethrin II, cinerin II, and jasmolin II are esters of chrysanthemum dicarboxylic acid and the same three alcohols.

Since analysis is based on the isolation and quantitative estimation of the chrysanthemum mono- and di- carboxylic acids, only the total and not the individual pyrethrins, cinerins, and jasmolins are determined. However, by convention the total "mono-" acids are reported as "pyrethrin I" and the total "di-" acids as "pyrethrin II."

Pyrethrins are viscous liquids, practically insoluble in water, but soluble in alcohol, petroleum ether, kerosene, carbon tetrachloride, ethylene dichloride, nitromethane, and acetone. They are stable in water-base aerosols where modern emulsifiers give neutral water systems. Pyrethrins are oxidized rapidly and become inactive. Stored flowers may lose 20% of their activity in a year. Impregnated and stabilized dusts are less susceptible to oxidation than dusts made from ground flowers. Oxidation is not a problem in stabilized oil concentrates. Antioxidants such as hydroquinone, pyrogallol, etc. can be used to inhibit oxidation. Pyrethrins are incompatible with lime and ordinary soaps because acids and alkalis speed the process of hydrolysis.

Because of its low order of toxicity to warm-blooded animals, pyrethrin extracts are used extensively in stock sprays, pet sprays, household sprays and aerosols, industrial sanitation sprays, and to protect stored food in warehouses.

The use of a synergist, such as piperonyl butoxide, increases the effectiveness of pyrethrin formulations, enabling the user to maintain rapid action against insects and to reduce costs.

Pyrethrin formulations available include: concentrated oil extracts, impregnated and stabilized dusts, and dilute dusts made from ground flowers. A low color 20% extract in oil has recently become the "standard" item of the industry.

Determination of Pyrethrins in Formulations by Gas-Liquid Chromatography (FID)

For description, structure, and technical data on pyrethrins, see Pyrethrins EPA-1.

Principle of the Method:

The active ingredients in some commercial mixtures of pyrethrins, piperonyl butoxide (PBO) and n-octylbicycloheptenedicarboximide (NOBD), especially when present in small amounts (in the range of 0.05-0.50 percent pyrethrin concentrations) can be measured simultaneously by gas chromatography. A Florisil cleanup procedure is used with all samples to remove oil-based materials and other substances that would interfere with the GC analysis of the NOBD compound of the formulation.

Reagents:

1. Pyrethrin primary standard, or extract of known assay
2. Piperonyl butoxide standard of known assay
3. n-Octylbicycloheptenedicarboximide standard of known assay
4. Sodium sulfate, anhydrous
5. Florisil, 60-80 mesh heated for 16 hours at 130° prior to use
6. Hexane, ACS
7. Acetone, ACS
8. Carbon disulfide, ACS

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 5' x 1/8" ID borosilicate glass, packed with 5% SE-30 on 60-80 mesh Chromosorb W AW DMCS

3. Chromatographic column for Florisil cleanup - 20 mm x 400 mm borosilicate glass with Ultramax stopcock and 300 ml reservoir
4. Precision liquid syringe: 10 µl
5. Mechanical shaker
6. Centrifuge or filtration equipment
7. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	190°C
Injection temperature:	205°C
Detector temperature:	205°C
Carrier gas:	Nitrogen
Carrier gas flow rate:	25 ml/min
Hydrogen flow rate:	25 ml/min
Air flow rate:	200 ml/min
Chart speed:	0.5 in/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Prepare a mixed standard in carbon disulfide to contain 0.4 µg/µl for pyrethrin I and 1.1 µg/µl each for PBO and NOBD. This mixed standard is used to quantitate these components in the sample. Separate standards should be made to identify the individual peaks.

The linearity range for pyrethrin I is 0.2 to 2.2 μg, for PBO 0.6 to 5.6 μg, and for NOBD 0.3 to 1.7 μg, with a minimum detectability of about 0.06 μg for each of the three components.

Preparation of Sample:

A chromatographic column is packed with 5 grams anhydrous sodium sulfate, followed by 20 grams Florisil, and topped with 5 grams anhydrous sodium sulfate. The column is prewashed with 100 ml hexane, leaving enough solvent in the column to just cover the packing.

An appropriate weight of sample or sample extract (10 mg pyrethrin I for a final volume of 25 ml - 0.4 μg/μl) is transferred to the column with 5-10 ml hexane. The column is washed with 75 ml hexane and the eluate discarded. The pyrethrin and the synergistic compounds are then eluted from the column with 125 ml acetone.

The acetone eluate is evaporated nearly to dryness using a stream of air and a warm steam bath. The residue is diluted to about 10 ml with carbon disulfide and passed through a small column of anhydrous sodium sulfate. The sodium sulfate is washed with a small amount of carbon disulfide, and the combined eluates are made to a definite volume for chromatographic analysis.

GC Determination:

Using the appropriate attenuation settings, 2 or 3 μl of standard and sample are alternately injected for pyrethrin I and PBO. Smaller amounts or an additional dilution is needed to keep the NOBD within the linear range (0.3-1.7 μg for NOBD).

The pyrethrin I component of the pyrethrum fraction of the formulation is the only predominant peak of the pyrethrum fraction appearing in the chromatogram under the conditions of this method.

Other pyrethrum components do not interfere with the simultaneous recording of the NOBD and PBO components of the mixture.

Calculations:

Use an average of at least three injections of standard and sample to determine the peak height of each component.

$$\% \text{ component} = \frac{(\text{peak ht. sample})(\text{conc. std})(\mu\text{l std injected})(100)}{(\text{peak ht. std})(\text{conc. sample})(\mu\text{l sample injected})}$$

The amount of pyrethrin I calculated is multiplied by a factor of two since pyrethrin I and II usually occur in approximately equal amounts in formulations.

This method is based on "Analytical Studies of Pyrethrin Formulations by Gas Chromatography" by A. Bevenue, Y. Kawano, and F. DeLano, Journal of Chromatography, 50 (1970), 49-58 and "Analytical Methods for Pesticides and Plant Growth Regulators," edited by Gunter Zweig, Vol. 6 Gas Chromatographic Analysis, pages 461-464.

Determination of Pyrethrins I & II by Hydrolysis, Steam Distillation, and Titration (Seil Method)

For definition, structure, and technical data on pyrethrins, see Pyrethrins EPA-1.

Principle of the Method:

The pyrethrins are hydrolyzed with alcoholic sodium hydroxide to release the mono- and di- carboxylic acids which together are extracted with ether and steam-distilled for separation. The monocarboxylic acid "pyrethrin I" is extracted from the distillate while the dicarboxylic acid "pyrethrin II" is extracted from the residue. Both are titrated with standard alkali.

Reagents:

1. Petroleum ether, ACS
2. Ethanolic sodium hydroxide solution, 0.5N in ethyl alcohol
3. Barium chloride solution, 10% w/v
4. Phenolphthalein indicator solution, 0.5% in 50% alcohol
5. Sulfuric acid solution, 1N
6. Neutral petroleum ether - neutralize with 0.02N NaOH to faint phenolphthalein pink
7. Standard sodium hydroxide solution, 0.02N
8. Concentrated hydrochloric acid
9. Sodium chloride, ACS
10. Ethyl ether, ACS

Equipment:

1. Soxhlet extraction apparatus
2. Extraction thimbles and cotton or glass wool
3. Dry ice chamber (for aerosols)
4. Water bath
5. Steam bath
6. Reflux apparatus
7. Steam distillation apparatus

   Any standard steam distillation apparatus can be used if the flow of steam and the amount of heat to the distilling flask can be adjusted so that the volume in the flask remains constant for most of the distillation but can be reduced to about 20 ml at the end.

   A picture and description of a steam distillation apparatus is on pages 312-313 of the AOAC 12th Ed. 1975, 18.046 and Fig. 18:02.

8. Filter-cell
9. Filtration apparatus
10. Gooch crucible
11. Titration apparatus
12. Usual laboratory glassware

Procedure:

Preparation of Sample:

For solutions, sprays, extracts, and concentrates - Weigh an amount of sample equivalent to 0.2 gram total pyrethrins into a 250 ml Erlenmeyer flask.

For dusts, powders, flowers, and mosquito coils - Weigh an amount of sample (finely ground or pulverized if necessary) equivalent to 0.2 gram total pyrethrins into a Soxhlet thimble, plug with cotton or glass wool, and place in the Soxhlet extractor. Add 125 ml petroleum ether and a few boiling chips to a 250 ml flask and connect to the Soxhlet. Reflux for 6-8 hours. Evaporate the ether to about 40 ml, stopper the flask, and place in a refrigerator at 0-5°C for several hours, preferably overnight. Place a piece of cotton in the stem of a glass funnel, wet the cotton with cold petroleum ether, and filter the cold extract, collecting the filtrate in a 250 ml Erlenmeyer flask. Wash flask several times with cold ether using a rubber policeman to dislodge any resinous material in the flask. Add several small glass beads and evaporate the ether on a water bath until just less than 1 ml remains. Do not attempt to remove the last trace of solvent.

For aerosols - Place weighed aerosol can in a dry ice chamber until well chilled (at least 30 minutes). Punch several holes in the top of the can and allow the contents to warm slowly to room temperature. Cut the can open and heat gently on steam bath until the propellant and other volatile substances are removed so that the sample can be handled at room temperature without further loss. Cool, weigh, and transfer the "non-volatile" portion to a bottle. Rinse the can with ether, dry, and weigh. Calculate percent non-volatile. Weigh a portion of the non-volatile equivalent to 0.2 gram total pyrethrins into a 250 ml Erlenmeyer flask.

$$\frac{(.2 \text{ gram pyrethrins})(\% \text{ non-volatile})}{(\% \text{ claim on label})} = \text{grams of non-volatile needed}$$

$$\% \text{ non-volatile} = \frac{(\text{wt. can \& contents after heating}) - (\text{wt. empty can})}{(\text{wt. full can}) - (\text{wt. empty can})}$$

Hydrolysis and Steam Distillation

Add 15 ml of 0.5N ethanolic sodium hydroxide solution to the sample in the Erlenmeyer flask and reflux for 1 hour. It may be necessary to add extra 0.5N ethanolic NaOH solution (up to 50 ml) with samples containing much perfume or other saponifiable ingredients. Transfer to a large beaker (600-800 ml); wash the flask with two 25 ml portions of water, adding them to the contents of the beaker. Add 1 ml deodorized kerosene and dilute to about 200 ml. Place a few glass beads or a boiling tube in the beaker and boil until the volume is reduced to about 150 ml. If more than 15 ml of ethanolic NaOH solution has been used, sufficient water must be added to insure that all the ethanol is removed when the volume is reduced to 150 ml. Add 1 gram filter-cel and transfer the mixture quantitatively to a 250 ml volumetric flask. (It is more convenient to add the filter-cel to the dry flask first.) Add 10 ml 10% barium chloride solution, make to volume with water, and mix thoroughly. Filter through fluted filter paper.

Measure exactly 200 ml of the clear filtrate and transfer quantitatively to the 500 ml distilling flask of a steam distillation apparatus. Add one drop of phenolphthalein solution, neutralize with 1N sulfuric acid solution, and add 1 ml in excess. Connect to the steam distillation apparatus and, using a 500 ml separatory funnel to collect the distillate, steam distill until the volume remaining in the flask is about 20 ml. The volume of distillate should be 250-350 ml.

Use the distillate for the determination of Pyrethrin I and the residue for the determination of Pyrethrin II.

Determination of Pyrethrin I

Add 50 ml neutral petroleum ether to the separatory funnel containing the distillate and shake thoroughly for one minute. (If an emulsion forms, add a few crystals of sodium chloride and

shake again.) After the liquids have separated, draw off the aqueous layer into a second 500 ml separatory funnel to which has been added a second 50 ml of neutral petroleum ether. Shake for 1 minute and allow to separate, then discard the aqueous layer. Wash the petroleum ether in the first separatory funnel by shaking with 10 ml water; using the same 10 ml water, wash the petroleum ether in the second separatory funnel. Repeat the washing procedure with a second 10 ml portion of water. Combine the petroleum ether extracts. Neutralize 15 ml water containing one drop of phenolphthalein indicator solution with 0.02N sodium hydroxide solution and add it to the combined petroleum ether extracts. Titrate with small portions of the 0.02N NaOH solution, shaking thoroughly after each addition, until the aqueous layer obtains a pale but permanent pink.

Calculation: The milliequivalent weight of pyrethrin I is 0.3284.

$$\% \text{ pyrethrin} = \frac{(\text{ml } 0.02\text{N NaOH})(\text{N } 0.02\text{N NaOH})(.3284)(100)}{(\text{grams sample})(200/250)}$$

Determination of Pyrethrin II

Cool the flask containing the residue from the steam distillation and filter the solution through a Gooch crucible. Wash the flask with three 10 ml portions of water using each successively to wash the Gooch crucible. Transfer the filtrate to a 500 ml separatory funnel, add 5 ml concentrated hydrochloric acid, and saturate with sodium chloride. (Acidified aqueous layer must contain visible NaCl crystals throughout the following extractions.)

Extract the mixture with 50 ml ethyl ether, shaking thoroughly for one minute. Draw off the aqueous layer into a second separatory funnel and extract again with 50 ml ethyl ether. Repeat for a third and fourth extraction using 25 ml ethyl ether each time. Wash the ether extracts successively with two 10 ml portions of distilled

water. Combine the ether solutions, draw off any water that separates, and filter through a plug of cotton (previously wetted with ether) into a 300 ml Erlenmeyer flask. Wash the separatory funnel and cotton with 10 ml ether. Evaporate the ether on a water bath and dry the residue at 100°C for 10 minutes. Blow gently into the flask several times to remove vapors.

Add 30 ml distilled water, boil to dissolve the residue, and cool. Add a drop of phenolphthalein indicator and titrate with 0.02N NaOH solution to the first pale but permanent pink.

Calculation: The milliequivalent weight of pyrethrin II is 0.1862.

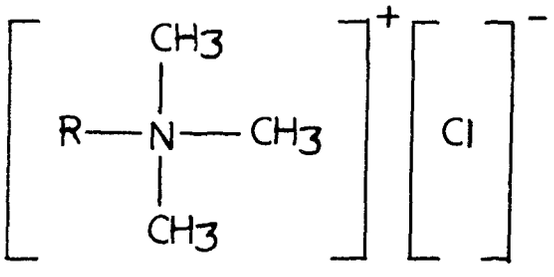
$$\% \text{ pyrethrin II} = \frac{(\text{ml } 0.02\text{N NaOH})(\text{N } 0.02\text{N NaOH})(.1862)(100)}{(\text{grams sample})(200/250)}$$

Definition, Structure, Technical Data,
Halogen and Nitrogen Conversion Factors

A quaternary ammonium compound is an organic nitrogen compound in which the molecular structure consists of a central pentavalent nitrogen atom joined to four organic groups and an acidic or basic radical. The most usual or common of these compounds are salts of mineral acids.

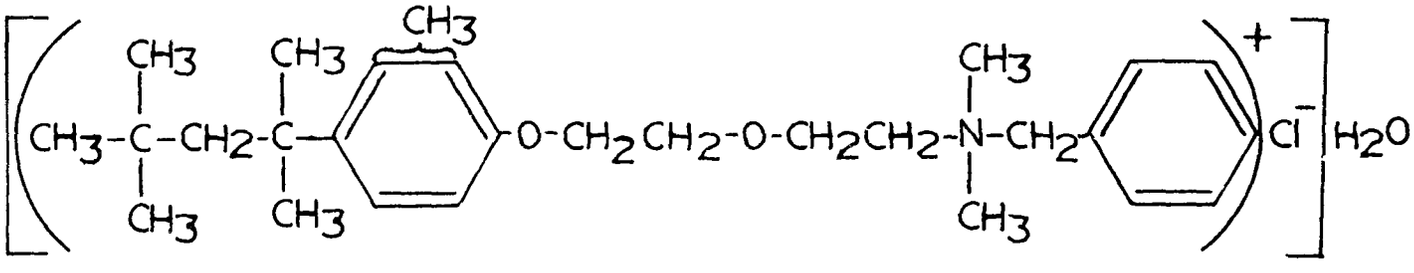
Two examples of the chemical structure are:

(1) a relatively simple salt - alkyl trimethyl ammonium chloride



where "R" represents a long hydrocarbon chain of the length found in the various fatty acids in which these "quaternaries" have their origin.

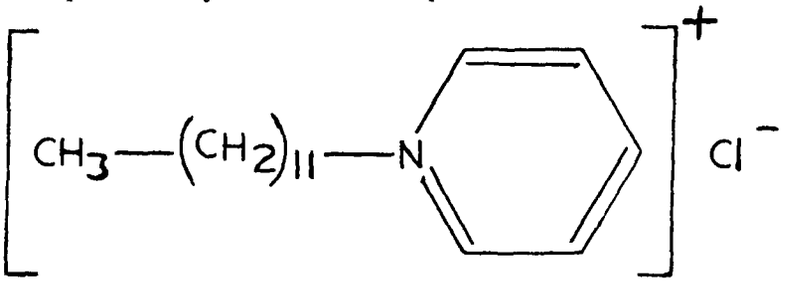
(2) a relatively complex salt - di-isobutyl cresoxy ethoxy ethyl dimethyl benzyl ammonium chloride, monohydrate



The great number of quaternary compounds possible becomes apparent when consideration is given to the many different organic radicals that can be attached to the nitrogen, and to the many inorganic radicals that can form salts.

One popular type of quaternary is the water-soluble type which contains a long carbon chain radical similar to the carbon chain found in fatty acids. This long chain (alkyl) group imparts surface activity.

In addition to the usual quaternaries, some pentavalent nitrogen ring compounds such as lauryl pyridinium chloride (structure below) are also considered quaternary ammonium compounds.



Most quaternary salts are water-soluble or water-dispersible, but depending on structure, some are oil-soluble. Many are cationic in character and are not compatible with soap, anionic wetting agents, or synthetic detergents.

Quaternary ammonium compounds have many different uses. In the general field of pesticides, such uses are as disinfectants, cleansers, sterilizers, deodorants, emulsion stabilizers, fungicides, and algicides.

CONVERSION FACTORS FOR VARIOUS QUATERNARY AMMONIUM COMPOUNDS

The tables of conversion factors (pages 4 to 9) are based on the following atomic weights:

Carbon - 12.011	Hydrogen - 1.008	Oxygen - 16.000
Sulfur - 32.064	Nitrogen - 14.007	Chlorine - 35.453
Bromine - 79.909		

Percent halogen in the table refers only to the ionic halogen; where additional halogen is present in the molecule but not figured in the factor, they are keyed with (*).

Under the percent halogen column there are several materials that contain no halogen and another element is listed; these are keyed with (°).

Percent nitrogen in the table refers only to quaternary nitrogen; where additional nitrogen is present in the molecule but not figured in the factor, they are keyed with (').

The list is not complete as to all known quaternary materials but contains the most frequently occurring quaternaries. If specific compounds are not listed, the class name should be checked; i.e., octadecyl dimethyl benzyl ammonium chloride will be found under alkyl dimethyl benzyl ammonium chloride -- 100%-C18.

Finally, group names have in some cases been inverted and should be checked if a particular compound cannot be found; i.e., alkyl dimethyl methylnaphthyl ammonium chloride will be found under alkyl dimethyl naphthylmethyl ammonium chloride.

FACTORS FOR VARIOUS QUATERNARY COMPOUNDS

				M.W.	%HALOGEN(FACTOR)	% N (FACTOR)	
ALKENYL DIMETHYL ETHYL AMMONIUM BROMIDE							
%C18	%C16						
100			$C_{22}H_{46}NBr$	404.53	19.75 %Br(5.062)	3.463	(28.88)
90	10	(Onyxide)		401.7	19.89 %Br(5.027)	3.487	(28.68)
15	85	(ST-50)		380.7	20.99 %Br(4.764)	3.679	(27.18)
80	20	(LQ-750)		398.9	20.03 %Br(4.992)	3.511	(28.48)
ALKENYL DIMETHYL ETHYL AMMONIUM CHLORIDE							
100%-C18			$C_{22}H_{46}NCl$	360.07	9.846%Cl(10.16)	3.890	(25.71)
90%-C18, 10%-C16				357.3	9.923%Cl(10.08)	3.921	(25.51)
ALKENYL 1-HYDROXYETHYL-1-ETHYL IMIDAZOLINIUM BROMIDE							
100%-C12			$C_{19}H_{37}ON_2Br$	389.42	20.52 %Br(4.873)	3.597	(27.802)'
ALKENYL TRIMETHYL AMMONIUM CHLORIDE							
100%-C18		(Aliquat 11)	$C_{21}H_{44}NCl$	346.04	10.25 %Cl(9.761)	4.048	(24.71)
ALKYL 1-BENZYL-1-HYDROXYETHYL IMIDAZOLINIUM CHLORIDE							
100%-C13			$C_{25}H_{43}ON_2Cl$	423.09	8.380%Cl(11.93)	3.311	(30.21)'
ALKYLBENZYL TRIMETHYL AMMONIUM CHLORIDE							
%C9	%C10	%C11	%C12	%C13	%C14	%C15	
			100				$C_{22}H_{40}NCl$	354.02	10.01 %Cl(9.986)	3.957	(25.27)
	4	27	56	9	3	1		351.6	10.08 %Cl(9.918)	3.983	(25.10)
4	4	23	56	9	3	1		350.5	10.11 %Cl(9.887)	3.996	(25.02)
ALKYL DIMETHYL BENZYL AMMONIUM CHLORIDE							
%C12	%C14	%C16	%C18				
			100	(Onyx 4002)		$C_{27}H_{50}NCl$	424.16	8.358%Cl(11.96)	3.302	(30.28)
14	58	28					372.0	9.531%Cl(10.49)	3.765	(26.55)
		100		(Onyx T)		$C_{25}H_{46}NCl$	396.10	8.950%Cl(11.17)	3.536	(28.28)
10	60	30					382.1	9.279%Cl(10.78)	3.666	(27.28)
	100			(Hyamine 1450, BTC 927)		$C_{23}H_{42}NCl$	368.05	9.633%Cl(10.38)	3.806	(26.28)
65	30	5					351.2	10.09 %Cl(9.907)	3.988	(25.07)
50	30	17	3	(BTC 50, BQL 50, LC 5373)			360.5	9.835%Cl(10.17)	3.886	(25.74)

						M.W.	%HALOGEN(FACTOR)	% N (FACTOR)
ALKYL DIMETHYL BENZYL AMMONIUM CHLORIDE (CONT.)								
%C12	%C14	%C16	%C18					
100					$C_{21}H_{38}NCl$	340.00	10.43 %Cl(9.590)	4.120 (24.27)
61	23	11	5	(LC 6215)		356.8	9.936 %Cl(10.06)	3.925 (25.47)
40	50	10		(Hyamine 3500, BQM 50, MC 5410)		359.6	9.858 %Cl(10.14)	3.895 (25.67)
5	90	5		(Dibactol)		368.0	9.633 %Cl(10.38)	3.806 (26.28)
5	60	30	5	(BTC 824, MC 6355)		377.9	9.382 %Cl(10.66)	3.707 (26.98)
ALKYL DIMETHYLBENZYL DIMETHYL AMMONIUM CHLORIDE								
100%-C12					$C_{23}H_{42}NCl$	368.05	9.633 %Cl(10.38)	3.806 (26.28)
50%-C12, 30%-C14, 17%-C16, 3%-C18 (BTC 927)						388.5	9.125 %Cl(10.96)	3.605 (27.74)
ALKYL DIMETHYL 3,4-DICHLOROBENZYL AMMONIUM CHLORIDE								
%C12	%C14	%C16	%C18					
100					$C_{21}H_{36}Cl_2NCl$	408.88	8.671 %Cl(11.53)*	3.426 (29.19)
50	30	17	3	(ADC-60, BQL-50)		429.4	8.257 %Cl(12.11)*	3.262 (30.65)
23	55	20	2			437.2	8.109 %Cl(12.33)*	3.204 (31.21)
5	60	30	5	(Guardsan 50-50)		446.8	7.936 %Cl(12.60)*	3.135 (31.90)
ALKYL DIMETHYL ETHYL AMMONIUM BROMIDE								
100%-C16					$C_{20}H_{44}NBr$	378.49	21.11 %Br(4.736)	3.701 (27.02)
50%-C12, 30%-C14, 17%-C16, 3%-C18						342.9	23.31 %Br(4.291)	4.085 (24.48)
ALKYL DIMETHYL ETHYLBENZYL AMMONIUM BROMIDE								
100%-C16					$C_{27}H_{50}NBr$	468.61	17.05 %Br(5.864)	2.989 (33.46)
50%-C12, 30%-C14, 17%-C16, 3%-C18						433.0	18.46 %Br(5.418)	3.235 (30.91)
ALKYL DIMETHYL ETHYLBENZYL AMMONIUM CHLORIDE								
100%-C16					$C_{27}H_{50}ClN$	424.16	8.358 %Cl(11.96)	3.302 (30.28)
50%-C12, 30%-C14, 17%-C16, 3%-C18 (BTC 471)						388.5	9.125 %Cl(10.96)	3.605 (27.74)
ALKYL DIMETHYL FURFURYL AMMONIUM CHLORIDE								
100%-C18					$C_{25}H_{48}NOCl$	414.12	8.561 %Cl(11.68)	3.382 (29.57)
50%-C14, 30%-C16, 20%-C18						377.6	9.388 %Cl(10.65)	3.709 (26.96)
5%-C14, 30%-C16, 65%-C18						402.9	8.800 %Cl(11.36)	3.477 (28.76)

		M.W.	%HALOGEN(FACTOR)	% N (FACTOR)
ALKYL DIMETHYL NAPHTHYLMETHYL AMMONIUM CHLORIDE				
100%-C12	$C_{25}H_{40}NCl$	390.06	9.089 %Cl(11.00)	3.591 (27.85)
98%-C12, 2%-C14		390.6	9.076 %Cl(11.02)	3.586 (27.89)
100%-C12, monohydrate	$C_{25}H_{40}NCl \cdot H_2O$	408.07	8.688 %Cl(11.51)	3.432 (29.13)
98%-C12, 2%-C14, monohydrate		408.6	8.676 %Cl(11.53)	3.428 (29.17)
ALKYLDODECYLBENZYL TRIMETHYL AMMONIUM CHLORIDE				
100%-C12	$C_{34}H_{64}NCl$	522.35	6.787 %Cl(14.73)	2.682 (37.29)
95%-C12, 5%-C18 (DBC-50)		526.6	6.733 %Cl(14.85)	2.660 (37.59)
N-ALKYL N-ETHYL MORPHOLINIUM ETHYL SULFATE				
100%-C12	$C_{20}H_{39}NSO_5$	405.60	7.905 %S(12.65)°	3.453 (28.96)
92%-C12, 8%-C16		410.1	7.819 %S(12.79)°	3.416 (29.28)
92%-C8, 8%-C16(Alkyl from soy beans)		358.5	8.945 %S(11.18)°	3.907 (25.59)
ALKYL ISOQUINOLINIUM BROMIDE				
100%-C12	$C_{21}H_{32}NBr$	378.40	21.12 %Br(4.735)	3.702 (27.02)
50%-C12, 30%-C14, 17%-C16, 3%-C18		398.9	20.03 %Br(4.992)	3.512 (28.48)
61%-C12, 23%-C14, 11%-C16, 5%-C18 (LIB 75)		395.2	20.22 %Br(4.946)	3.544 (28.22)
2-ALKYL 1-METHYL 1-HYDROXYLETHYL IMIDAZOLINIUM CHLORIDE				
100%-C13	$C_{19}H_{39}ON_2Cl$	346.99	10.22 %Cl(9.787)	4.037 (24.77)'
ALKYL METHYL ISOQUINOLINIUM CHLORIDE				
100%-C12	$C_{22}H_{34}NCl$	347.97	10.19 %Cl(9.815)	4.025 (24.84)
25%-C12, 55%-C14, 17%-C16, 3%-C18 (Ammonyx 781)		375.5	9.442 %Cl(10.59)	3.731 (26.81)
ALKYLNAPHTHYLMETHYL PYRIDINIUM CHLORIDE				
100%-C12	$C_{28}H_{38}NCl$	424.07	8.360 %CL(11.96)	3.303 (30.28)
ALKYL TOLYLMETHYL DIMETHYL AMMONIUM CHLORIDE				
100%-C12	$C_{22}H_{40}NCl$	354.02	10.01 %Cl(9.986)	3.957 (25.27)
ALKYLTOLYLMETHYL TRIMETHYL AMMONIUM CHLORIDE				
100%-C12	$C_{23}H_{42}NCl$	368.05	9.633 %Cl(10.38)	3.806 (26.28)
ALKYL TRIMETHYL AMMONIUM BROMIDE				
100%-C16	$C_{19}H_{42}NBr$	364.46	21.93 %Br(4.561)	3.843 (26.02)

		M.W.	%HALOGEN(FACTOR)	% N (FACTOR)	
ALKYL TRIMETHYL AMMONIUM CHLORIDE					
100%-C16	$C_{19}H_{42}NCl$	320.01	11.08 %Cl(9.026)	4.377	(22.85)
5%-C16, 95%-C18		346.7	10.23 %Cl(9.778)	4.041	(24.75)
BENZYL DODECYLCARBAMYLMETHYL DIMETHYL AMMONIUM CHLORIDE (Urolocide)	$C_{23}H_{41}N_2OCl$	397.05	8.929 %Cl(11.20)	3.528	(28.35)'
CETYL PYRIDINIUM BROMIDE	$C_{21}H_{38}NBr$	384.45	20.78 %Br(4.811)	3.643	(27.45)
monohydrate		402.47	19.85 %Br(5.037)	3.480	(28.73)
CETYL PYRIDINIUM CHLORIDE	$C_{21}H_{38}NCl$	340.00	10.43 %Cl(9.590)	4.120	(24.27)
monohydrate		358.01	9.903 %Cl(10.10)	3.912	(25.56)
2-CHLOROETHYL TRIMETHYL AMMONIUM CHLORIDE	$C_5H_{13}ClNCl$	158.07	22.43 %Cl(4.459)*	8.861	(11.29)
DIALKYL DIMETHYL AMMONIUM BROMIDE					
100%-C12 (Use for dicoco-)	$C_{26}H_{56}NBr$	462.65	17.27 %Br(5.790)	3.028	(33.03)
DIALKYL DIMETHYL AMMONIUM CHLORIDE					
100%-C12 (Use for dicoco-)	$C_{26}H_{56}NCl$	418.19	8.478 %Cl(11.80)	3.349	(29.86)
4%-C14, 26%-C16, 70%-C18		567.4	6.248 %Cl(16.01)	2.468	(40.51)
DI-n-ALKYL METHYL BENZYL AMMONIUM CHLORIDE					
100%-C12	$C_{32}H_{60}NCl$	494.29	7.172 %Cl(13.94)	2.834	(35.29)
5%-C12, 60%-C14, 30%-C16, 5%-C18 (BTC 776)		570.0	6.219 %Cl(16.08)	2.457	(40.70)
DI(ALKYL OXYPROPYL) DIMETHYL AMMONIUM CHLORIDE					
100%-C10	$C_{28}H_{60}O_2NCl$	478.25	7.413 %Cl(13.49)	2.929	(34.14)
60%-C8, 40%-C10 (Q-Dox)		444.6	7.974 %Cl(12.54)	3.151	(31.74)
p-DIISOBUTYLCRESOXYETHOXYETHYL DIMETHYL BENZYL AMMONIUM CHLORIDE	$C_{28}H_{44}O_2NCl$	462.12	7.672 %Cl(13.03)	3.031	(32.99)
monohydrate		480.14	7.384 %Cl(13.54)	2.917	(34.28)
p-DIISOBUTYLPHENOXYETHOXYETHYL DIMETHYL BENZYL AMMONIUM CHLORIDE	$C_{27}H_{42}O_2NCl$	448.09	7.912 %Cl(12.64)	3.126	(31.99)
monohydrate		466.11	7.593 %Cl(13.17)	3.000	(33.33)

		M.W.	%HALOGEN(FACTOR)	% N (FACTOR)
DIQUAT DIBROMIDE	$C_{12}H_{12}N_2Br_2$	344.06	46.45 %Br(2.153)	4.071 (24.56)'
monohydrate		362.08	44.14 %Br(2.266)	3.868 (25.85)'
DODECYLACETAMIDYL DIMETHYL BENZYL AMMONIUM CHLORIDE (NOPCO, DBC)	$C_{23}H_{41}N_2OCl$	397.05	8.929 %Cl(11.20)	3.528 (28.35)'
DODECYLBENZYL TRIMETHYL AMMONIUM CHLORIDE (Barquat, TC-50, DBQ, GT-50, LQ-150)	$C_{22}H_{40}NCl$	354.02	10.01 %Cl(9.986)	3.957 (25.27)
DODECYLBENZYL TRIMETHYL AMMONIUM 2-ETHYLHEXOATE	$C_{30}H_{55}NO_2$	461.78		3.033 (32.97)
DODECYL DIMETHYL BENZYL AMMONIUM CYCLOPENTANE CARBOXYLATE SALT	$C_{27}H_{47}NO_2$	417.68		3.354 (29.82)
FURFURYL TRIMETHYL AMMONIUM IODIDE	$C_8H_{14}NOI$	267.11	47.51 %I (2.105)	5.244 (19.07)
2-HEPTADECENYL-1-ETHANOL-1-ETHYL IMIDAZOLINIUM BROMIDE	$C_{24}H_{47}ON_2Br$	459.76	17.39 %Br(5.751)	3.047 (32.82)'
2-HEPTADECYL-1-METHYL-1-(2-(STEAROYLAMIDO)ETHYL) IMIDAZOLINIUM METHYL SULFATE (Arqual S)	$C_{42}H_{85}N_3O_5S$	744.23	4.308 %S(23.21)°	1.882 (53.13)'
1,3-bis(2-HYDROXYETHYL)-2-HEPTADECENYL IMIDAZOLINIUM CHLORIDE	$C_{24}H_{47}N_2O_2Cl$	431.11	8.224 %Cl(12.16)	3.249 (30.78)'
1,3-bis(2-HYDROXYETHYL)-2-HEPTADECENYL IMIDAZOLINIUM BROMIDE	$C_{24}H_{47}N_2O_2Br$	475.56	16.80 %Br(5.951)	2.945 (33.95)'
METHYLALKYLBENZYL TRIMETHYL AMMONIUM CHLORIDE 100%-C12	$C_{23}H_{42}NCl$	368.05	9.633 %Cl(10.38)	3.806 (26.28)
METHYLDODECYLBENZYL TRIMETHYL AMMONIUM CHLORIDE	$C_{23}H_{42}NCl$	368.05	9.633 %Cl(10.38)	3.806 (26.28)
METHYLDODECYLXYLYLENE bis(TRIMETHYL AMMONIUM CHLORIDE)	$C_{27}H_{52}N_2Cl_2$	475.63	14.91 %Cl(6.708)	2.945 (33.96)'
METHYLDODECYLBENZYL TRIMETHYL AMMONIUM CHLORIDE(80%) METHYLDODECYLXYLYLENE bis(TRIMETHYL AMMONIUM CHLORIDE) (20%) (Hyamine 2389)		331.7	10.69 %Cl(9.356)	4.223 (23.68)

		M.W.	%HALOGEN(FACTOR)	% N (FACTOR)
OCTADECYL TRIMETHYL AMMONIUM PENTACHLOROPHENATE	$C_{27}H_{52}Cl_5NO$	577.9		2.424 %N(41.26)
PARAQUAT DICHLORIDE (1,1'-DIMETHYL-4,4'-BIPYRIDINIUM DICHLORIDE)	$C_{12}H_{14}N_2Cl_2$	257.16	27.57 %Cl(3.627)	5.447 (18.36)'
PARAQUAT DI OR bis METHYL SULFATE (1,1'-DIMETHYL-4,4'-BIPYRIDINIUM DIMETHYL SULFATE)	$C_{14}H_{20}O_8N_2S_2$	408.46	15.70 %S(6.369)°	3.429 (29.16)'
TRIMETHYL OCTADECENYL AMMONIUM CHLORIDE	$C_{21}H_{44}NCl$	346.04	10.25 %Cl(9.761)	4.048 %N(24.71)
TRIMETHYL OCTADECADIENYL AMMONIUM CHLORIDE	$C_{21}H_{42}NCl$	344.03	10.31 %Cl(9.704)	4.071 %N(24.56)

Determination of Quaternary Ammonium Compounds
Qualitative (Auerbach)* Tests

For definition, structure, and technical data on these compounds - see Quaternary Ammonium Compounds EPA-1.

Principle of the Method:

Bromophenol blue indicator forms a salt with quaternary ammonium compounds. This salt is soluble in ethylene dichloride and colors it blue.

Reagents:

1. Sodium carbonate, 10% solution
2. Bromophenol blue, 0.04% solution
3. Ethylene dichloride, reagent grade

Equipment:

1. Glass-stoppered test tube or cylinder
2. Pipettes - 1, 5, and 10 ml

Procedure:

Transfer a portion of sample equivalent to 1-2 mg quaternary ammonium compound into a glass-stoppered tube or cylinder. Add 5 ml 10% sodium carbonate solution, 1 ml bromophenol blue solution, and 10 ml ethylene dichloride. Shake steadily for 1 to 2 minutes and allow the layers to separate.

A blue color in the ethylene dichloride layer indicates the presence of a quaternary ammonium compound.

Soaps or anionic detergents, if present, may cause the test to fail.

*This test is based on Auerbach, Industrial & Engineering Chemistry, Analytical Edition, Vol. 15, Pg. 492 (1943) and Vol. 16, Pg. 739 (1944).

Determination of Quaternary Ammonium Compounds by the Ferricyanide Method

For definition, structure, and technical data on these compounds - see Quaternary Ammonium Compounds EPA-1.

Principle of the Method:

Excess ferricyanide solution is reacted with the quaternary ammonium compound to form an insoluble precipitate which is filtered from the sample solution. The excess ferricyanide in the filtrate is determined by titration with standard thiosulfate, and the percent quaternary is calculated from the amount of ferricyanide used.

Reagents:

1. Buffer solution - dissolve 130 grams sodium acetate in about 400 ml water, add 42 ml acetic acid, and make to 500 ml.
2. Ferricyanide solution - dissolve 6.6 grams potassium ferricyanide in water and make to one liter. (approx. 0.02N)
3. Zinc sulfate solution - dissolve 20 grams zinc sulfate heptahydrate in 180 ml water.
4. Sodium thiosulfate, 0.02N standard solution - dilute 100 ml 0.1N standard sodium thiosulfate to 500 ml.
5. Hydrochloric acid, (1+1)
6. Potassium iodide, ACS, crystals
7. Starch indicator solution

Equipment:

1. Steam bath
2. Filtration apparatus
3. Titration apparatus
4. Usual laboratory glassware

Procedure:

Weigh a portion of sample equivalent to 0.5 gram quaternary ammonium compound into a 100 ml volumetric flask and dissolve in about 50 ml water. If the sample is not readily soluble, warm on a steam bath for about 10 minutes with occasional mixing; cool, and add 5 ml of the buffer solution. Add exactly, by pipette, 30 ml of the ferricyanide solution, swirling the flask during the addition. Make to volume with water, mix thoroughly, and let stand for one-half hour, with occasional mixing.

Filter, discarding the first 10 ml of the filtrate. Pipette 50 ml of the filtrate into a 300 ml glass-stoppered Erlenmeyer flask, add 10 ml water, 1-2 grams potassium iodide, and 10 ml (1+1) hydrochloric acid. Mix well and let stand 2 minutes. Add 10 ml zinc sulfate solution, mix well, and let stand 2-5 minutes longer.

Titrate with standard 0.02N sodium thiosulfate solution, adding starch indicator solution near the end of the titration.

Repeat the above procedure exactly, using an identical portion (30 ml) of ferricyanide solution as was used with the sample. This will serve as a blank for the reagents and provide a basis for calculation.

Calculate the percent nitrogen and percent quaternary ammonium compounds as follows:

$$\%N = \frac{(\text{Blank ml} - \text{Sample ml})(N\ Na_2S_2O_3)(.0140)(100)}{(\text{grams sample})}$$

0.0140 = milliequivalent weight of nitrogen

% Quaternary = % nitrogen X nitrogen to quaternary factor

The reactions involved in this method are:

1. Precipitation of quaternary with ferricyanide

$$3[R_1R_2R_3R_4N]X + K_3Fe(CN)_6 \longrightarrow 3KX + [R_1R_2R_3R_4]_3Fe(CN)_6\downarrow$$

2. Reaction of excess ferricyanide with potassium iodide

$$\text{Excess } 2K_3Fe(CN)_6 + 2KI \longrightarrow 2K_4Fe(CN)_6 + I_2$$

3. Removal of $K_4Fe(CN)_6$ by zinc sulfate to speed oxidation of KI

$$2K_4Fe(CN)_6 + 3ZnSO_4 \longrightarrow K_2Zn_3[Fe(CN)_6]_2\downarrow + 3K_2SO_4$$

4. Titration of released iodine by sodium thiosulfate

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

Determination of Quaternary Ammonium Compounds by the Epton Titration Method

This method is most applicable to formulations containing 0.1% to 1.0% quaternary ammonium compounds.

For definition, structure, and technical data on these compounds - see Quaternary Ammonium Compounds EPA-1.

Principle of the Method:

An aqueous solution containing a quaternary ammonium compound (QAC) is reacted with an excess of anionic detergent (AD) in the presence of methylene blue and chloroform. The excess AD reacts with methylene blue to form a salt that is soluble in the chloroform (lower) layer and colors it blue. Since a QAC and an AD react to form an undissociated salt, any QAC in the sample reduces the AD by an equivalent amount. The excess AD is titrated by a standard QAC solution. When all of the AD has reacted with the QAC, the methylene blue is free to dissolve in the aqueous (upper) layer. The endpoint is therefore the point of equal color intensity in the two layers when viewed by diffused, reflected light.

Reagents:

1. Standard QAC, 0.005M solution - dissolve 0.005 gram molecular weight (usually 2-2.5 grams) of a pure QAC in water and make to one liter.
2. Standard AD, 0.005M solution - dissolve 0.005 gram molecular weight (usually 2-2.5 grams) of a pure AD in water and make to one liter.

3. Methylene blue indicator solution - dissolve 50 grams sodium sulfate (anhydrous), 12 ml sulfuric acid, and 0.03 gram methylene blue in water and make to one liter.

4. Chloroform

Equipment:

1. Glass-stoppered cylinders, 100 ml (plain without graduation markings is preferred)

2. Burettes and pipettes

3. Source of diffused light

Procedure:

Preparation of Sample:

For best results, dissolve and/or dilute the sample so that a 10 ml aliquot will contain 0.02-0.04 gram of QAC. (Very low percent products requiring extremely large sample amounts may require a cylinder larger than 100 ml.)

Determination:

Place the sample aliquot in a 100 ml glass-stoppered cylinder, add 25 ml methylene blue indicator solution, 15 ml chloroform, and exactly, by pipette, 25 ml of AD solution. Shake thoroughly and allow to settle; the blue color should be in the bottom layer, indicating an excess of AD.

Titrate with standard QAC solution in small amounts, shaking thoroughly after each addition, and allowing time for the layers to separate. The rate of separation becomes slower as the endpoint is approached. When color begins to appear in both layers, add the standard QAC solution in very small increments. The endpoint is taken as equal color or equal intensity in both layers when viewed by reflected diffused light. (Should the endpoint be passed,

additional AD solution may be added, and the titration continued; however, that extra amount must be accounted for in the calculations.)

Repeat the titration using 10 ml water as blank and the same quantity of AD solution as was used for the sample.

Calculation:

The difference between the volume of QAC solution used for the blank and that used for the sample is the amount equivalent to the QAC present in the sample.

$$\% \text{ QAC Nitrogen} = \frac{(\text{Blank ml} - \text{Sample ml})(M)(.0140)(100)}{(\text{grams sample})(\text{any dilution factors})}$$

M = molarity of QAC solution
0.0140 = milliequivalent weight of nitrogen

% QAC = % nitrogen X nitrogen to QAC factor

Determination of Quaternary Chlorides and Bromides in Mixed Quaternary Formulations by Potentiometric Titration

For definition, structure, and technical data on these compounds - see Quaternary Ammonium Compounds EPA-1.

Reagents:

1. Inorganic chloride and bromide salts of known halogen content
2. Nitric acid, (1+1)
3. Barium nitrate, crystals, ACS
4. Silver nitrate, 0.1N standard solution

Equipment:

1. Potentiometric titrimeter equipped with a glass reference electrode and a silver electrode
2. 25 ml burette
3. Usual laboratory glassware

Procedure:

Standardization of Titrimeter:

Prepare a standard solution of chloride and bromide in the same ratio as expected in the sample. This solution should contain approximately one milliequivalent total halides (35 mg chloride or 80 mg bromine) in 10 ml solution.

Pipette 10 ml of the prepared standard halide solution into a 250 ml beaker, add 0.5 ml (1+1) hydrochloric acid, and 0.5 gram barium nitrate (removes iodate in Volhard titration). Place the electrodes in the solution and set the potential on the titrimeter at 0.7 or 0.8 volt. Add 0.1N silver nitrate solution in small

increments and record the new potential after each addition. The increments should be smallest when the change in potential is greatest. Continue the addition of silver nitrate and recording of potential until 3.5 volts is reached.

Plot a curve of each addition of 0.1N silver nitrate against each potential reading. The plotted curve will indicate two inflection points; the first will be the bromide end point, and the second will be the chloride end point. Record the potential where each end point occurs.

Sample Titration:

Into a 250 ml beaker weigh a portion of sample equal to 1 milliequivalent of total halides. Dilute to 150-200 ml with distilled water, add 0.5 ml (1+1) nitric acid, and 0.5 gram barium nitrate. Test the pH of the solution with methyl red. Adjust the pH by adding small amounts of nitric acid until the solution is red. Titrate with 0.1N silver nitrate solution and record the volume added when each potentiometric end point is reached.

Calculations:

Calculate the percent chloride and/or bromide as follows:

$$\% \text{ Chloride} = \frac{(A-B)(N \text{ of } AgNO_3)(.03546)(100)}{(\text{grams of sample})}$$

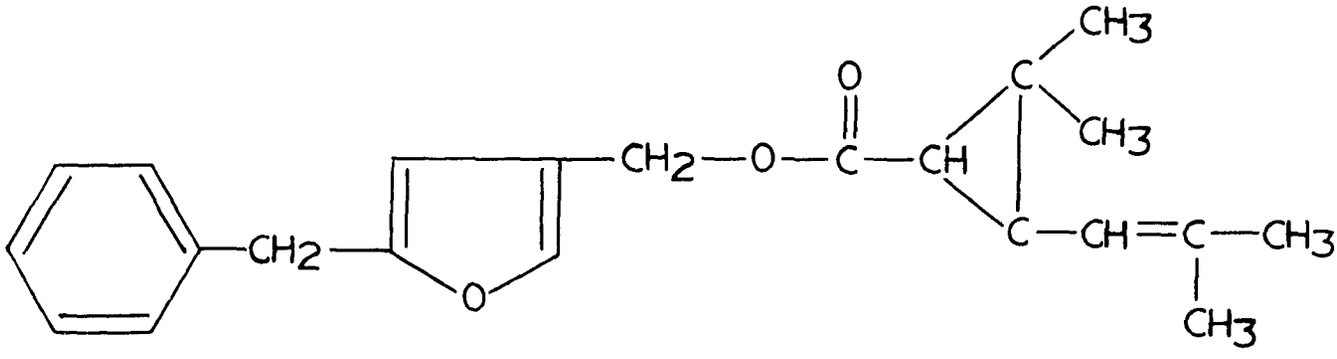
$$\% \text{ Bromide} = \frac{(B)(N \text{ of } AgNO_3)(.07992)(100)}{(\text{grams of sample})}$$

A = ml of $AgNO_3$ for second (chloride) end point on titration curve

B = ml of $AgNO_3$ for first (bromide) end point on titration curve

Determination of Resmethrin in Aerosol Formulations by Infrared Spectroscopy

Resmethrin is the common name for (5-benzyl-3-furyl)methyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate (approx. 70% trans, 30% cis isomers), a registered insecticide having the chemical structure:



Molecular formula: $C_{22}H_{26}O_3$

Molecular weight: 338

Melting point: 43 to 48°C

Physical state, color, and odor: waxy off-white to tan solid with a characteristic chrysanthemate odor

Solubility: insoluble in water; soluble in all common organic solvents

Stability: decomposes fairly rapidly on exposure to air and light; somewhat more stable than pyrethrins

Other names: Synthrin, Crysan, benzofuraline, NIA 17370, FMC 17370, NRDC 104, SBP 1382

This method is for 1-2% aerosol formulations in which resmethrin is the only active ingredient.

Reagents:

1. Resmethrin standard of known % purity
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm KBr or NaCl cells
2. Freezer or dry-ice chest
3. Warm water bath
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.06 gram resmethrin standard into a 10 ml volumetric flask; dissolve in and make to volume with carbon disulfide. Add a small amount anhydrous sodium sulfate to insure dryness. (final conc 6 mg/ml)

Preparation of Sample:

Record the gross weight of a full aerosol can with cap. Place the can in a freezer overnight or in a dry-ice chest for at least 2 hours. Remove can and immediately punch several holes in the top to relieve pressure. Open the can top with a can opener and allow to warm to room temperature. Remove any remaining propellants by placing can in a water bath at about 35-40°C. Dissolve the residue, transfer to a 100 ml volumetric flask, and make to volume with carbon disulfide.

Dry the can and weigh with cap. Subtract this weight from the gross weight to obtain the net weight, which is both the net contents of the sample and the sample weight. From the declared percent of resmethrin and the sample weight, calculate the apparent concentration of resmethrin in the 100 ml volumetric flask. Dilute an aliquot of this solution to obtain a solution of approximately 6 mg/ml. Add a small amount of anhydrous sodium sulfate to insure dryness.

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1800 cm^{-1} to 1600 cm^{-1} (5.6 μ to 6.25 μ).

Determine the absorbance of standard and sample using the peak at 1720 cm^{-1} (5.82 μ) and baseline from 1765 cm^{-1} to 1660 cm^{-1} (5.67 μ to 6.02 μ).

Calculation:

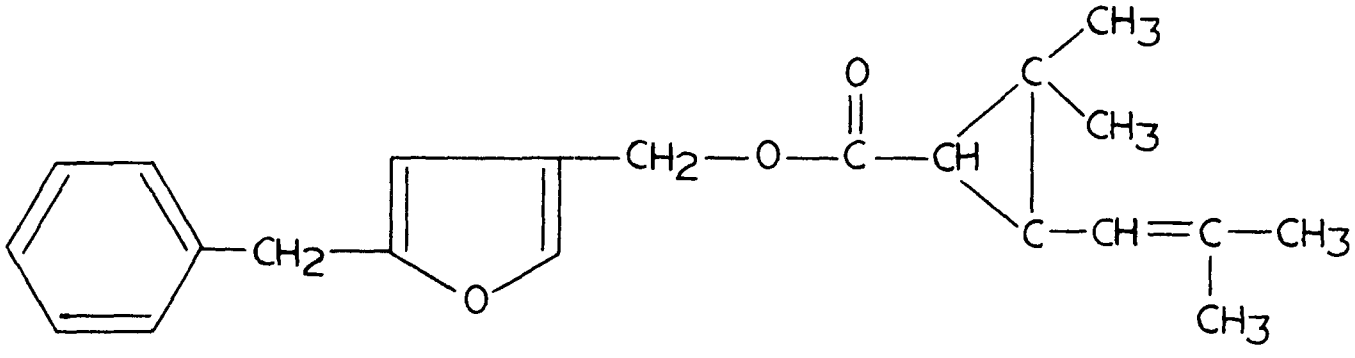
From the above absorbances and using the standard and sample solution concentrations, calculate the percent resmethrin as follows:

$$\% = \frac{\text{(abs. sample)(conc. std in mg/ml)(\% purity std)}}{\text{(abs. std)(conc. sample in mg/ml)}}$$

Method submitted by Mark Law and Jack Looker, EPA Beltsville Chemistry Laboratory, TSD, OPP, Beltsville, Maryland.

Determination of Resmethrin in Aerosol Formulations by Gas-Liquid Chromatography (TCD)

Resmethrin is the common name for (5-benzyl-3-furyl)methyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate (approx. 70% trans, 30% cis isomers), a registered insecticide having the chemical structure:



Molecular formula: $C_{22}H_{26}O_3$

Molecular weight: 338

Melting point: 43 to 48°C

Physical state, color, and odor: waxy off-white to tan solid with a characteristic chrysanthemate odor

Solubility: insoluble in water; soluble in all common organic solvents

Stability: decomposes fairly rapidly on exposure to air and light; somewhat more stable than pyrethrins

Other names: Synthrin, Crysan, benzofuraline, NIA 17370, FMC 17370, NRDC 104, SBP 1382

This method is for 1-2% aerosol formulations in which resmethrin is the only active ingredient.

Reagents:

1. Resmethrin standard of known % purity
2. Carbon disulfide, pesticide or spectro grade

   (Methanol could be substituted for the carbon disulfide in this method if it is desired to use the same sample solutions for High Pressure Liquid Chromatography -- see EPA-4.)

Equipment:

1. Gas chromatograph with thermal conductivity detector
2. 4' x 1/4" column packed with 10% SP-2100 on Chromosorb 750, 80/100 mesh (or equivalent column)
3. 25 µl precision syringe
4. Freezer or dry-ice chest
5. Warm water bath
6. Usual laboratory glassware

Determination using Thermal Conductivity Detector:

Operating Conditions:

Column temperature:	260°C
Injection temperature:	290°C
Detector temperature:	270°C
Filament current:	200 ma
Carrier gas:	Helium
Flow rate:	55 ml/min

Operating conditions for filament current, column temperature, or gas flow should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.06 gram resmethrin standard into a 10 ml volumetric flask; dissolve in and make to volume with carbon disulfide. Add a small amount anhydrous sodium sulfate to insure dryness. (final conc 6 mg/ml)

Preparation of Sample:

Record the gross weight of a full aerosol can with cap. Place the can in a freezer overnight or in a dry-ice chest for at least 2 hours. Remove can and immediately punch several holes in the top to relieve pressure. Open the can top with a can opener and allow to warm to room temperature. Remove any remaining propellants by placing can in a water bath at about 35-40°C. Dissolve the residue, transfer to a 100 ml volumetric flask, and make to volume with carbon disulfide.

Dry the can and weigh with cap. Subtract this weight from the gross weight to obtain the net weight, which is both the net contents of the sample and the sample weight. From the declared percent of resmethrin and the sample weight, calculate the apparent concentration of resmethrin in the 100 ml volumetric flask. Dilute an aliquot of this solution to obtain a solution of approximately 6 mg/ml.

Determination:

Using a precision liquid syringe, alternately inject three 10-20 µl portions of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

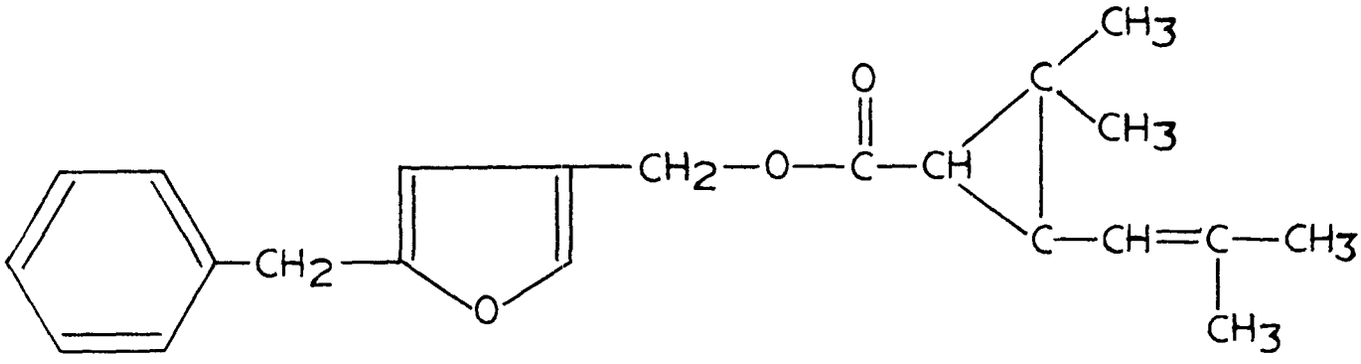
From the average peak height or peak area, calculate the percent resmethrin as follows:

$$\% = \frac{\text{(pk. ht. or area sample)(wt. std injected)(\% purity of std)}}{\text{(pk. ht. or area standard)(wt. sample injected)}}$$

Method submitted by Mark Law and Jack Looker, EPA-OPP-TSD Beltsville Chemistry Laboratory, Beltsville, Maryland.

Determination of Resmethrin in Aerosol Formulations by Gas-Liquid Chromatography (TCD - Internal Standard)

Resmethrin is the common name for (5-benzyl-3-furyl) methyl 2,2-dimethyl-3-(2-methylpropenyl) cyclopropanecarboxylate (approx. 70% trans, 30% cis isomers), a registered insecticide having the chemical structure:



Molecular formula: $C_{22}H_{26}O_3$

Molecular weight: 338

Melting point: 43 to 48°C

Physical state, color, and odor: waxy off-white to tan solid with a characteristic chrysanthemate odor

Solubility: insoluble in water; soluble in all common organic solvents

Stability: decomposes fairly rapidly on exposure to air and light; somewhat more stable than pyrethrins

Other names: Synthrin, Crysan, benzofuraline, NIA 17370, FMC 17370, NRDC 104, SBP 1382

This method is for 1-2% aerosol formulations in which resmethrin is the only active ingredient.

Reagents:

1. Resmethrin standard of known % purity
2. Dieldrin standard of known HEOD content
3. Benzene, pesticide or spectro grade
4. Internal Standard solution - weigh 0.2 gram dieldrin standard into a 10 ml volumetric flask; dissolve in and make to volume with benzene. (conc 20 mg dieldrin/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector
2. 6' x 1/8" stainless steel column packed with 10% SE 30 on 80/100 Diatoport S (or equivalent column)
3. Precision liquid syringe: 10 or 25 μl
4. Freezer or dry-ice chest
5. Warm water bath
6. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	230°C
Injection temperature:	250°C
Detector temperature:	250°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas pressure:	25 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.16 gram resmethrin into a 10 ml volumetric flask; dissolve in and make to volume with benzene. Pipette 5 ml of this solution and 5 ml internal standard solution into a small flask or vial and mix thoroughly. (conc 8 mg resmethrin and 10 mg dieldrin/ml)

Preparation of Sample:

Record the gross weight of a full aerosol can with cap. Place the can in a freezer overnight or in a dry-ice chest for at least 2 hours. Remove can and immediately punch several holes in the top to relieve pressure. Open the can top with a can opener and allow to warm to room temperature. Remove any remaining propellants by placing can in a water bath at about 35-40°C. Dissolve the residue, transfer to a 100 ml volumetric flask, and make to volume with benzene.

Dry the can and weigh with cap. Subtract this weight from the gross weight to obtain the net weight, which is both the net contents of the sample and the sample weight. From the declared percent of resmethrin and the sample weight, calculate the apparent concentration of resmethrin in the 100 ml volumetric flask. Dilute an aliquot of this solution to obtain a concentration of 16 mg/ml. Pipette 5 ml of this diluted solution and 5 ml internal standard solution into a small flask or vial and mix thoroughly. (conc 8 mg resmethrin and 10 mg dieldrin/ml)

Determination:

Inject 5-10 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within 10 minutes and peak heights of from 1/2 to 3/4 full scale. The elution time of dieldrin is 3.5 minutes and that of resmethrin 6.0 minutes.

Proceed with the determination, making at least three injections each of standard and sample solutions.

Calculation:

Measure the peak heights or areas of resmethrin and dieldrin from both the standard-internal standard solution and the sample-internal standard solutions.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. dieldrin})(\%\text{ purity dieldrin})(\text{pk. ht. or area resmethrin})}{(\text{wt. resmethrin})(\%\text{ purity resmethrin})(\text{pk. ht. or area dieldrin})}$$

Determine the percent resmethrin for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. dieldrin})(\%\text{ purity dieldrin})(\text{pk. ht. or area resmethrin})\cancel{(100)}}{(\text{wt. sample})(\text{pk. ht. or area dieldrin})(RF)} \quad (1-1)$$

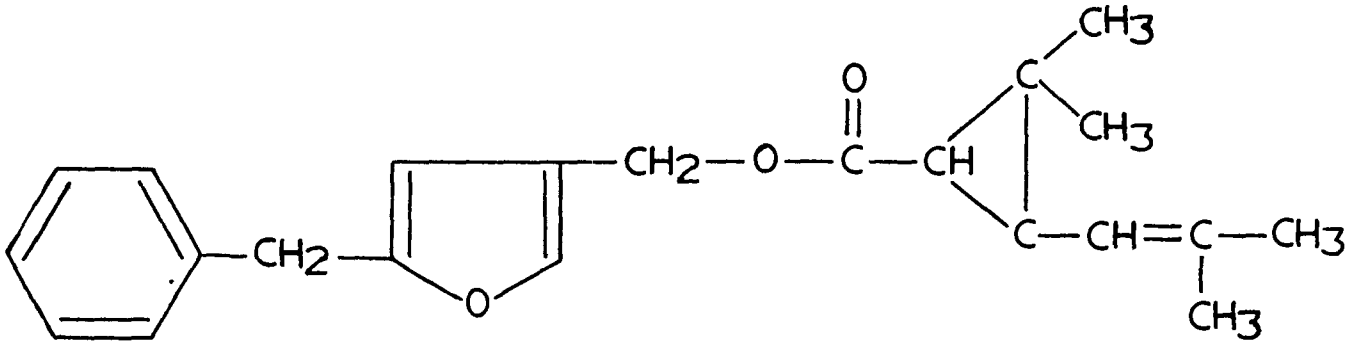
Method submitted by Stelios Gerazounis, EPA Region II, New York, New York.

September 1975

Resmethrin EPA-4
(Tentative)

Determination of Resmethrin in Aerosol Formulations by High Pressure Liquid Chromatography

Resmethrin is the common name for (5-benzyl-3-furyl)methyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate (approx. 70% trans, 30% cis isomers), a registered insecticide having the chemical structure:



Molecular formula: $C_{22}H_{26}O_3$

Molecular weight: 338

Melting point: 43 to 48°C

Physical state, color, and odor: waxy off-white to tan solid with a characteristic chrysanthemate odor

Solubility: insoluble in water; soluble in all common organic solvents

Stability: decomposes fairly rapidly on exposure to air and light; somewhat more stable than pyrethrins

Other names: Synthrin, Crysan, benzofuraline, NIA 17370, FMC 17370, NRDC 104, SBP 1382

This method is for 1-2% aerosol formulations in which resmethrin is the only active ingredient.

Reagents:

1. Resmethrin standard of known % purity
2. Methanol, pesticide or spectro grade

Equipment:

1. High pressure liquid chromatograph
2. High pressure liquid syringe
3. Liquid chromatographic column such as DuPont's ODS Permaphase 1 meter x 2.1 m I.D. (or equivalent column)
4. Freezer or dry-ice chest
5. Warm water bath
6. Usual laboratory glassware

Operating Conditions for DuPont Model 830:

Mobile phase:	70% methanol + 30% water
Column temperature:	65°C
Column pressure:	1000 psi
Observed flow rate:	1-2 ml/min
Detector:	UV at 254 nm
Chart speed:	5 min/in
Injection:	5 µl

Procedure:

Preparation of Standard:

Weigh 0.06 gram resmethrin standard into a 10 ml volumetric flask; dissolve in and make to volume with methanol. (final conc 6 mg/ml)

Preparation of Sample:

Record the gross weight of a full aerosol can with cap. Place the can in a freezer overnight or in a dry-ice chest for at least 2 hours. Remove can and immediately punch several holes in the top to relieve pressure. Open the can top with a can opener and allow to warm to room temperature. Remove any remaining propellants by placing can in a water bath at about 35-40°C. Dissolve the residue, transfer to a 100 ml volumetric flask, and make to volume with methanol.

Dry the can and weigh with cap. Subtract this weight from the gross weight to obtain the net weight, which is both the net contents of the sample and the sample weight. From the declared percent of resmethrin and the sample weight, calculate the apparent concentration of resmethrin in the 100 ml volumetric flask. Dilute an aliquot of this solution to obtain a solution of approximately 6 mg/ml.

Determination:

Using a high pressure liquid syringe, alternately inject three 5 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area, calculate the percent resmethrin as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

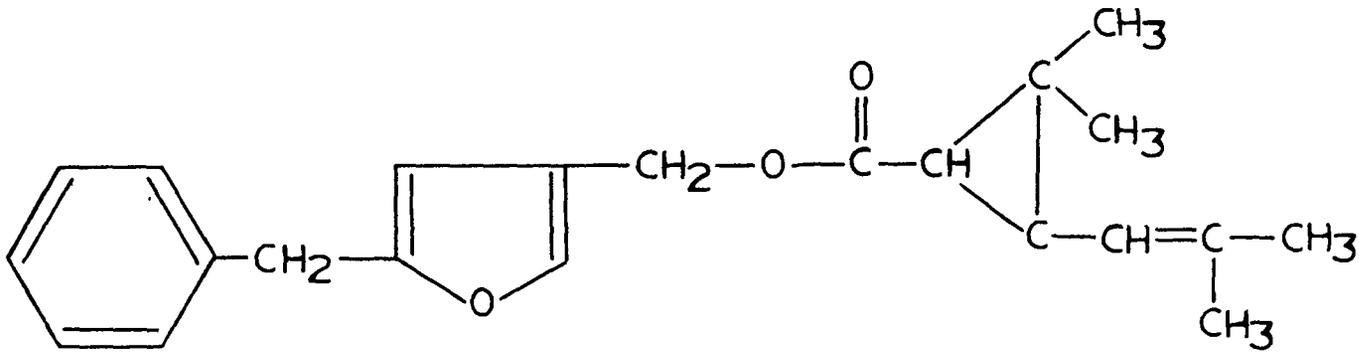
Method submitted by Elmer Hayes, EPA-OPP-TSD Beltsville Chemistry Laboratory, Beltsville, Maryland.

October 1975

Resmethrin EPA-5
(Tentative)

Determination of Resmethrin by Gas-Liquid Chromatography (FID - Internal Standard)

Resmethrin is the common name for (5-benzyl-3-furyl) methyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate (approx. 70% trans, 30% cis isomers), a registered insecticide having the chemical structure:



Molecular formula: $C_{22}H_{26}O_3$

Molecular weight: 338

Melting point: 43 to 48°C

Physical state, color, and odor: waxy off-white to tan solid with a characteristic chrysanthemate odor

Solubility: insoluble in water; soluble in all common organic solvents

Stability: decomposes fairly rapidly on exposure to air and light; somewhat more stable than pyrethrins

Other names: Synthrin, Crysan, benzofuraline, NIA 17370, FMC 17370, NRDC 104, SBP 1382

Reagents:

1. Resmethrin standard of known % purity
2. Dipentyl phthalate, practical*
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.1 gram dipentyl phthalate into a 100 ml volumetric flask; dissolve in and make to volume with acetone. (conc 1 mg dipentyl phthalate/ml)

* #P2473 Eastman Catalog #48, Eastman Organic Chemicals, Rochester, N. Y. 14650

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm ID glass column packed with 5% SE-30 on 80/100 Chromosorb W HP (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	210°
Injection temperature:	260°
Detector temperature:	260°
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi
Hydrogen pressure:	20 psi
Air pressure:	30 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram resmethrin standard into a small glass-stoppered flask or screw-cap tube. Add by pipette 25 ml of the internal standard solution and shake to dissolve. (final conc 2 mg resmethrin and 1 mg dipentyl phthalate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.05 gram resmethrin into a small glass-stoppered flask or screw-cap tube. Add by pipette 25 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the resmethrin. For coarse or granular materials, shake or tumble mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 2 mg resmethrin and 1 mg dipentyl phthalate/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is dipentyl phthalate, then resmethrin.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of resmethrin and dipentyl phthalate from both the standard-internal standard solution and the sample-internal standard solutions.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

DPP = dipentyl phthalate = internal standard

$$RF = \frac{(\text{wt. DPP})(\%\text{ purity DPP})(\text{pk. ht. or area resmethrin})}{(\text{wt. resmethrin})(\%\text{ purity resmethrin})(\text{pk. ht. or area DPP})}$$

Determine the percent resmethrin for each injection of the sample-internal standard solution as follows and calculate the average:

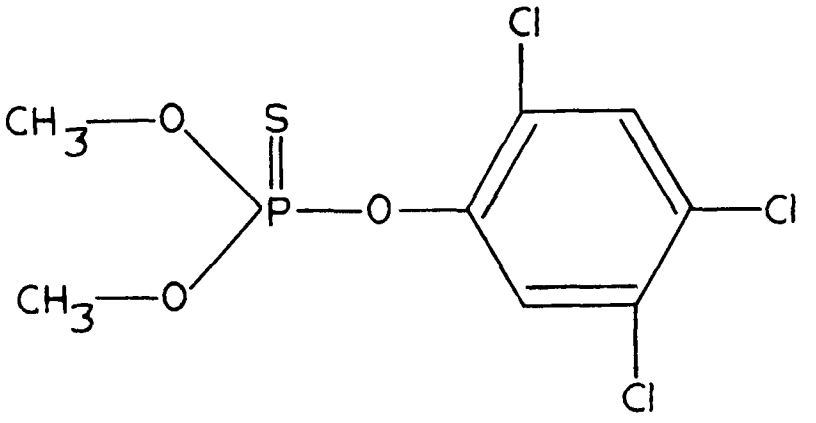
$$\% = \frac{(\text{wt. DPP})(\%\text{ purity DPP})(\text{pk. ht. or area resmethrin})(100)}{(\text{wt. sample})(\text{pk. ht. or area DPP})(RF)} \qquad (4-1)$$

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Note! This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Chemistry Lab. Any comments, criticism, suggestion, data, etc. concerning this method will be appreciated.

Determination of Ronnel by Infrared Spectroscopy

Ronnel is the accepted common name for O,O-dimethyl O-(2,4,5-trichlorophenyl) phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_8H_8Cl_3O_3PS$

Molecular weight: 321.5

Melting point: softens at 35 to 37°C with full melt at 40-42°C

Physical state and color: white crystalline powder

Solubility: 40 ppm in water at RT; readily soluble in most organic solvents including refined kerosene

Stability: stable at temperatures to 60°C, and in neutral or acidic media; hydrolyzed by alkali to the desmethyl compound; not compatible with alkaline pesticides

Other names: fenchlorphos (common name accepted by ISO and BSI); Trolene (drug grade) and Korlan (tech. grade)(Dow Chemical Co.); Nankor, Ectoral, Etrolene, Viozene

Reagents:

1. Ronnel standard of known % purity
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps. These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.05 gram ronnel into a small glass-stoppered flask or screw-cap bottle, add 10 ml carbon disulfide by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc. 5 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.125 gram ronnel into a glass-stoppered flask or screw-cap bottle. Add 25 ml carbon disulfide and 1-2 grams anhydrous sodium sulfate. Close

tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 5 mg ronnel/ml)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1020 cm^{-1} to 890 cm^{-1} (9.8 μ to 11.3 μ).

Determine the absorbances of the standard and sample using the peak at 960 cm^{-1} (10.42 μ) and basepoint at 920 cm^{-1} (10.87 μ).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent ronnel as follows:

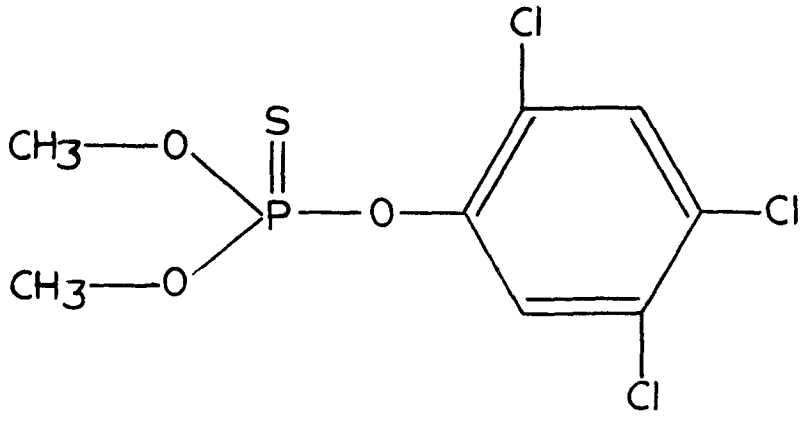
$$\% = \frac{\text{(abs. sample)(conc. std in mg/ml)(\% purity std)}}{\text{(abs. std)(conc. sample in mg/ml)}}$$

(A concentration of 1 mg ronnel/ml carbon disulfide gives an absorbance of approx. 0.08 in a 0.5 mm cell.)

Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services.

Determination of Ronnel by Gas-Liquid Chromatography (FID - Internal Standard)

Ronnel is the accepted common name for O,O-dimethyl O-(2,4,5-trichlorophenyl) phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_8H_8Cl_3O_3PS$

Molecular weight: 321.5

Melting point: softens at 35 to 37°C with full melt at 40-42°C

Physical state and color: white crystalline powder

Solubility: 40 ppm in water at RT; readily soluble in most organic solvents including refined kerosene

Stability: stable at temperatures to 60°C, and in neutral or acidic media; hydrolyzed by alkali to the desmethyl compound; not compatible with alkaline pesticides

Other names: fenchlorphos (common name accepted by ISO and BSI); Trolene (drug grade) and Korlan (tech. grade)(Dow Chemical Co.); Nankor, Ectoral, Etrolene, Viozene

Reagents:

1. Ronnel standard of known % purity
2. Diisobutylphthalate
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.07 gram diisobutylphthalate into a 100 ml volumetric flask, dissolve in, and make to volume with acetone. (conc 0.7 mg/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 4 mm ID glass, packed with 3% OV-1 on 60/80 mesh Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	180°C
Injection temperature:	250°C
Detector temperature:	250°C
Carrier gas:	Nitrogen
Carrier gas pressure:	(not stated in method)
Hydrogen pressure:	24 psi
Air pressure:	30 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram ronnel standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 25 ml of the internal standard solution and shake to dissolve. (final conc 2 mg ronnel and 0.7 mg diisobutylphthalate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.05 gram ronnel into a small glass-stoppered flask or screw-cap bottle. Add by pipette 25 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the ronnel. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 2 mg ronnel and 0.7 mg diisobutylphthalate/ml)

Determination:

Inject 3-4 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is diisobutylphthalate, then ronnel.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of ronnel and diisobutylphthalate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

I.S. = internal standard = diisobutylphthalate

$$RF = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area Ronnel})}{(\text{wt. Ronnel})(\%\text{ purity Ronnel})(\text{pk. ht. or area I.S.})}$$

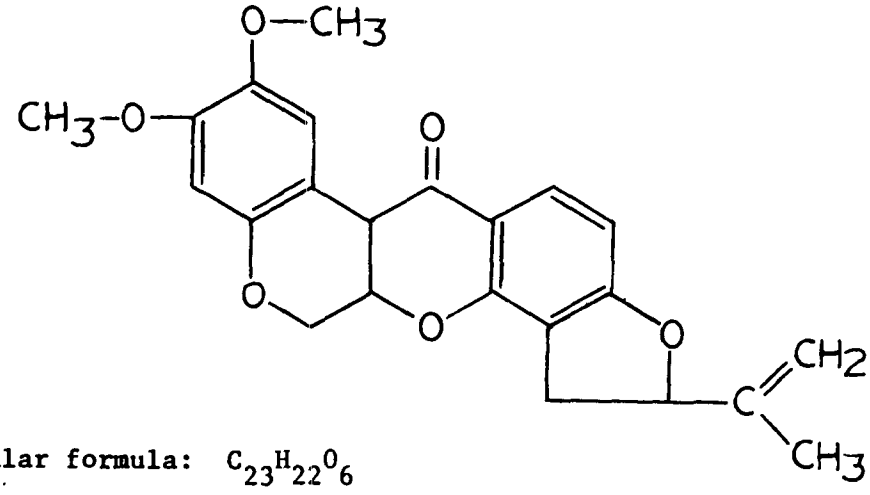
Determine the percent Ronnel for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area Ronnel})(\cancel{100})}{(\text{wt. sample})(\text{pk. ht. or area I.S.})(\text{RF})} \qquad (4\text{-}1)$$

Method submitted by Division of Regulatory Services, Kentucky Agricultural Experiment Station, University of Kentucky, Lexington, Kentucky 40506.

Determination of Rotenone in Pesticides - Qualitative tests

Rotenone is a registered insecticide having the chemical structure:



Molecular formula: $C_{23}H_{22}O_6$

Molecular weight: 394.4

Melting point: 163°C (a dimorphoric form melts at 181°C)

Physical state and color: colorless crystals; crystallizes with solvent of crystallization

Solubility: 15 ppm in water at 100°C; slightly soluble in petroleum oils, carbon tetrachloride; soluble in polar organic solvents

Stability: readily oxidized, especially in presence of light or alkali

Other names: Protex, Derris, Lonchocarpus, Barbasco (Spanish-speaking countries of So. Am.), Cube (Peru), Haiari (British Guiana), Nekos (Dutch Guiana), Timbo (Brazil), Nicouline, tubatoxin

Reagents:

1. Chloroform, ACS
2. Thymol solution - dissolve 10 grams of thymol in 100 ml of chloroform.
3. Nitric acid-hydrochloric acid mixture - add 0.2 ml of concentrated nitric acid to 100 ml of concentrated hydrochloric acid.

Equipment:

1. Glass-stoppered test tubes or small flasks
2. Usual laboratory glassware

Preparation of Sample:

Dilute an amount of liquid sample, or extract an amount of dry sample with chloroform to give 0.01-0.25 mg of rotenone per ml of solution.

This method is sensitive to 0.01 mg of rotenone per ml, but if too much rotenone is present the characteristic blue color will not develop. If the test fails on a sample believed to contain rotenone, repeat on a diluted portion of the sample.

Qualitative Determination:

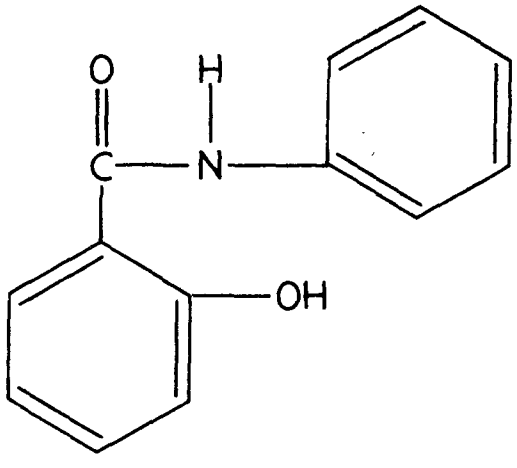
Place 5 ml of sample solution, 5 ml of thymol solution, and 3 ml mixed acid solution in a glass-stoppered test tube or small flask. Agitate for about 30 seconds and allow to stand.

The presence of rotenone is indicated by the appearance of a bluish-green to blue color. The color usually appears in from 30 seconds to 2 minutes and deepens on standing.

In the presence of the yellow coloring matter of pyrethrum flowers and of derris extract, the developed color may be green at first but on standing will become bluish-green and finally blue.

Determination of Salicylanilide by Ultraviolet Spectroscopy

Salicylanilide is a registered fungicide having the chemical structure:



Molecular formula: $C_{13}H_{11}NO_2$

Molecular weight: 213.3

Melting point: 135°C

Physical state and color: cream-colored powder

Solubility: almost insoluble in water (55 ppm at 25°), slightly soluble in organic solvents

Stability: slightly volatile in steam; forms water-soluble salts with alkali metals, ammonia, amines, and forms insoluble salts with copper and zinc

Other names: Shirlan (ICI Ltd)

Reagents:

1. Salicylanilide standard of known % purity
2. Sodium hydroxide, 0.1N solution (this need not be standardized)

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Soxhlet extraction apparatus
3. Rotary evaporator or steam bath and compressed air source
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram salicylanilide into a 100 ml volumetric flask; dissolve in and make to volume with 0.1N sodium hydroxide solution. Mix thoroughly, pipette 10 ml into a second 100 ml volumetric flask, and make to volume with the 0.1N NaOH solution. Again, mix thoroughly, and pipette 10 ml into a third 100 ml volumetric flask. Make to volume with 0.1N NaOH solution and mix well. (final conc 10 µg/ml)

Preparation of Sample:

For salicylanilide formulations, weigh a portion of sample equivalent to 0.01 gram salicylanilide into a 100 ml volumetric flask, make to volume with 0.1N sodium hydroxide solution, and mix thoroughly. Pipette 10 ml into a second 100 ml volumetric flask, again make to volume with the 0.1N sodium hydroxide solution, and mix well. (final conc 10 µg salicylanilide/ml)

For salicylanilide-treated products* weigh a portion of sample equivalent to 0.01 gram salicylanilide into a Soxhlet thimble, plug with cotton or glass wool, and extract with ethanol for about two hours. Evaporate to dryness using a rotary evaporator or a steam

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*Salicylanilide is used to prevent mildew on such things as rope, canvass, upholstery and mattress filling, tiles, in rubber backing (0.5%) for carpets and carpet underlays.

bath with a gentle stream of air. **Dissolve** residue, transfer to a 100 ml volumetric flask, and make to volume with 0.1N sodium hydroxide solution, and mix thoroughly. Pipette 10 ml into a second 100 ml volumetric flask; make to volume with the 0.1N sodium hydroxide solution. (final conc 10 µg salicylanilide/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 338 nm with 0.1N sodium hydroxide solution in each cell. Scan both the standard and sample from 360 nm to 250 nm with 0.1N NaOH solution in the reference cell. Measure the absorbance of both standard and sample at 338 nm.

If an untreated product is available, it can be carried through the extraction procedure and used as a blank. The absorbance at 338 nm would then be subtracted from the sample absorbance at 338 nm.

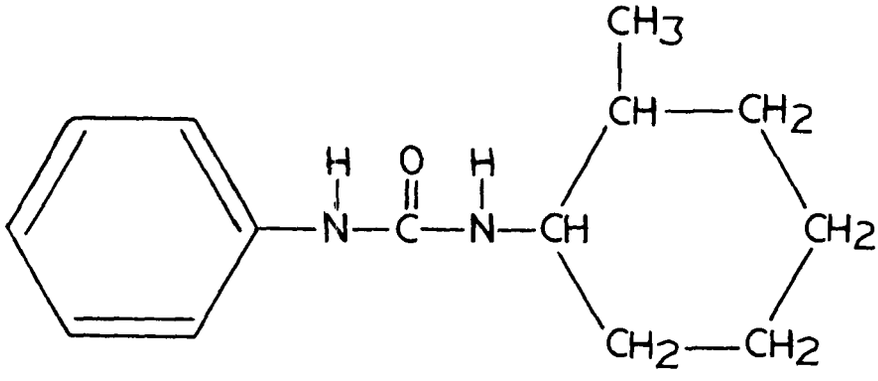
Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent salicylanilide as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

Determination of Siduron by Ultraviolet Spectroscopy

Siduron is the accepted common name for 1-(2-methylcyclohexyl)-3-phenylurea, a registered herbicide having the chemical structure:



Molecular formula: $C_{14}H_{20}N_2O$

Molecular weight: 232.3

Melting point: 133 to 138°C

Physical state, color, and odor: odorless, white, crystalline solid

Solubility: 18 ppm in water at 25°C; soluble to the extent of 10% or more in cellosolve, dimethylacetamide, dimethylformamide, ethanol, isophorone, methylene chloride

Stability: stable up to its m.p. in water; slowly decomposed by acids and bases; non-corrosive

Other names: Tupersan (DuPont)

Reagents:

1. Siduron standard of known % purity
2. Methanol, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm silica cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram siduron standard into a 100 ml volumetric flask, add 100 ml methanol by pipette, and mix thoroughly. Pipette 10 ml into a second 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette 5 ml into a third 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. (final conc 5 µg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram siduron into a 250 ml glass-stoppered or screw-cap flask, add 100 ml methanol by pipette, and shake on a mechanical shaker for 30 minutes. Allow to settle; centrifuge or filter if necessary, taking precautions to prevent evaporation. Pipette 10 ml into a 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette 5 ml of this solution into another 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. (final conc 5 µg siduron/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen at 0 and 100% transmission at 240 nm with

methanol in each cell. Scan both the standard and sample from 300 nm to 200 nm with methanol in the reference cell.

Measure the absorbance of standard and sample at 240 nm.

Calculation:

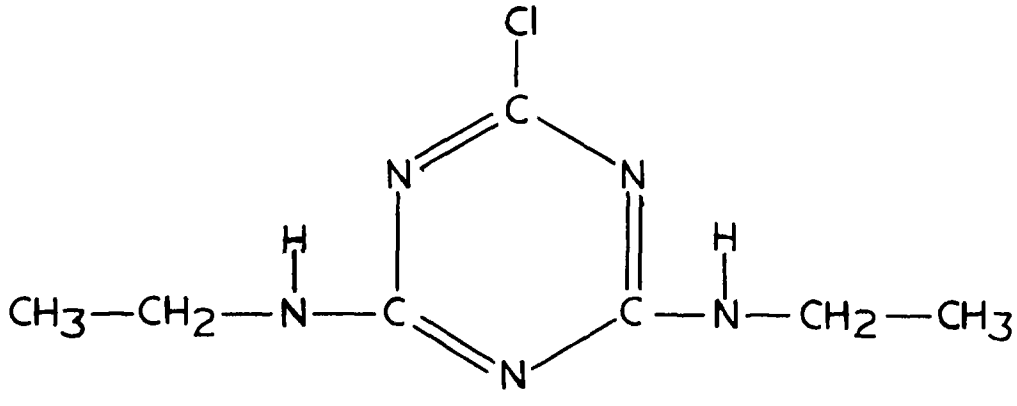
From the above absorbances and using the standard and sample concentrations, calculate the percent siduron as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

Method submitted by Stelios Gerazounis, EPA Region II, New York, N. Y.

Determination of Simazine in 0.1% Aqueous Suspension by Ultraviolet Spectroscopy

Simazine is the accepted common name for 2-chloro-4,6-bis (ethylamino)-s-triazine, a registered herbicide having the chemical structure:



Molecular formula: $C_7H_{12}ClN_5$

Molecular weight: 201.7

Melting point: 225 to 227°C

Physical state and color: white, crystalline solid

Solubility: at 20°C, 2 ppm in petroleum ether, 5 ppm in water, 400 ppm in methanol, and 900 ppm in chloroform; considered slightly soluble in chloroform, dioxane, and ethylcellosolve

Stability: stable in neutral or slightly acidic or basic media; hydrolyzed by stronger acids and bases, especially at higher temperatures; non-corrosive

Other names: Princep, Gesatop, Primatol, and Printop (CIBA-GEIGY); Simanex

This method is designed specifically for 0.1% aqueous suspensions; however, it may be used for other simazine formulations with appropriate modifications when there is no interference at the 263 mμ maxima.

Reagents:

1. Simazine standard of known purity
2. Methanol - ACS

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm silica cells
2. Steam bath
3. Flow of dry, clean air
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.05 gram of simazine standard into a 100 ml volumetric flask; dissolve and make to volume with methanol. Mix thoroughly. Pipette 5 ml into a second 100 ml volumetric flask, make to volume, and mix well. (final conc 25 μg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.0025 gram simazine (2.5 g of 0.1% formulation) from a weighing buret into a 50 ml beaker and take to dryness on a steam bath with a current of clean, dry air. Transfer the residue to a 100 ml volumetric

flask with small portions of methanol, make to volume with methanol, and mix thoroughly. Filter through Whatman No. 5 just prior to UV determination. (final conc 25 µg simazine/ml)

UV Determination:

Using the optimum quantitative settings for the particular UV instrument being used, adjust the 0 and 100% settings at 263 mµ with methanol in both cells. Scan both standard and sample from 360 mµ to 230 mµ.

Calculation:

Measure the absorbance (A) of both standard and sample at 263 mµ (maxima) and 300 mµ (base point). Calculate the percent of simazine as follows:

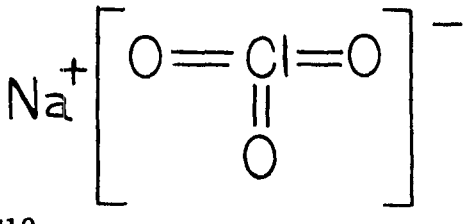
$$\% = \frac{(A_{263}-A_{300}\ \text{sample})(\text{conc. std in } \mu g/ml)(\%\ \text{purity std})}{(A_{263}-A_{300}\ \text{std})(\text{conc. sample in } \mu g/ml)}$$

The absorbance is linear for the concentration range of 0-50 µg/ml in methanol.

Method submitted by Dean Hill, EPA Region IX, San Francisco, California.

Determination of Sodium Chlorate in Herbicides by Reduction and Titration

Sodium chlorate is a registered herbicide, having the chemical structure:



Molecular formula: $NaClO_3$

Molecular weight: 106.4

Melting point: 248°C; decomposes about 300°C with evolution of oxygen

Physical state, color, odor, and taste: white to pale yellow, odorless crystals with a salty taste

Solubility: soluble in water 79 g/100 ml at 0°C and 230 g/100 ml at 100°C; somewhat soluble in alcohol and glycerol

Stability: DANGEROUSLY FLAMMABLE!; strong oxidizing agent, hence serious fire hazard with organic matter, e.g., vegetation, clothing, shoes (easily ignited by friction or heat as on shoestrings or cloth apron strings); DO NOT BURN contaminated clothing or containers. Somewhat corrosive to zinc and mild steel

Other names: Atlacide, Atratole, De-Fol-Ate, Drop-Leaf, Klorex, Fall, Rasikal, Shed-a-Leaf

Principle of the Method:

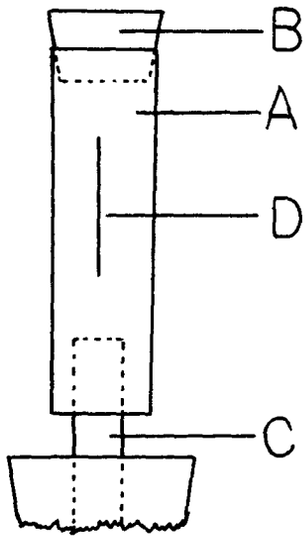
The sodium chlorate in a portion of sample is reacted (reduced) with a known amount (in excess) of ferrous sulfate solution. The ferrous sulfate not used by the sodium chlorate is titrated with standard potassium permanganate solution. An identical amount of ferrous sulfate solution without sample is titrated and the difference used to calculate the sodium chlorate in the sample.

Reagents:

1. Potassium permanganate, 0.1N standard solution
2. Ferrous sulfate solution - dissolve 30 grams of ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) in 900 ml water and make to one liter with concentrated sulfuric acid.
3. Manganese sulfate solution - weigh 14 grams of manganous sulfate tetrahydrate ($MnSO_4.4H_2O$) into 200 ml volumetric flask, add 25 ml sulfuric acid and 25 ml 85% phosphoric acid, and make to volume with water.

Equipment:

1. 300 ml Erlenmeyer flask with rubber stopper fitted with a Bunsen valve (described below)



The Bunsen valve is a short 2-4" length of rubber tubing (A) stoppered at one end (B) and fitted over a piece of glass tubing (C) at the other end. A 1/2-3/4" slit (D) is made with a razor blade along the length of the tubing. This slit allows internal pressure to be relieved by allowing gases to escape, but is sealed as outside pressure pushes in since the sides of the slit are pressed together.

2. Mechanical shaker
3. Filtration apparatus
4. Titration apparatus
5. Usual laboratory glassware

Procedure:

Weigh a portion of sample equivalent to 0.6 gram sodium chlorate into a 500 ml glass-stoppered or screw-cap flask, add exactly 250 ml water, shake on a mechanical shaker for two hours, and filter. Pipette a 25 ml aliquot into a 300 ml Erlenmeyer flask, add by pipette 30 ml ferrous sulfate solution, close tightly with a rubber stopper fitted with a Bunsen valve (to prevent oxidation by air), and boil 10 minutes.

Cool, dilute to about 100 ml with water, add 10 ml of the manganese sulfate solution, and mix well. Titrate with 0.1N potassium permanganate solution to the first distinct pink color. The endpoint is not permanent due to the oxidation of the chloride by the permanganate.

Repeat the same procedure using an identical 30 ml portion of the ferrous sulfate solution but no sample solution. The difference between these two titrations in ml of 0.1N potassium permanganate represents the sodium chlorate in the aliquot of sample solution.

Calculation:

From the difference in titration, calculate the percent sodium chlorate as follows:

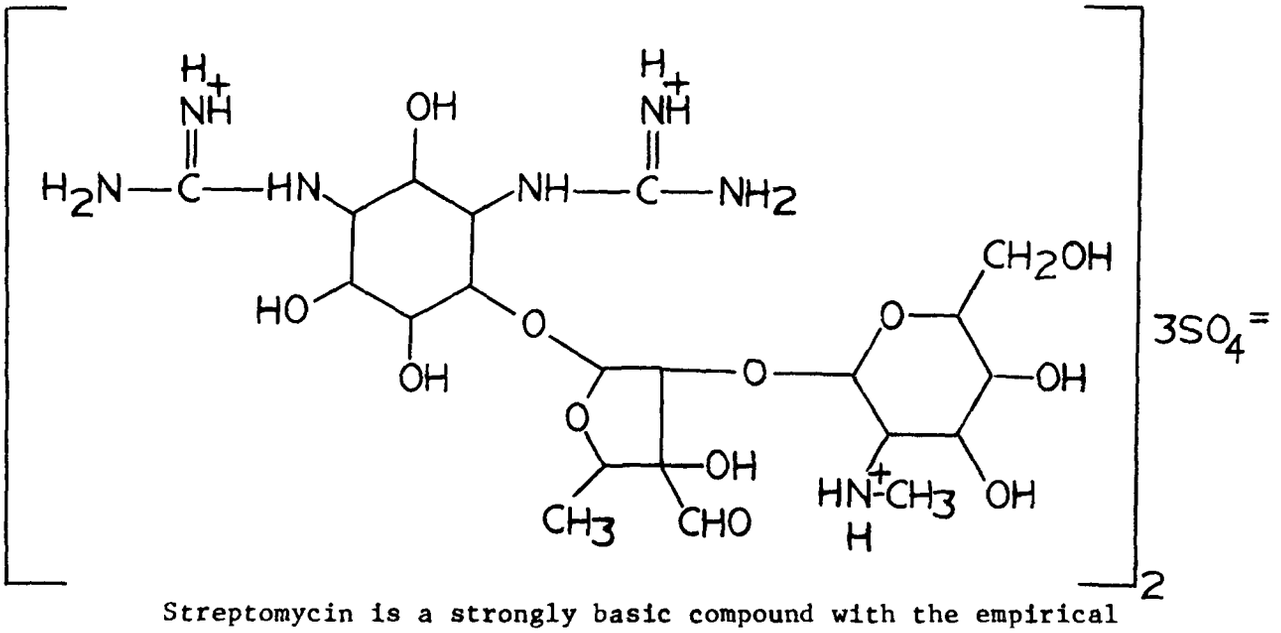
net ml 0.1N $KMnO_4$ = ml used for $FeSO_4$ alone - ml used for $FeSO_4$ and sample

$$\% \ NaClO_3 = \frac{(\text{net ml } KMnO_4)(\text{N } KMnO_4)(0.01774)(100)}{(\text{gram sample})(25/250)}$$

0.01774 = milliequivalent weight of $NaClO_3$

Determination of Streptomycin by Ultraviolet or Colorimetric Spectroscopy

Streptomycin is a registered plant bactericide used for the control of commercially important bacterial plant pathogens. It is usually marketed as the sulfate, nitrate, or hydrochloride. The structure of di-base tris-sulfate is:



Streptomycin is a strongly basic compound with the empirical formula $C_{21}H_{39}N_7O_{12}$; molecular weight 581.6; it is triacidic and forms salts with acids (as above where 2 molecules of the base combine with 3 molecules of sulfuric acid); it is not affected seriously by exposure to light and air, but is hygroscopic and quite readily deliquesces; its solutions are reasonably stable over the pH range 3 to 7; it is stable when dry.

Streptomycin sulfate molecular formula: $(C_{21}H_{39}N_7O_{12})_2 \cdot 3H_2SO_4$ (molecular weight: 1457.44) is a white or practically white powder; it is odorless or has a very faint odor; it is hygroscopic, but stable toward air and light; it is very slightly soluble in alcohol and

practically insoluble in chloroform, but is freely soluble in water; its solutions are acid to nearly neutral litmus.

Other names: Agrimycin, Agri-Strep, streptomycine (France), streptomycin sulfate, streptomycin nitrate, streptomycin hydrochloride

Principle of the Method:

Streptomycin compounds are subjected to an aqueous alkaline hydrolysis to form maltol which is determined by UV at 324 nm in the aqueous alkaline solution. Alternatively, the aqueous alkaline maltol solution can be neutralized with acid, treated with ferric chloride to produce a purple-red color, and determined by reading in the visible range at 530 nm.

Reagents:

1. Streptomycin (base or salt) standard of known % purity
2. Sodium hydroxide, 1N solution
3. Hydrochloric acid, 1.2N solution
4. Hydrochloric acid, 0.1N solution
5. Ferric chloride, 10% solution
6. Ferric chloride, 0.25% solution - prepare fresh daily by pipetting 2.5 ml 10% ferric chloride solution and 10 ml 0.1N hydrochloric acid solution into a 100 ml volumetric flask and make to volume with water.

Equipment:

1. Ultraviolet-visible spectrophotometer, double beam ratio recording with matched 1 cm silica cells
2. Boiling water bath
3. Ice water bath
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.12 gram streptomycin base or 0.15 gram streptomycin sulfate into a 250 ml volumetric flask; dissolve in and make to volume with water, and mix thoroughly. This solution must be stored in a refrigerator and should be made fresh at least every 2 weeks. (conc 0.48 mg streptomycin base or 0.6 mg streptomycin sulfate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.12 gram streptomycin base or 0.15 gram streptomycin sulfate into a 250 ml volumetric flask, dissolve in, make to volume with water, and mix thoroughly. (conc 0.48 mg streptomycin base or 0.6 mg streptomycin sulfate/ml)

Determination:

Pipette 10 ml of standard solution into a 25 ml volumetric flask, 10 ml of sample solution into a second 25 ml volumetric flask, and 10 ml water (for blank) into a third 25 ml volumetric flask. Add, by pipette, 2 ml 1N sodium hydroxide solution to each of the 3 flasks and heat in a boiling water bath for 10 minutes. Cool in an ice water bath for three minutes.

A determination in the ultraviolet region can be made at this point by making each of the 3 flasks to volume with water, mixing well, and diluting a 10 ml aliquot of each to 50 ml with water. Standard and sample solutions are scanned from 360 nm to 260 nm using the blank solution as reference. Measure the analytical peak at 324 nm.

For a colorimetric determination in the visible region, a purple-red color is developed as follows: to each of the 3 flasks, add 2 ml 1.2N hydrochloric acid to neutralize the sodium hydroxide,

add 5 ml 0.25% ferric chloride solution, make to volume with water, and mix thoroughly. Scan the standard and sample solutions from 650 nm to 450 nm using the blank solution as reference. Measure the analytical peak at 530 nm.

Calculations:

From the absorbances and concentrations of standard and sample, calculate the percent streptomycin base or streptomycin sulfate as follows:

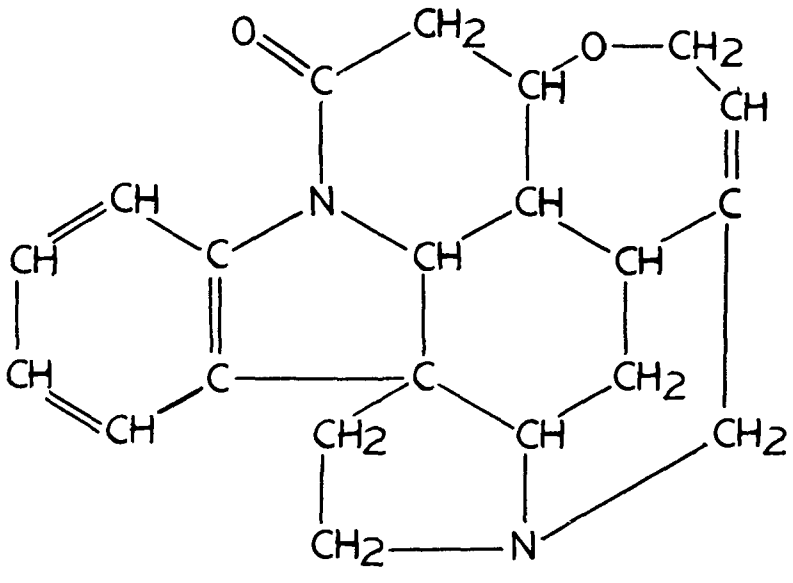
$$\% = \frac{(\text{abs. sample})(\text{conc. standard})(\% \text{ purity standard})}{(\text{abs. standard})(\text{conc. sample})}$$

% streptomycin sulfate = 1.253 x % streptomycin

% streptomycin = 0.7978 x % streptomycin sulfate

Determination of Strychnine in Poisoned Baits (Picric acid precipitation)

Strychnine is a registered rodenticide having the chemical structure:



Molecular formula: $C_{21}H_{22}N_2O_2$

Molecular weight: 334.4

Melting point: 268 to 290°C (depending on the speed of heating) with decomposition; b.p. 270°C at 5 mm

Physical state, color, and odor: hard white crystals or powder, very bitter taste; very poisonous!

Solubility: practically insoluble in water, alcohol, ether; slightly soluble in benzene, chloroform

Stability: forms salts with acids; ppt by alkaloid precipitants (e.g., picric acid as in this method)

Other names: Kwik-kil, Mouse-tox, Ro-Dec

Strychnine generally is used as the sulfate; poison baits usually are colored grain containing 0.5 to 1% strychnine sulfate.

Strychnine sulfate is a white crystalline powder containing 5 moles of water of crystallization lost at 110°C; moderately soluble in water and alcohol, insoluble in ether; mol. formula: $(C_{21}H_{22}N_2O_2)_2$-$H_2SO_4.5H_2O$; mol. wt. 856.96; m.p. above 199°C.

Principle of the Method:

Strychnine is extracted from the poison bait formulations using an ether-chloroform solvent mixture with some ammonium hydroxide solution to convert salts to the free alkaloid. After lead acetate and sodium oxalate treatments, the strychnine is precipitated with picric acid and weighed as strychnine picrate.

Reagents:

1. Ether-chloroform mixture (2 parts ~~ethanol~~ ether + 1 part chloroform)
2. Ammonium hydroxide, 10% solution
3. Corn syrup (such as white Karo)
4. Ethyl ether
5. Hydrochloric acid, 0.5% solution
6. Acetic acid
7. Neutral lead acetate, 10% aqueous solution
8. Sodium oxalate, 3% aqueous solution
9. Picric acid, saturated aqueous solution (1 g/100 ml)

All chemicals and solvents, ACS or reagent grade

Equipment:

1. Usual laboratory glassware
2. Filter paper (Whatman No. 1 and No. 30 or equivalent)
3. Gooch crucible, prepared with filter pad, dried, and weighed

Procedure:

Weigh a portion of finely ground sample equivalent to about 0.1 gram strychnine or 0.13 gram of strychnine sulfate into a 300 ml Erlenmeyer flask. Add (conveniently at 3:00 p.m.) 150 ml of (2+1) ether-chloroform mixture and stopper tightly. Allow to stand 30 minutes with occasional agitation. Add 25 ml of 10% ammonium hydroxide solution, shake one hour, and allow to stand overnight.

In the morning, shake for 15 minutes, add about 5 ml corn syrup (such as white Karo) to clarify the solution, shake again for 15 minutes, and allow to settle. Pour off 100 ml of the solvent layer and transfer to a 250 ml separatory funnel. Add enough ether (approx. 50 ml) to cause the solvent layer to rise to the top in the subsequent extractions. Extract with 0.5% hydrochloric acid, using a 50 ml portion for the first extraction and a 25 ml portion for each of six additional extractions. Collect the extracts in a 400 ml beaker. (A milky emulsion will be formed on shaking, but this should be entirely drained off each time.)

Evaporate the combined extracts to 50 ml, cool, and make alkaline with ammonium hydroxide, avoiding an excess. Make slightly acid with acetic acid and warm gently for a few minutes until a flocculation of the suspended matter takes place. Cool, add 2 ml of 10% neutral lead

acetate solution, transfer to a 100 ml volumetric flask, make to volume, and shake thoroughly. Filter through dry paper (Whatman #1 or equivalent) into a dry 100 ml glass-stoppered graduated cylinder without washing and note the volume obtained. Add 3.0 ml of 3% sodium oxalate solution, shake thoroughly, and allow to stand for 15 minutes. Again filter through a dry paper (Whatman No. 30 or equivalent) into a dry 100 ml glass-stoppered cylinder without washing and note the volume obtained.

Transfer to a 250 ml beaker, evaporate to 70 ml, and cool. Add 25 ml of a recently filtered saturated picric acid solution and allow to stand for 3 hours with occasional stirring during the first half hour. Filter on a tared Gooch crucible and wash with 50-80 ml cold water. Dry at 105°C and weigh.

Calculations:

$$\% \text{ strychnine} = \frac{(\text{grams strychnine picrate})(0.5934)(100)}{(\text{gm sample})(100/150)(X/100)(Y/X + 3)}$$

where: 0.5934 = factor for strychnine picrate to strychnine

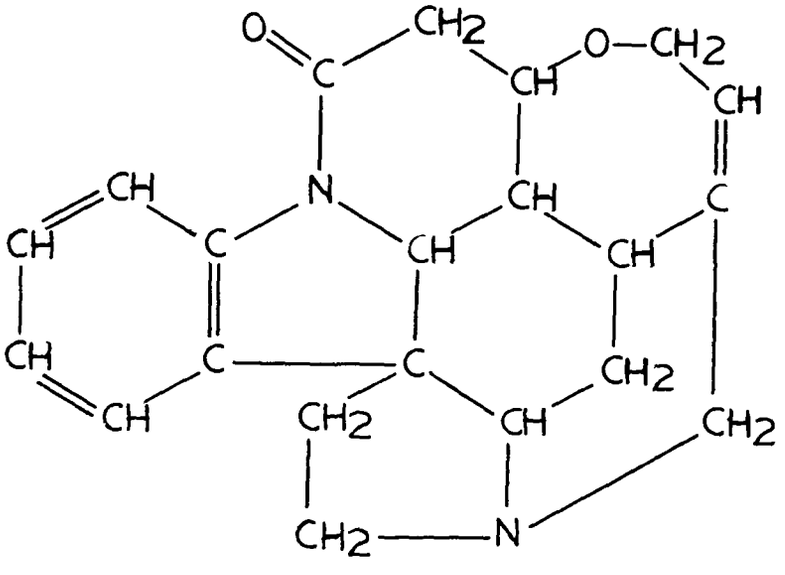
X = ml collected from first filtration (after lead acetate addition)

Y = ml collected from 2nd filtration (after sodium oxalate addition)

% strychnine sulfate = % strychnine X 1.281

Determination of Strychnine in Commercial Bait Formulations by Ultraviolet Spectroscopy

Strychnine is a registered rodenticide having the chemical structure:



Molecular formula: $C_{21}H_{22}N_2O_2$

Molecular weight: 334.4

Melting point: 268 to 290°C (depending on the speed of heating) with decomposition; b.p. 270°C at 5 mm

Physical state, color, and odor: hard white crystals or powder, very bitter taste; very poisonous!

Solubility: practically insoluble in water, alcohol, ether; slightly soluble in benzene, chloroform

Stability: forms salts with acids; ppt by alkaloid precipitants (e.g., picric acid as in this method)

Other names: Kwik-kil, Mouse-tox, Ro-Dec

Principle of the Method:

Strychnine is extracted from the sample with a 0.5% sulfuric acid solution. The extract is cleaned up and the strychnine determined by the difference in absorbance at 254 and 287 nm using a concentration of 10-20 µg/ml.

This method is not suitable for commercial strychnine sulfate formulations. The rodenticide seems to be complexed or associated with the carrier in these products, and the strychnine sulfate is not quantitatively extracted by the sulfuric acid solution. (Use EPA-1 for the sulfate)

Reagents:

1. Strychnine standard of known % purity
2. Sulfuric acid solution, 0.5% V/V solution
3. Concentrated ammonium hydroxide
4. Chloroform, ACS
5. Ethyl ether, ACS

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm absorption cells
2. Mechanical shaker
3. Ultrasonic cleaner (useful for dissolving standard but not essential)
4. Steam bath
5. Hot plate
6. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram strychnine standard into a 100 ml volumetric flask, add about 90 ml 0.5% sulfuric acid solution, stopper tightly, and shake to dissolve the strychnine. (Dissolution of the strychnine may be hastened by placing the volumetric flask in an ultrasonic bath for a few minutes.) Make to volume and mix thoroughly. Pipette 15 ml into a second 100 ml volumetric flask, make to volume with the 0.5% sulfuric acid solution, and mix thoroughly.

Prepare three dilutions by pipetting 5, 10, and 15 ml into separate 100 ml volumetric flasks and making each to volume with 0.5% sulfuric acid. Mix each flask thoroughly. (final concs 7.5, 15.0, and 22.5 µg/ml)

(If a direct standard - sample comparison is to be made, use 15 µg/ml conc for the standard.)

Preparation of Sample:

Uniformly coated bait materials may be used directly but non-uniform materials should be ground to a fine powder.

Weigh a portion of sample equivalent to 0.025 gram of strychnine into a 250 ml glass-stoppered or screw-cap flask, add by pipette 100 ml 0.5% sulfuric acid solution, and shake on a mechanical shaker for 6 hours. Let sample stand overnight. Shake an additional half-hour the next day, allow to settle, and filter. Transfer a 25 ml aliquot into a 100 ml volumetric flask, and make to volume with 0.5% sulfuric acid solution. Mix thoroughly and pipette 25 ml into a 125 ml separatory funnel.

Add 2 ml concentrated ammonium hydroxide to the separatory funnel and shake. The solution should be basic; if not, add more ammonium hydroxide. Extract with four 25 ml portions of chloroform,

draining each extract through plug of cotton (prewashed with chloroform) into 400 ml beaker. Transfer all emulsions which form during the extraction onto the cotton. Extract the solution once more with 50 ml chloroform and drain through the cotton. Wash the cotton with 15 ml chloroform and squeeze out the excess.

Add three glass beads to the beaker and evaporate the chloroform extract to dryness on a steam bath. Heat until all the chloroform vapor is dissipated. Cool, dry the exterior of the beaker, and add 40 ml 0.5% sulfuric acid solution. Weigh the beaker (with a stirring rod) to two decimal places. Heat on steam bath 20-30 min, bringing liquid into contact with the residue on the side of the beaker, and re-weigh. Add an amount of water to the beaker equal to the weight of that evaporated. (Note: It is desirable to keep the environment of the sample close to, or identical with, that of the reference standard in absorption spectroscopy. For this reason the evaporated water is added twice in handling the sample. The acid concentrations in the standard and sample are, for all practical purposes, the same. However, no appreciable analytical error would be expected if the acid concentration in the sample was significantly weaker than that of the standard.)

Transfer the solution to 250 ml separatory funnel, washing the beaker with two 10 ml portions of 0.5% sulfuric acid solution and adding the liquid to the separatory funnel. Add 50 ml ethyl ether to the separatory funnel and shake for 1 min. (The extraction with ether removes fatty acids or oils which may be present in the strychnine sample.) Drain the aqueous layer into a 250 ml beaker. Wash the ethyl ether layer with two 5 ml portions of 0.5% sulfuric acid solution and add to the beaker. Add three glass beads to beaker and weigh beaker to two decimal places. Heat the liquid to boiling on a hot plate to remove dissolved ether and evaporate to ca 40 ml. Cool to room temperature, dry exterior of beaker, and weigh. Return an amount of water to the beaker equal to that evaporated (see note above).

Transfer the solution to a 100 ml volumetric flask and make to volume with 0.5% sulfuric acid solution; mix thoroughly. (final conc 15.6 µg strychnine/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 254 nm with 0.5% sulfuric acid in each cell. Scan the standard and sample solutions from 350 nm to 225 nm with 0.5% sulfuric acid solution in the reference cell.

Calculation:

Determine the difference in absorbance at 254 and 287 nm (A = abs(254 nm) - abs(287 nm)) for standards and sample. Plot an absorbance vs. concentration curve for the three standards (Beer's law is obeyed), and calculate the percentage strychnine in the sample from the standard curve as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. standard})(\text{purity of standard})(100)}{(\text{abs. stand.})(\text{conc. sample})}$$

The percent strychnine may be determined using a direct standard - sample comparison (without using a standard curve) as follows:

$$\% = \frac{(\text{abs. spl})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. stand.})(\text{conc. sample in } \mu g/ml)}$$

or using dilution factors:

$$\% = \frac{(\text{abs. spl})(g \quad \text{std})(\text{purity std})(1/100)(15/100)(10/100)(100)}{(\text{abs. stand.})(g \quad \text{sample})(1/100)(25/100)(25/100)}$$

Method developed by Lawrence A. Wapensky (Journal of the AOAC, Vol. 52, No. 5, 1969, pages 1015-1016).

(The format of the method has been changed somewhat to conform to the general format as used for the methods in this manual.)

Determination of Free Sulfur in Sulfur Formulations (CS_2 Extraction)

Sulfur is a registered fungicide and acaricide.

Molecular (atomic) formula: S

Molecular (atomic) weight: 32.06

Melting point: 115°C; b.p. 444.6°C

Physical state and color: yellow solid, melting at 115°C to a yellow mobile liquid which darkens and becomes viscous about 160°C. It exists in two allotropic forms: rhombic, m.p. 112.8°C, and monoclinic, m.p. 119°C.

Solubility: practically insoluble in water, slightly soluble in ethanol and ether; the crystalline forms are soluble in carbon disulfide whereas the amorphous forms are not.

Stability: compatible with most other pesticides, except petroleum oils; slowly hydrolyzed by water (detectable when a product of hydrolysis is removed, as in the tarnishing of silver or its reaction with alkalis)

Other names: Brimstone; Flowers of sulfur (= sublimed sulfur); Flour sulfur (= ground rock sulfur); precipitated sulfur

Reagents:

1. Carbon disulfide, ACS

Equipment:

1. Filtration apparatus
2. Exhaust hood
3. Steam bath
4. Drying oven (100-105°C)
5. Usual laboratory glassware

Procedure:

Weigh a portion of sample equivalent to about 0.1 gram of sulfur and transfer to a funnel fitted with dry filter paper. Wash the sample with small portions of dry carbon disulfide, catching the filtrate in a dry weighed beaker. Continue washing until the sulfur is apparently all extracted. (see note at end of procedure)

Evaporate the carbon disulfide in an exhaust hood either over a steam bath or spontaneously at room temperature. (CAUTION - carbon disulfide is extremely flammable!) When the carbon disulfide is completely evaporated, heat the beaker and residue for 15-20 minutes at 100-105°C and weigh. Subtract to determine the weight of elemental sulfur.

Using the above weight, calculate the percent sulfur in the sample as follows:

$$\% \text{ sulfur} = \frac{(\text{wt. elemental sulfur})(100)}{(\text{wt. sample})}$$

Note:

A portion of the sulfur may be present as flowers of sulfur and is not soluble in carbon disulfide. In such cases, the sulfur must be determined by oxidation and precipitation as barium sulfate - see method Sulfur EPA-2. The determined sulfur, calculated to elemental sulfur, is added to the above result to obtain total free sulfur.

If there are any sulfates present in the sample, determine these on a hydrochloric acid solution of the original sample and subtract from the total sulfur determined on the carbon disulfide washed residue. The difference, calculated to elemental sulfur, represents the sulfur from the undissolved flowers of sulfur. This should be added to the carbon disulfide soluble sulfur to give the total free sulfur in the sample.

Determination of Sulfur by Oxidation and Precipitation as Barium Sulfate

Sulfur is a registered fungicide and acaricide.

Molecular (atomic) formula: S

Molecular (atomic) weight: 32.06

Melting point: 115°C; b.p. 444.6°C

Physical state and color: yellow solid, melting at 115°C to a yellow mobile liquid which darkens and becomes viscous about 160°C. It exists in two allotropic forms: rhombic, m.p. 112.8°C, and monoclinic, m.p. 119°C.

Solubility: practically insoluble in water, slightly soluble in ethanol and ether; the crystalline forms are soluble in carbon disulfide whereas the amorphous forms are not.

Stability: compatible with most other pesticides, except petroleum oils; slowly hydrolyzed by water (detectable when a product of hydrolysis is removed, as in the tarnishing of silver or its reaction with alkalis)

Other names: Brimstone; Flowers of sulfur (= sublimed sulfur); Flour sulfur (= ground rock sulfur); precipitated sulfur

Reagents:

1. Fuming nitric acid (specific gravity 1.49-1.50)
2. Concentrated hydrochloric acid
3. 10% Barium chloride solution

Equipment:

1. 300 ml Erlenmeyer soil flask with an air condenser connected by ground glass joints
2. Steam bath
3. Hot plate
4. Filtration apparatus
5. Platinum Gooch crucible, previously ignited and weighed
6. Muffle furnace
7. Usual laboratory glassware

Procedure:

Weigh a portion of sample equivalent to 0.025 to 0.035 gram sulfur into a 300 ml Erlenmeyer soil flask fitted with an air condenser by means of a ground glass joint. Add cautiously (through the condenser) 25 ml fuming nitric acid in small portions, taking about 15 minutes to make the addition so that the reaction does not become violent. Let stand for one-half hour, swirling gently from time to time to mix thoroughly. Heat gently on a covered steam bath, and when the reaction slows, heat in direct contact with steam for one hour.

Cool, wash down the inside of the condenser, and quantitatively transfer the contents of the flask to a beaker. Evaporate to dryness, add 3 ml hydrochloric acid, and again evaporate to dryness. Repeat the addition of hydrochloric acid and the evaporation to dryness two more times. Dissolve the residue in about 5 ml water and 5 ml hydrochloric acid, quantitatively transfer to a 250 ml volumetric flask, make to volume with water, and mix thoroughly.

Pipette a 50 ml aliquot into a 600 ml beaker, dilute to about 400 ml with water, and add 10 ml hydrochloric acid. Heat nearly to boiling and add slowly, dropwise with stirring, sufficient 10% barium chloride solution to precipitate the sulfur as barium sulfate. Wash down the sides of the beaker, and heat just under the boiling point for one hour.

Filter through a previously ignited and weighed Gooch crucible, wash, dry, and ignite in a muffle furnace at 550-650°C. Weigh as barium sulfate.

Calculate the percent sulfur in the sample as follows:

$$\% \text{ Barium sulfate} = \frac{(\text{wt. of precipitate})(100)}{(\text{wt. sample})(50/250)}$$

$$\% \text{ Sulfur} = (0.1374)(\% \text{ barium sulfate})$$

Determination of Sulfur in Dusting Mixtures in the Presence of Acetone-Soluble Pesticides

Sulfur is a registered fungicide and acaricide.

Molecular (atomic) formula: S

Molecular (atomic) weight: 32.06

Melting point: 115°C; b.p. 444.6°C

Physical state and color: yellow solid, melting at 115°C to a yellow mobile liquid which darkens and becomes viscous about 160°C. It exists in two allotropic forms: rhombic, m.p. 112.8°C, and monoclinic, m.p. 119°C.

Solubility: practically insoluble in water, slightly soluble in ethanol and ether; the crystalline forms are soluble in carbon disulfide whereas the amorphous forms are not.

Stability: compatible with most other pesticides, except petroleum oils; slowly hydrolyzed by water (detectable when a product of hydrolysis is removed, as in the tarnishing of silver or its reaction with alkalis)

Other names: Brimstone; Flowers of sulfur (= sublimed sulfur); Flour sulfur (= ground rock sulfur); precipitated sulfur

Reagents:

1. Acetone, sulfur-saturated - prepare by adding an excess of sulfur to acetone, warm gently to effect solution, then cool to room temperature. Filter before using.
2. Carbon disulfide, ACS

Equipment:

1. 125 ml glass-stoppered flask, preferably with a pour-out lip
2. Filter paper equivalent to S&S No. 590 or Whatman No. 40
3. Short-stemmed funnel
4. Dry, weighed 150 ml beaker

Procedure:

Weigh a portion of sample equivalent to about 0.2-0.3 gram sulfur into a glass-stoppered 125 ml Erlenmeyer flask (preferably with pour-out lip), add 50 ml of the sulfur-saturated acetone, stoppered tightly, and shake for several minutes to dissolve all the acetone-soluble pesticides and other acetone-soluble substances. Filter, transferring the insoluble residue containing the sulfur to the paper with small portions of sulfur-saturated acetone. Wash the residue several times with small portions of the sulfur-saturated acetone to remove all traces of acetone-soluble substances.

Allow the acetone to volatilize from the original flask and filter paper, place a dry, weighed 150 ml beaker under the funnel, and wash the flask and residue with carbon disulfide. Continue the washing of the residue with carbon disulfide until all the sulfur has apparently been removed. Evaporate the carbon disulfide gently on a steam bath. When the odor of carbon disulfide is no longer present, dry in an oven at 105°C for 15 minutes. CAUTION - carbon disulfide is extremely flammable!

Cool, weigh, and calculate the percent carbon disulfide soluble sulfur as follows:

$$\% \text{ Sulfur} = \frac{(\text{wt. residue})(100)}{(\text{wt. sample})}$$

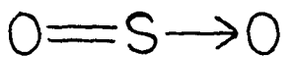
Note: The recovered sulfur should be free of plant extractives; however, if it appears to contain small quantities, they may be removed as follows:

Add 25 ml of the sulfur-saturated acetone and with the aid of a rod flattened on one end, disintegrate the residue in such a manner that acetone comes in contact with all the sulfur crystals. Filter the dissolved plant extractives through a weighed Gooch crucible that has been fitted with a disk of filter paper. Rinse the sulfur from the beaker into the paper and wash under suction with the sulfur-saturated acetone. Allow the acetone to evaporate under suction for about 10 minutes; then dry the crucible in an oven at 105°C for 15 minutes. Cool, weigh, and re-calculate the percent sulfur as above.

Should the sample contain flowers of sulfur or be below the declared percentage, determine sulfur by EPA-2.

Determination of Sulfur Dioxide in Fumigants by Iodometry

Sulfur dioxide is a registered fumigant, having the chemical structure:



Molecular formula: SO_2

Molecular weight: 64.07

Boiling point: -10°C

Physical state, color, and odor: colorless gas with a strong suffocating odor characteristic of burning sulfur; under pressure condenses readily to a colorless liquid

Solubility: soluble in water, alcohol, ether, chloroform; forms sulfurous acid, H_2SO_3, with water

Stability: nonflammable; an outstanding oxidizing and reducing agent; CAUTION - extremely irritating to eyes and respiratory tract

Other names: sulfurous acid anhydride, sulfurous oxide

Reagents:

1. Iodine solution, 0.1N standardized solution
2. Sodium thiosulfate solution, 0.1N standardized solution
3. Acetic acid, ACS

Equipment:

1. Titration apparatus
2. Usual laboratory glassware

Principle of the Method:

Since sulfur dioxide is volatile, the product container should not be opened until just before the sample portion is to be removed. Loss of sulfur dioxide is minimized by weighing the sample, by difference, directly in a known amount of acidified iodine solution. The excess is titrated and the sulfur dioxide calculated from the iodine solution used.

Procedure:

Pipette 50 ml 0.1N iodine solution into a 125 ml glass-stoppered flask, add 5 ml acetic acid, stopper, and weigh accurately.

Transfer a portion of sample equivalent to 0.1 gram sulfur dioxide into the flask with swirling, restopper, weigh, and obtain the sample weight by difference.

Titrate the excess iodine solution with 0.1N sodium thiosulfate solution. Starch indicator is usually not necessary, but may be used close to the end of the titration.

Calculation:

Calculate the sulfur dioxide as follows:

$$\% = \frac{[(\text{ml } I_2)(\text{N}I_2) - (\text{ml } Na_2S_2O_3)(\text{N } Na_2S_2O_3)](0.03203)(100)}{(\text{wt. sample in grams})}$$

If an identical 50 ml portion of the 0.1N iodine solution is titrated (without sample), then calculate the sulfur dioxide as follows:

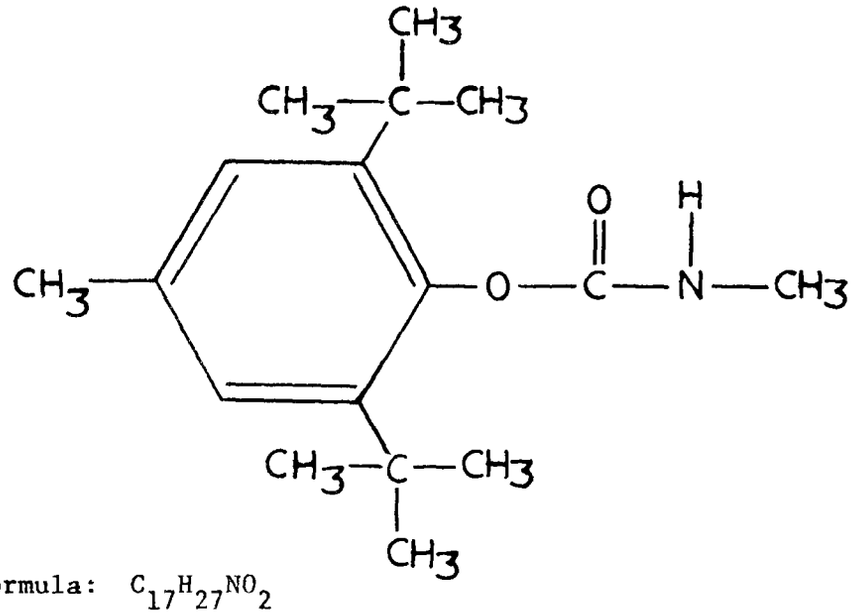
$$\% = \frac{(\text{ml difference } Na_2S_2O_3)(\text{N } Na_2S_2O_3)(0.03203)(100)}{(\text{wt. sample in grams})}$$

December 1975

Terbutol EPA-1
(Tentative)

Determination of Terbutol by Infrared Spectroscopy

Terbutol is the common name (WSSA) for 2,6-di-tert-butyl-p-tolyl methylcarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{17}H_{27}NO_2$

Molecular weight: 277.4

Melting point: 200 to 201°C; the technical product is 95% and has a mp of 185 to 190°C

Physical state, color, and odor: white, odorless, crystalline solid

Solubility: 7 ppm in water at 25°C; insoluble in hexane and kerosene; slightly soluble in benzene and toluene; soluble in acetone and ethanol

Stability: decomposes at melting point; nonflammable; compatible with hard water, other pesticides, and fertilizer; non-corrosive; stable on storage

Other names: Azak (Hercules, Inc.), Hercules 9573, Terbucarb

Reagents:

1. Terbutol standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker
3. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.08 gram terbutol standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, close tightly, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 8 mg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.8 gram terbutol into a glass-stoppered flask or screw-cap tube. Add 100 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precautions to prevent evaporation. (final conc 8 mg terbutol/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1925 cm^{-1} to 1580 cm^{-1} (5.2 μ to 6.3 μ).

Determine the absorbance of standard and sample using the peak at 1754 cm^{-1} (5.7 μ) and a baseline from 1835 cm^{-1} to 1695 cm^{-1} (5.45 μ to 5.9 μ).

Calculation:

From the above absorbances and using the standard and sample solution concentrations, calculate the percent terbutol as follows

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Beer's law is obeyed over the range 1-14 mg/ml.

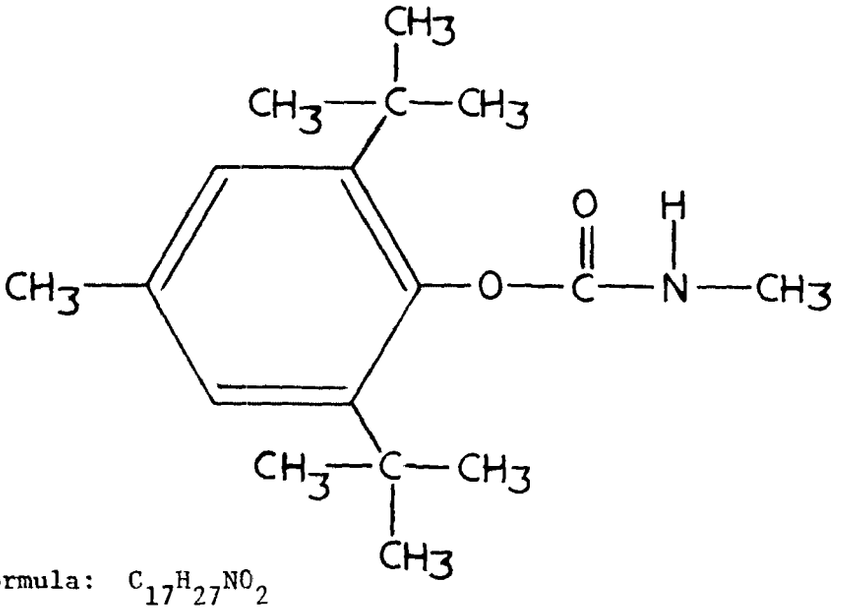
Method submitted by Dean Hill, EPA Region IX, San Francisco, Calif.

December 1975

Terbutol EPA-2
(Tentative)

Determination of Terbutol by Gas-Liquid Chromatography (FID - Internal Standard)

Terbutol is the common name (WSSA) for 2,6-di-tert-butyl-p-tolyl methylcarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{17}H_{27}NO_2$

Molecular weight: 277.4

Melting point: 200 to 201°C; the technical product is 95% and has a mp of 185 to 190°C

Physical state, color, and odor: white, odorless, crystalline solid

Solubility: 7 ppm in water at 25°C; insoluble in hexane and kerosene; slightly soluble in benzene and toluene; soluble in acetone and ethanol

Stability: decomposes at melting point; nonflammable; compatible with hard water, other pesticides, and fertilizer; non-corrosive; stable on storage

Other names: Azak (Hercules, Inc.), Hercules 9573, Terbucarb

Reagents:

1. Terbutol standard of known % purity
2. Diazinon standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.2 gram diazinon into a 100 ml volumetric flask; dissolve in and make to volume with acetone. (conc 2 mg diazinon/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm I.D. glass column packed with 5% SE-30 on 80/100 Chromosorb W HP (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	165°C
Injection temperature:	215°C
Detector temperature:	215°C
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi (adjusted for specific GC)
Hydrogen pressure:	20 psi (adjusted for specific GC)
Air pressure:	30 psi (adjusted for specific GC)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram terbutol standard into a small glass-stoppered flask or screw-cap bottle, add by pipette 25 ml of the internal standard solution, and shake to dissolve. (final conc 2 mg terbutol and 2 mg diazinon/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.05 gram terbutol into a small glass-stoppered flask or screw-cap bottle; add by pipette 25 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the terbutol. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour (final conc 2 mg terbutol and 2 mg diazinon/µl)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is diazinon, then terbutol.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of terbutol and diazinon from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. diazinon})(\%\text{ purity diazinon})(\text{pk. ht. or area terbutol})}{(\text{wt. terbutol})(\%\text{ purity terbutol})(\text{pk. ht. or area diazinon})}$$

Determine the percent terbutol for each injection of the sample-internal standard solution as follows and calculate the average:

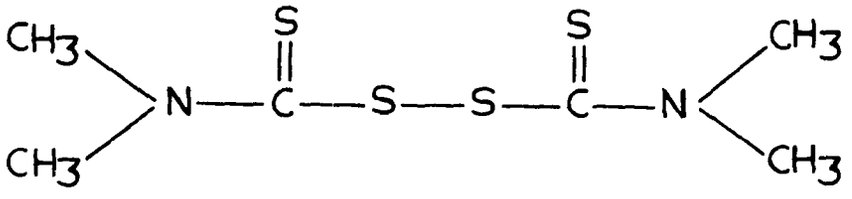
$$\% = \frac{(\text{wt. diazinon})(\%\text{ purity diazinon})(\text{pk. ht. or area terbutol})\cancel{(100)}}{(\text{wt. sample})(\text{pk. ht. or area diazinon})(RF)} \quad (4-1)$$

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

Note: This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Chemistry Lab. Any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated.

Determination of Thiram by Ultraviolet Spectroscopy

Thiram is the official common name for tetramethylthiuram disulfide, a registered fungicide having the chemical structure:



Molecular formula: $C_6H_{12}N_2S_4$

Molecular weight: 240.44

Melting point: 155 to 156°C

Physical state and color: colorless crystals

Solubility: about 30 ppm in water at RT; slightly soluble in ethanol, ether, carbon disulfide; soluble in acetone, chloroform

Stability: stable in storage; in the form of a fine dust it gives explosive mixtures with air.

Other names: Arasan (DuPont), Nomersan (Plant Protection Ltd.), Pomarsol (I. G. Farb.), Tersan, Thylate Spotrete, Thimar, Mercuram, Tuads, Vancide, Hexathir, Fermide, Bis(dimethylthiocarbamoyl)disulphide, TMTD

Reagents:

1. Thiram standard of known % purity
2. Chloroform, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm silica cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram thiram standard into a 100 ml volumetric flask, add 100 ml chloroform by pipette, and mix thoroughly. Pipette 10 ml into a second 100 ml volumetric flask, make to volume with chloroform, and mix thoroughly. Pipette 10 ml into a third 100 ml volumetric flask, make to volume with chloroform, and mix thoroughly. (final conc 10 µg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram thiram into a 250 ml glass-stoppered or screw-cap flask, add 100 ml chloroform by pipette, and shake on a mechanical shaker for 30 minutes. Allow to settle; centrifuge or filter if necessary, taking precautions to prevent evaporation. Pipette 10 ml into a 100 ml volumetric flask, make to volume with chloroform, and mix thoroughly. Pipette 10 ml of this solution into another 100 ml volumetric flask, make to volume with chloroform, and mix thoroughly. (final conc 10 µg thiram/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen at 0 and 100% transmission at 280 nm with

chloroform in each cell. Scan both the standard and sample from 350 nm to 250 nm with chloroform in the reference cell.

Measure the absorbance of standard and sample at 280 nm.

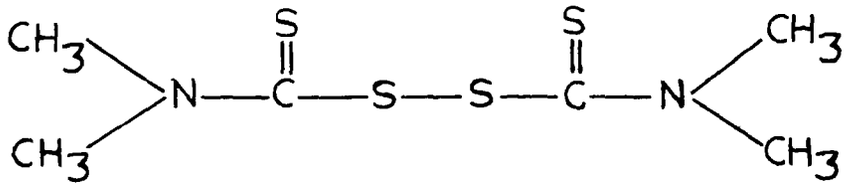
Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent thiram as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

Determination of Thiram by Infrared Spectroscopy

Thiram is the official common name for tetramethylthiuram disulfide, a registered fungicide having the chemical structure:



Molecular formula: $C_6H_{12}N_2S_4$

Molecular weight: 240.44

Melting point: 155 to 156°C

Physical state and color: colorless crystals

Solubility: about 30 ppm in water at RT; slightly soluble in ethanol, ether, carbon disulfide; soluble in acetone, chloroform

Stability: stable in storage; in the form of a fine dust it gives explosive mixtures with air.

Other names: Arasan (DuPont), Nomersan (Plant Protection Ltd.), Pomarsol (I. G. Farb.), Tersan, Thylate, Spotrete, Thimar, Mercuram, Tuads, Vancide, Hexathir, Fermide, Bis(dimethylthiocarbamoyl)disulphide, TMTD

Reagents:

1. Thiram standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.065 gram thiram standard into a small glass-stoppered flask or screw-cap bottle, add 10 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 6.5 mg/ml)

Preparation of Sample:

For dusts, granules, and wettable powder, weigh a portion of sample equivalent to 0.325 gram thiram into a glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 6.5 mg thiram/ml) For very low percent formulations requiring larger samples, use more solvent and evaporate an aliquot to a smaller volume to give a concentration close to 6.5 mg thiram/ml.

For water suspensions a tentative procedure is as follows: weigh a portion of sample equivalent to 0.325 gram thiram into a glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and sufficient anhydrous sodium sulfate to absorb the water and dry and clarify the chloroform solution; shake thoroughly. (final conc 6.5 mg thiram/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both standard and sample from 1430 cm^{-1} to 1300 cm^{-1} (7 μ to 7.7 μ).

Determine the absorbance of standard and sample using the peak at 1380 cm^{-1} (7.25 μ) and baseline from 1400 cm^{-1} to 1350 cm^{-1} (7.14 μ to 7.41 μ).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent thiram as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

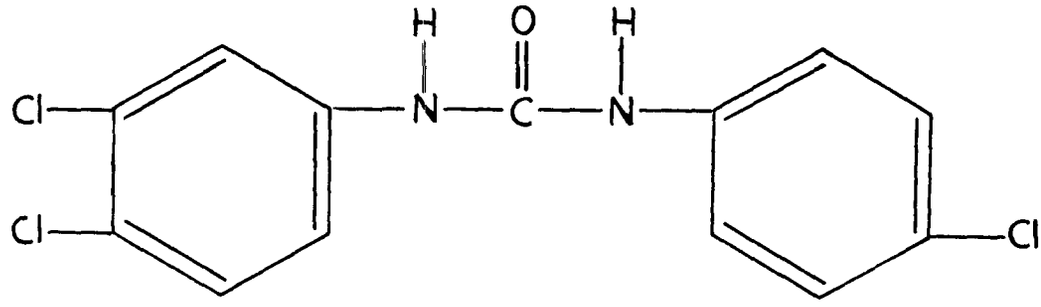
(A concentration of 1 mg thiram/ml chloroform gives an absorbance of approx. 0.046 in a .2 mm cell.)

Method submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services.

(The procedure for water suspensions has successfully been used by EPA's Beltsville Chemistry Lab.)

Determination of Trichlorocarbanilide in Detergents by Ultraviolet Spectroscopy

Trichlorocarbanilide is 3,4,4'-trichlorocarbanilide, a registered bacteriostat and fungistat having the chemical structure:



Molecular formula: $C_{13}H_9Cl_3N_2O$

Molecular weight: 315.6

Melting point: 250°C (minimum)

Physical state, color, and odor: fine white powder; no odor or a slight characteristic odor

Solubility: slightly soluble in dioxane, propylene glycol; soluble in acetone, methyl isobutyl ketone, dimethyl formamide, alcohol

Stability: stable to light and heat; does not discolor by reaction with other materials

Other names: TCC

Reagents:

1. 3,4,4'-trichlorocarbanilide standard of known % purity
2. Ethanol, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Steam bath
3. Filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.07 gram trichlorocarbanilide standard into a 100 ml volumetric flask; dissolve in (warming if necessary) and make to volume with ethanol; mix thoroughly. Pipette 10 ml into a second 100 ml volumetric flask, make to volume with ethanol, and mix thoroughly. Pipette 5 ml into a third 100 ml volumetric flask, make to volume with ethanol, and again mix thoroughly. (final conc 3.5 µg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.0035 gram trichlorocarbanilide (0.7 gram for a 0.5% formulation) into a 100 ml beaker, add 40 ml ethanol, cover with a watch glass, and warm on a steam bath. Filter, collecting the filtrate in a 100 ml volumetric flask. Wash the residue in the beaker by adding another 40 ml ethanol, warming, filtering, and adding the filtrate to the volumetric flask. Transfer the residue from the beaker into the filter and wash with warm alcohol. Cool the extracts and washing in the volumetric flask, make to volume with ethanol, and mix thoroughly. Pipette 5 ml into a 50 ml volumetric, make to volume with alcohol, and mix thoroughly. (final conc 3.5 µg trichlorocarbanilide/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 265 nm with ethanol in each cell. Scan both the standard and sample from 300 nm to 210 nm with distilled water in the reference cell. Measure the absorbance of both standard and sample at 265 nm. (A slight shift to a lower wavelength may occur if moderate interference is present.)

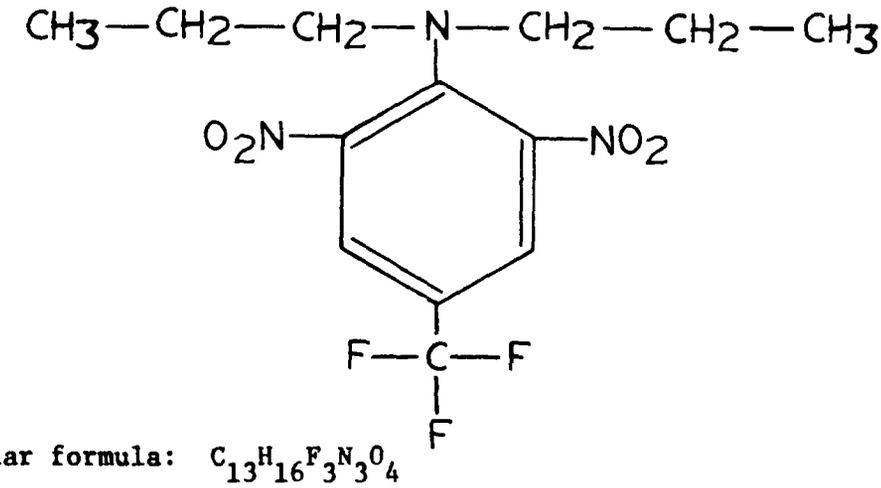
Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent trichlorocarbanilide as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu\text{g/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu\text{g/ml})}$$

Determination of Trifluralin by Gas-Liquid Chromatography (FID - Internal Standard)

Trifluralin is the accepted common name for α,α,α-trifluoro-2,6-dinitro - N,N-dipropyl-p-toluidine, a registered herbicide having the chemical structure:



Molecular formula: $C_{13}H_{16}F_3N_3O_4$

Molecular weight: 335.3

Melting point: 48.5 to 49.0°C (tech. product is at least 95% pure and has a mp greater than 42°C)

Physical state, color, and odor: orange crystalline solid; no appreciable odor

Solubility: less than 1 ppm in water at 27°C; 7% in ethanol, 40% in acetone, 58% in xylene; soluble in other organic solvents

Stability: stable but susceptible to photochemical decomposition

Other names: Treflan (Eli Lilly), Trefanocide, Treficon, Triflurex, Su Seguro Carpidor

Reagents:

1. Trifluralin standard of known % purity
2. Diisobutylphthalate
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.3 gram of diisobutylphthalate into a 25 ml volumetric flask, dissolve in, and make to volume with acetone. (conc 12 mg diisobutylphthalate/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 4 mm glass column packed with 5% SP-2401 on 80/100 mesh Supelcoport AW DMCS (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	200°C
Injection temperature:	210°C
Detector temperature:	275°C
Carrier gas:	Nitrogen
Carrier gas pressure:	(not stated in method)
Hydrogen pressure:	30 psi
Air pressure:	30 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.13 gram trifluralin standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 13 mg trifluralin and 12 mg diisobutylphthalate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.13 gram trifluralin into a small glass-stoppered flask or screw-cap bottle. Add by pipette 10 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the trifluralin. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 13 mg trifluralin and 12 mg diisobutylphthalate/ml)

Determination:

Inject 2-3 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is trifluralin, then diisobutylphthalate.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of trifluralin and diisobutylphthalate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

I.S. = internal standard = diisobutylphthalate

$$RF = \frac{\text{(wt. I.S.)(\% purity I.S.)(pk. ht. or area trifluralin)}}{\text{(wt. trifluralin)(\% purity trifluralin)(pk. ht. or area I.S.)}}$$

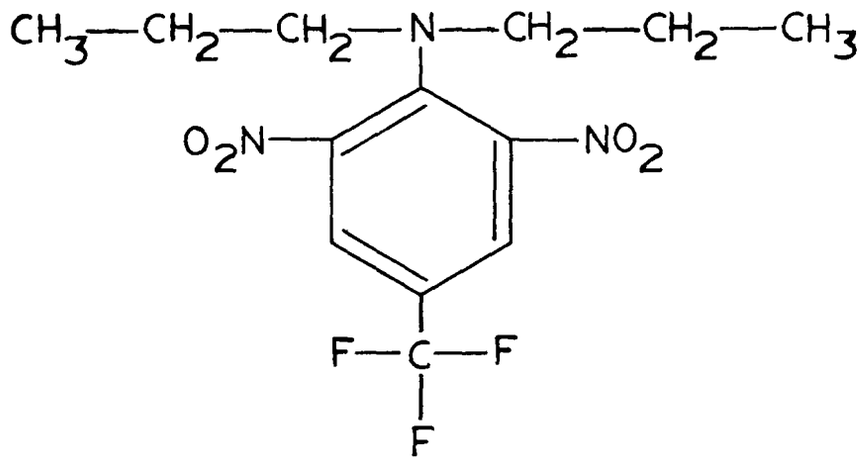
Determine the percent trifluralin for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{\text{(wt. I.S.)(\% purity I.S.)(pk. ht. or area trifluralin)}\cancel{(100)}}{\text{(wt. sample)(pk. ht. or area I.S.)(RF)}} \quad (41)$$

Method submitted by Division of Regulatory Services, Kentucky Agricultural Experiment Station, University of Kentucky, Lexington, Kentucky 40506.

Determination of Trifluralin by Infrared Spectroscopy

Trifluralin is the accepted common name for α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine, a registered herbicide having the chemical structure:



Molecular formula: $C_{13}H_{16}F_3N_3O_4$

Molecular weight: 335.3

Melting point: 48.5 to 49.0°C (tech. product is at least 95% pure and has a mp greater than 42°C)

Physical state, color, and odor: orange crystalline solid; no appreciable odor

Solubility: less than 1 ppm in water at 27°C; 7% in ethanol, 40% in acetone, 58% in xylene; soluble in other organic solvents

Stability: stable but susceptible to photochemical decomposition

Other names: Treflan (Eli Lilly), Trefanocide, Treficon, Triflurex, Su Seguro Carpidor

Reagents:

1. Trifluralin standard of known % purity
2. Acetone, pesticide or spectro grade
3. Carbon disulfide, pesticide or spectro grade
4. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.08 gram trifluralin into a small glass-stoppered flask or screw-cap bottle, add 20 ml carbon disulfide by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 4 mg/ml)

Preparation of Sample:

For emulsifiable concentrates, weigh a portion of sample equivalent to 0.04 gram trifluralin into a 10 ml volumetric flask, make to volume with carbon disulfide, and mix well. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 4 mg trifluralin/ml)

For granular formulations, weigh a portion of sample equivalent to 0.08 gram trifluralin into a glass-stoppered flask or screw-cap bottle. Add 50 ml acetone by pipette and 1-2 grams anhydrous sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. Evaporate a 25 ml aliquot to dryness on a water bath using a gentle stream of dry air; evaporate the last one or two ml with air only. Dissolve in about 4-5 ml carbon disulfide, transfer to a 10 ml volumetric flask, and make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 4 mg trifluralin/ml)

Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan the standard and sample from 1390 cm^{-1} to 1212 cm^{-1} (7.2 μ to 8.25 μ).

Determine the absorbance of standard and sample using the peak at 1300 cm^{-1} (7.69 μ) and baseline from 1315 cm^{-1} to 1264 cm^{-1} (7.6 μ to 7.91 μ).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent trifluralin as follows:

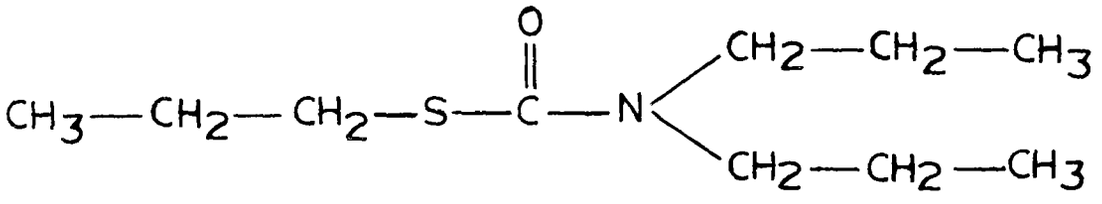
$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

(A concentration of 1 mg trifluralin/ml carbon disulfide gives an absorbance of approx. 0.079 in a 0.2 mm cell.)

Method contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services.

Determination of Vernolate by Infrared Spectroscopy

Vernolate is the common name for S-propyl dipropylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_{21}NOS$

Molecular weight: 203.4

Boiling point: 140°C at 20 mm Hg, 150°C at 30 mm Hg

Physical state, color, and odor: clear liquid with an aromatic odor

Solubility: about 100 ppm in water at 20-21°C; miscible with common organic solvents

Stability: stable; non-corrosive

Other names: Vernam (Stauffer), R-1607, S-propyl N,N-dipropyl thiocarbamate

The method described below is primarily that presently used by the State of Virginia but written into our standard format; however, it is followed by a different set of conditions from a tentative EPA method.

Reagents:

1. Vernolate standard of known % purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.1 mm NaCl or KBr cells
2. Mechanical shaker*
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, put in 1-2 grams anhydrous sodium sulfate, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Procedure:

Preparation of Standard:

Weigh 0.12 gram vernolate standard into a 10 ml volumetric flask, make to volume with chloroform, and mix well. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 12 mg/ml)

Preparation of Sample:

For emulsifiable concentrates, weigh a portion of sample equivalent to 0.6 gram vernolate into a 50 ml volumetric flask, make to volume with chloroform, and mix well. Add a few grams of anhydrous sodium sulfate to insure dryness and clarify the solution. (final conc 12 mg vernolate/ml)

For granular formulations, weigh a portion of sample equivalent to 0.6 gram vernolate into a glass-stoppered flask or

screw-cap bottle. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 12 mg vernolate/ml)

Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1850 cm^{-1} to 1500 cm^{-1} (5.4 μ to 6.7 μ).

Determine the absorbance of standard and sample using the peak at 1630 cm^{-1} (6.13 μ) and basepoint at 1800 cm^{-1} (5.56 μ).

Calculations:

From the above absorbances and using the standard and sample concentrations, calculate the percent vernolate as follows:

$$\% = \frac{\text{(abs. sample)(conc. std in mg/ml)(\% purity std)}}{\text{(abs. std)(conc. sample in mg/ml)}}$$

(A concentration of 1 mg vernolate/ml chloroform gives an absorbance of approx. 0.024 in a 0.1 mm cell.)

The above method was contributed by the Commonwealth of Virginia, Division of Consolidated Laboratory Services.

See EPA method on page 4.

The conditions below are those used in a tentative EPA method -- method developed by George Radan, EPA Region II, New York.

Procedure: same as described above

Solvent: carbon disulfide

Concentration of standard: 6 mg/ml

Concentration of sample: equivalent to 6 mg vernolate/ml

IR cell: 0.5 mm

Scan range: 1250 cm^{-1} to 950 cm^{-1} (8.0 μ to 10.5 μ)

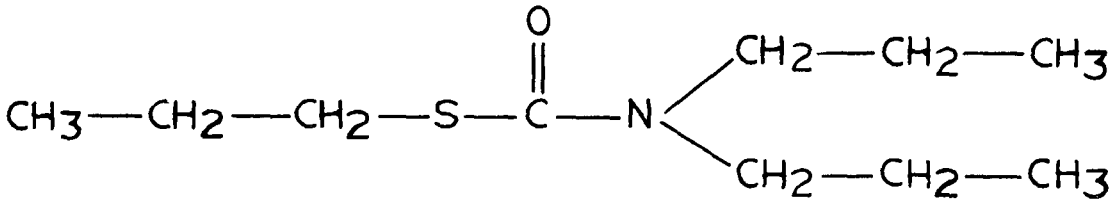
Analytical peak: 1105 cm^{-1} (9.05 μ)

Baseline: 1163 cm^{-1} to 1047 cm^{-1} (8.6 μ to 9.55 μ)

Calculation: same

Determination of Vernolate by Gas-Liquid Chromatography (FID - Internal Standard)

Vernolate is the common name for S-propyl dipropylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_{21}NOS$

Molecular weight: 203.4

Boiling point: 140°C at 20 mm Hg, 150°C at 30 mm Hg

Physical state, color, and odor: clear liquid with an aromatic odor

Solubility: about 100 ppm in water at 20-21°C; miscible with common organic solvents

Stability: stable; non-corrosive

Other names: Vernam (Stauffer), R-1607, S-propyl N,N-dipropyl thiocarbamate

Reagents:

1. Vernolate standard of known % purity
2. Cycloate standard of known % purity
3. Carbon disulfide, pesticide or spectro grade

Reagents (Cont.):

4. Chloroform, pesticide or spectro grade
5. Methanol, pesticide or spectro grade
6. Internal Standard solution - weigh 0.20 gram cycloate into a 50 ml volumetric flask; dissolve in and make to volume with a solvent mixture consisting of 80% carbon disulfide + 15% chloroform + 5% methanol. (conc 4 mg cycloate/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 4 mm glass column packed with 3% OV-1 on 60/80 Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	140°C
Injection temperature:	225°C
Detector temperature:	250°C
Carrier gas:	Nitrogen
Carrier gas pressure:	60 psi
Hydrogen pressure:	20 psi
Air pressure:	30 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.08 gram vernolate standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 4 mg vernolate and 4 mg cycloate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.08 gram vernolate into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the vernolate. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 4 mg vernolate and 4 mg cycloate/ml)

Determination:

Inject 2-3 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is vernolate, then cycloate.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of vernolate and cycloate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{\text{(wt. cycloate)(\% purity cycloate)(pk. ht. or area vernolate)}}{\text{(wt. vernolate)(\% purity vernolate)(pk. ht. or area cycloate)}}$$

Determine the percent vernolate for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{\text{(wt. cycloate)(\% purity cycloate)(pk. ht. or area vernolate)}\cancel{(100)}}{\text{(wt. sample)(pk. ht. or area cycloate)(RF)}} \quad (4\text{-}1)$$

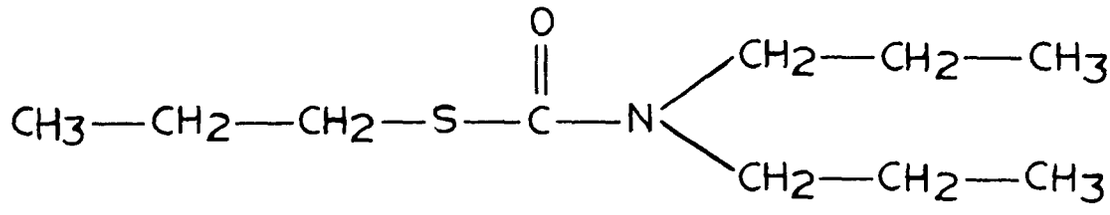
Method submitted by Division of Regulatory Services, Kentucky Agricultural Experiment Station, University of Kentucky, Lexington, Kentucky 40506.

October 1975

Vernolate **EPA-3**
(Tentative)

Determination of Vernolate by Gas-Liquid Chromatography (TCD - Internal Standard)

Vernolate is the common name for S-propyl dipropylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_{21}NOS$

Molecular weight: 203.4

Boiling point: 140°C at 20 mm Hg, 150°C at 30 mm Hg

Physical state, color, and odor: clear liquid with an aromatic odor

Solubility: about 100 ppm in water at 20-21°C; miscible with common organic solvents

Stability: stable; non-corrosive

Other names: Vernam (Stauffer), R-1607, S-propyl N,N-dipropyl thiocarbamate

Reagents:

1. Vernolate standard of known % purity
2. Butylate standard of known % purity
3. Carbon disulfide, pesticide or spectro grade

Reagents (Cont.):

4. Chloroform, pesticide or spectro grade
5. Acetone, pesticide or spectro grade
6. Internal Standard solution - weigh 0.25 gram butylate standard into a 25 ml volumetric flask, dissolve in, and make to volume with a solvent mixture consisting of 80% carbon disulfide + 15% chloroform + 5% acetone. (final conc 10 mg butylate/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 5' x 1/4" glass column packed with 5% PEG-1540 on 60/80 mesh Chromosorb W AW DMCS (or equivalent column)
3. Precision liquid syringe: 25 or 50 µl
4. Mechanical shaker
5. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	150°
Injection temperature:	200°
Detector temperature:	175°
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas flow rate:	30 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram vernolate standard into a small glass-stoppered flask or screw-cap tube. Add by pipette 10 ml of the internal standard solution and shake to dissolve. (final conc 10 mg vernolate and 10 mg butylate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram vernolate into a small glass-stoppered flask or screw-cap tube. Add by pipette 10 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the vernolate. For coarse or granular materials, shake or tumble mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 10 mg vernolate and 10 mg butylate/ml)

Determination:

Inject 10-15 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is butylate, then vernolate.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of vernolate and butylate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{\text{(wt. butylate)(\% purity butylate)(pk. ht. or area vernolate)}}{\text{(wt. vernolate)(\% purity vernolate)(pk. ht. or area butylate)}}$$

Determine the percent vernolate for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{\text{(wt. butylate)(\% purity butylate)(pk. ht. or area vernolate)}\cancel{(100)}}{\text{(wt. sample)(pk. ht. or area butylate)(RF)}} \qquad (4\text{-}1)$$

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Virginia 23219.

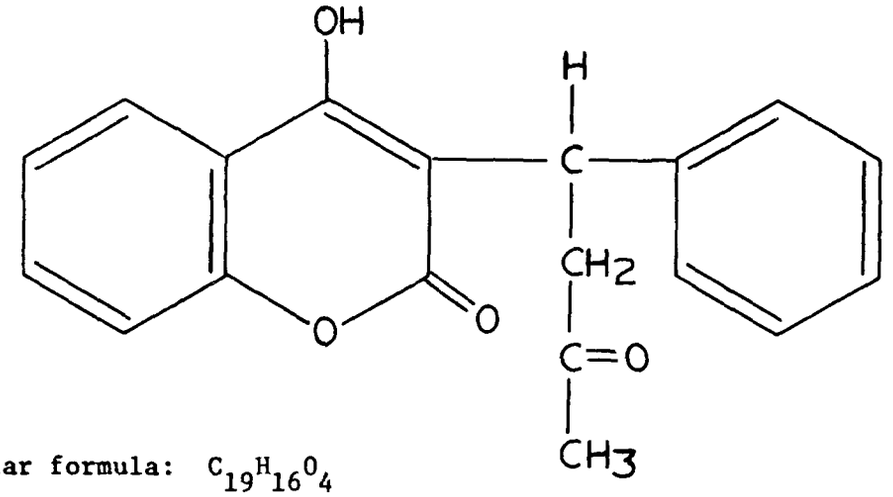
Note! This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Chemistry Lab. Any comments, criticism, suggestion, data, etc. concerning this method will be appreciated.

November 1975

Warfarin EPA-1
(Tentative)

Determination of Warfarin by High Pressure Liquid Chromatography

Warfarin is the official common name for 3-(alpha-acetonylbenzyl)-4-hydroxycoumarin, a registered rodenticide having the chemical structure:



Molecular formula: $C_{19}H_{16}O_4$

Molecular weight: 308.3

Melting point: (dl form) 159 to 161°C

Physical state, color, odor, taste: (dl form) colorless, tasteless, odorless crystals

Solubility: practically insoluble in water and benzene, moderately soluble in alcohols, readily soluble in acetone and dioxane; forms water-soluble salts with sodium

Stability: stable under normal conditions

Other names: WARF (Wisconsin Alumni Research Foundation), coumafene (France), zoocoumarin (Netherlands, USSR), Kypfarin

Reagents:

1. Warfarin standard of known % purity
2. Methanol, pesticide or spectro grade
3. Phosphorous acid solution, 0.0025M in water
4. Dioxane, pesticide or spectro grade

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm. If a variable wavelength UV detector is available, other wavelengths may be useful to increase sensitivity or eliminate interference. Warfarin is more easily determined at 308 nm.
2. Suitable column such as:
   a. DuPont ODS Permaphase, 1 meter x 2.1 mm ID
   b. Perkin-Elmer ODS Sil-X 11 RP, 1/2 meter x 2.6 mm ID
3. High pressure liquid syringe or sample injection loop
4. Usual laboratory glassware

Operating Conditions:

Mobile phase:	10% methanol + 90% 0.0025M H_3PO_4 in water
Column temperature:	50°C
Chart speed:	5 min/inch or equivalent
Flow rate:	0.5 to 1.5 ml/min (Perkin-Elmer 1/2 meter column)
Pressure:	500 psi (DuPont 1 meter column)
Attenuation:	Adjusted

Conditions may have to be varied by the analyst for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram warfarin standard into a 50 ml volumetric flask; dissolve in and make to volume with dioxane. Mix thoroughly, pipette 5 ml into a second 50 ml volumetric flask, make to volume with dioxane, and mix well. (final conc 0.1 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.005 gram warfarin into a glass-stoppered or screw-cap 125 ml Erlenmeyer flask, add 50 ml dioxane by pipette, close tightly, and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to avoid evaporation. (final conc 0.1 mg warfarin/ml)

Determination:

For a variable wavelength detector, use 308 nm rather than 254 nm. Warfarin is more easily detected at this wavelength and many interferences are eliminated or reduced to a negligible amount.

Alternately inject three 5 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

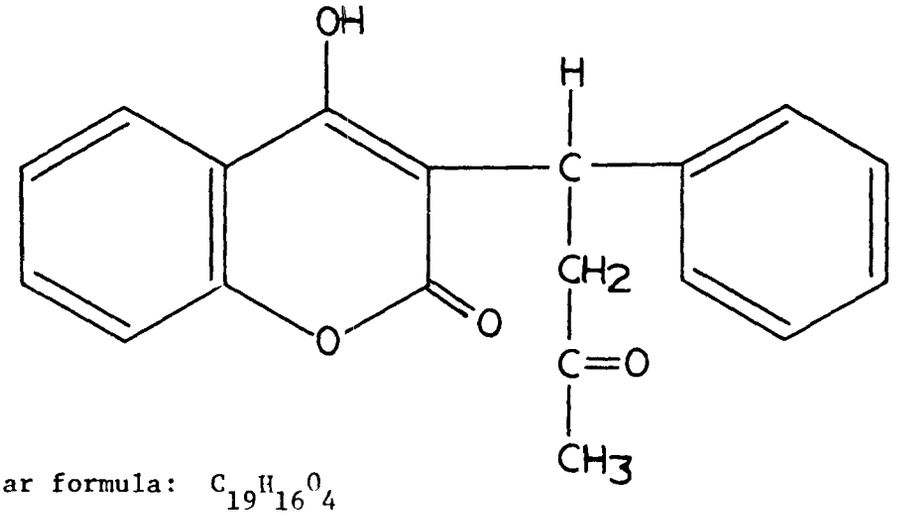
From the average peak height or peak area calculate the percent warfarin as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Elmer H. Hayes, EPA, Beltsville, Md.

Determination of Warfarin by Ultraviolet Spectroscopy

Warfarin is the official common name for 3-(alpha-acetonylbenzyl)-4-hydroxycoumarin, a registered rodenticide having the chemical structure:



Molecular formula: $C_{19}H_{16}O_4$

Molecular weight: 308.3

Melting point: (dl form) 159 to 161°C

Physical state, color, odor, taste: (dl form) colorless, tasteless, odorless crystals

Solubility: practically insoluble in water and benzene, moderately soluble in alcohols, readily soluble in acetone and dioxane; forms water-soluble salts with sodium

Stability: stable under normal conditions

Other names: WARF (Wisconsin Alumni Research Foundation), coumafene (France), zoocoumarin (Netherlands, USSR), Kypfarin

This method is applicable to most bait materials containing about 0.025% warfarin or its sodium salt. It is especially useful for bait materials that have a glazed coating or that have been made into pellets.

In such cases the extraction of warfarin in organic solvents (AOAC 12th Ed. 6.140-6.141 ether extraction) is retarded.

Reagents:

1. Warfarin standard of known % purity
2. Sodium pyrophosphate, 1% solution - dissolve 5 grams $Na_4P_2O_7.10H_2O$ in water and make to 500 ml.
3. Ether-hexane mixture - extract 200 ml n-hexane (bp 60—68°C) with three 20 ml portions of 1% pyrophosphate solution and add 50 ml ethyl ether, making a 20% ether-80% hexane mixture.
4. Hydrochloric acid, 2.5N solution - 20.6 ml hydrochloric acid diluted to 100 ml.

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm quartz cells
2. Centrifuge with 50 ml and 100 ml glass-stoppered tubes
3. Mechanical shaker
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram warfarin standard into a 100 ml volumetric flask; dissolve in and make to volume with 1% sodium pyrophosphate. Mix thoroughly, pipette 10 ml into a second 100 ml volumetric flask, and make to volume with 1% pyrophosphate solution. Again, mix thoroughly, pipette 10 ml of this solution into a third 100 ml volumetric flask, and make to volume with the 1% pyrophosphate solution. (final conc 10 µg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.0005 gram warfarin (2 grams for a 0.025% product) into a 125 ml glass-stoppered Erlenmeyer flask, add by pipette 50 ml 1% pyrophosphate solution, close tightly, and shake on a mechanical shaker for one hour. Transfer 30-35 ml to a glass-stoppered centrifuge tube and centrifuge for 5 minutes. Pipette 25 ml of clear solution into a second centrifuge tube, add 5 ml 2.5N hydrochloric acid and 50 ml ether-hexane solution, stopper tightly, and shake for 5 minutes. If an emulsion forms, centrifuge a few minutes to break the emulsion.

Pipette 20 ml of the ether layer into another centrifuge tube and add by pipette 10 ml 1% pyrophosphate solution. Shake for 2 minutes and remove the ether layer -- this is conveniently done by using a tube drawn into a fine tip and connected to a water aspirator. If the aqueous phase is not clear, centrifuge for a few minutes with the top off to remove any traces of the ether-hexane phase. **(final conc 10 µg warfarin/ml)**

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings, balance the 0 and 100% at 308 nm with the 1% pyrophosphate solution in each cell. Scan both standard and sample from 360 nm to 240 nm, using the 1% pyrophosphate solution in the reference cell. Measure the absorbance of both standard and sample at 308 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent warfarin as follows:

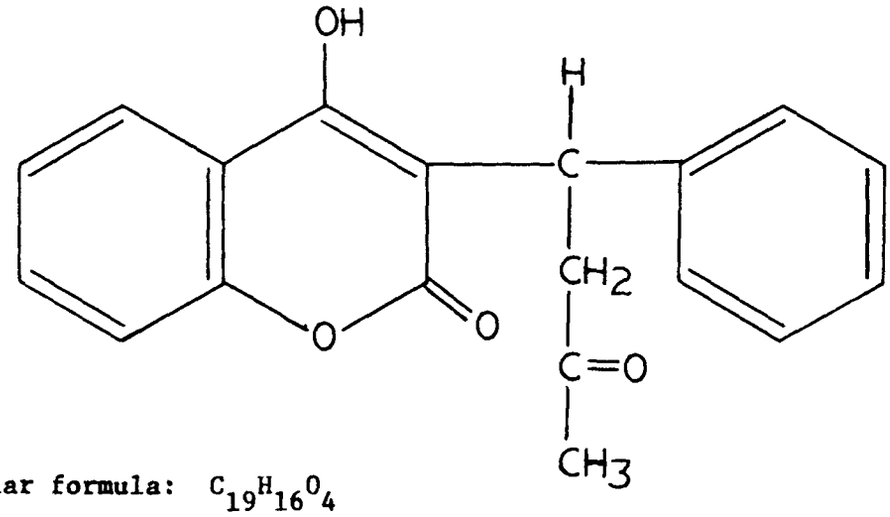
$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

December 1975

Warfarin EPA-3
(Tentative)

Determination of Warfarin, Sodium Salt by High Pressure Liquid Chromatography

Warfarin is the official common name for 3-(alpha-acetonylbenzyl)-4-hydroxycoumarin, a registered rodenticide having the chemical structure:



Molecular formula: $C_{19}H_{16}O_4$

Molecular weight: 308.3

Melting point: (dl form) 159 to 161°C

Physical state, color, odor, taste: (dl form) colorless, tasteless, odorless crystals

Solubility: practically insoluble in water and benzene, moderately soluble in alcohols, readily soluble in acetone and dioxane; forms water-soluble salts with sodium

Stability: stable under normal conditions

Other names: WARF (Wisconsin Alumni Research Foundation), coumafene (France), zoocoumarin (Netherlands, USSR), Kypfarin

Reagents:

1. Warfarin standard of known % purity
2. Methanol, pesticide or spectro grade
3. Phosphorous acid solution, 0.0025M in water
4. Sodium pyrophosphate, 1% solution - dissolve 10 grams $Na_4P_2O_7.10H_2O$ in water and make to 1000 ml.

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm. If a variable wavelength UV detector is available, other wavelengths may be useful to increase sensitivity or eliminate interference. Warfarin is more easily determined at 308 nm.
2. Suitable column such as:
   a. DuPont ODS Permaphase, 1 meter x 2.1 mm ID
   b. Perkin-Elmer ODS Sil-X 11 RP, 1/2 meter x 2.6 mm ID
3. High pressure liquid syringe or sample injection loop
4. Usual laboratory glassware

Operating Conditions:

Mobile phase:	10% methanol + 90% 0.0025M H_3PO_4 in water
Column temperature:	50°C
Chart speed:	5 min/inch or equivalent
Flow rate:	0.5 to 1.5 ml/min (Perkin-Elmer 1/2 meter column)
Pressure:	500 psi (DuPont 1 meter column)
Attenuation:	Adjusted

Conditions may have to be varied by the analyst for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram warfarin standard into a 50 ml volumetric flask; dissolve in and make to volume with sodium pyrophosphate solution. Mix thoroughly, pipette 5 ml into a second 50 ml volumetric flask, make to volume with sodium pyrophosphate solution, and mix well. (final conc 0.1 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.005 gram warfarin into a glass-stoppered or screw-cap 125 ml Erlenmeyer flask, add 50 ml sodium pyrophosphate solution by pipette, close tightly, and shake for one hour. Allow to settle; centrifuge or filter if necessary, taking precaution to avoid evaporation. (final conc 0.1 mg warfarin/ml)

Determination:

For a variable wavelength detector, use 308 nm rather than 254 nm. Warfarin is more easily detected at this wavelength and many interferences are eliminated or reduced to a negligible amount.

Alternately inject three 5 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent warfarin as follows:

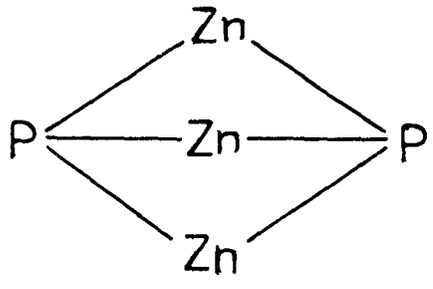
$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

% Sodium salt of warfarin = 1.071 x % warfarin

Method submitted by Elmer H. Hayes, EPA, Beltsville, Md.

Determination of Zinc Phosphide by the Phosphine Evolution Method

Zinc phosphide is a registered rodenticide having the chemical structure:



Molecular formula: Zn_3P_2

Molecular weight: 258.1

Melting point: 420°C (sublimes when heated in the absence of oxygen)

Physical state, color, and odor: gray powder, disagreeable odor (not offensive to rodents)

Solubility: practically insoluble in water and ethanol; soluble in benzene and carbon disulfide

Stability: stable when dry but decomposes slowly in moist air; reacts violently with acids with decomposition to the spontaneously inflammable phosphine

Other names: Kilrat, Mous-con, Rumetan

Principle of the Method:

A weighed portion of sample is initially washed with distilled water to remove any antimony potassium tartrate which would interfere with the quantitative evolution of phosphine from zinc phosphide. The

washed sample is treated with sulfuric acid under an atmosphere of nitrogen to release phosphine gas which is swept by the nitrogen into several absorption flasks containing standard potassium permanganate solution with which it reacts. The excess permanganate is titrated with oxalic acid solution and the zinc phosphide calculated from the amount of permanganate used by the phosphine from the sample.

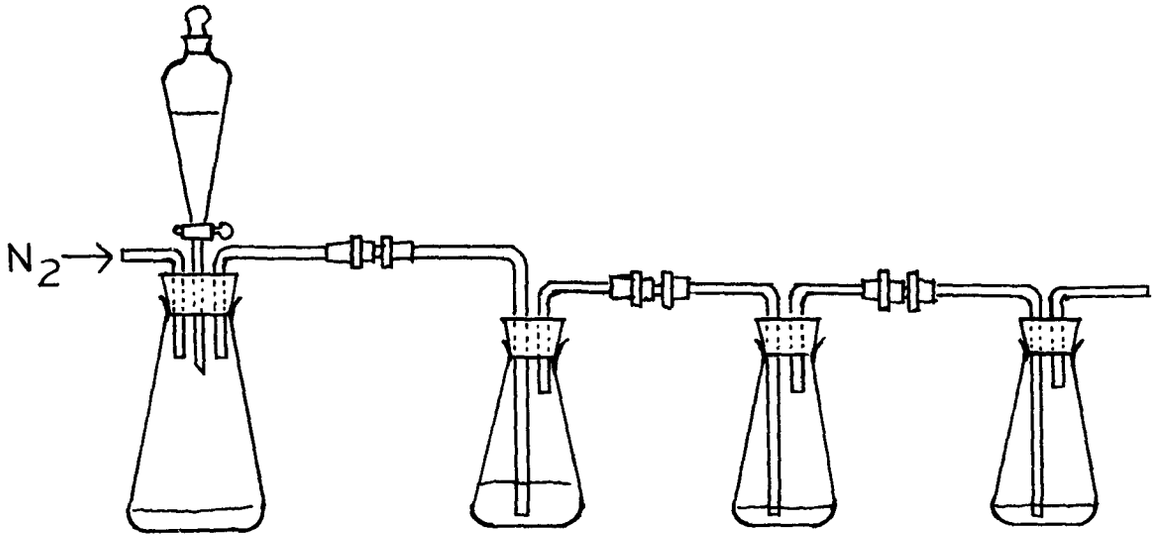
The antimony potassium tartrate in the wash solution may be determined by titration with iodine solution.

Reagents:

1. Potassium permanganate, 0.5N standard solution - 15.81 grams $KMnO_4$ per liter
2. Sulfuric acid, 10% solution - 1 volume concentrated sulfuric acid added to 9 volumes water
3. Oxalic acid, 0.5N standard solution - 31.52 grams $(COOH)_2.2H_2O$ per liter. This solution should contain 125 to 150 ml concentrated sulfuric acid.
4. Distilled water - freshly boiled and cooled to 15°C
5. Nitrogen gas
6. Sodium bicarbonate, saturated solution
7. Starch indicator solution
8. Iodine, 0.1N standard solution

Equipment:

1. Reaction train consisting of a 500 ml Erlenmeyer flask fitted with a three-hole stopper for: (1) an inlet tube for nitrogen, (2) a separatory funnel for adding acid, and (3) an outlet tube leading to three absorption flasks, each with an inlet tube extending to the bottom of the flask and an outlet tube leading to the next flask. It is very convenient to have the flasks connected with polyethylene tubing and polyethylene friction connectors.



2. Water bath maintained at 50°C
3. Titrating equipment
4. Usual laboratory glassware

Procedure:

Preparation of Sample:

Weigh a portion of ground sample equivalent to 0.005-0.010 gram zinc phosphide into a 250 ml beaker. Add 50-75 ml freshly boiled and cooled distilled water, stir, and filter with gentle suction through ashless, double acid washed filter paper. Transfer all the sample into the paper and wash five times with 15 ml portions of distilled water.

Use the residue for the determination of zinc phosphide and the filtrate for the determination of antimony potassium tartrate.

Determination of Antimony Potassium Tartrate:

If antimony potassium tartrate is to be determined, add 10 ml cold saturated solution of sodium bicarbonate and a few drops of 0.5% starch indicator solution to the combined filtrate and

titrate immediately with 0.1N iodine solution to a permanent blue color. Calculate the % antimony potassium tartrate as follows:

$$\% = \frac{(\text{ml iodine})(\text{N iodine})(0.1625)(100)}{(\text{wt. sample})}$$

Evolution and Absorption of Phosphine:

Transfer the filter paper and residue (from above) to the 500 ml reaction flask. Pipette 100 ml of 0.5N standard potassium permanganate into the first absorption flask, and pipette 50 ml into each of the other two. Add 100 ml of 10% sulfuric acid to the separatory funnel, connect the apparatus to a source of nitrogen, sweep the system with nitrogen for at least 10 minutes, and adjust the flow of nitrogen to one or two bubbles per second. Slowly add the acid to the reaction flask, regulating the rate so that a steady stream of bubbles appears in the absorbers. After all the acid has been added, place the reaction flask in the 50°C water bath and allow the reaction to continue for at least one hour, adjusting the flow of nitrogen to maintain a steady flow of bubbles at all times.

Determination of Phosphine and Calculation of Zinc Phosphide:

At the end of the reaction period, quantitatively transfer the potassium permanganate solution from the absorbers into a one-liter beaker. Accurately measure 225 ml of the 0.5N oxalic acid standard solution into a plastic squeeze wash bottle and rinse the absorbers and connecting tubes into the liter beaker. Carefully dissolve all the manganese dioxide and rinse with distilled water so as not to lose any of the oxalic acid solution. Finally, rinse the oxalic acid solution from the wash bottle into the same liter beaker.

Warm the oxalic-manganous solution to about 50°C and titrate the excess oxalic acid with the 0.5N potassium permanganate solution to the first permanent pink (persists for 60 seconds).

Calculate the zinc phosphide as follows:

meq's from $KMnO_4$ = N x (ml $KMnO_4$ added + ml used in titration)

\- meq's from oxalic acid = N x ml oxalic acid used

meq's difference = net meq's used by sample

$$\% \text{ zinc phosphide} = \frac{(\text{net meq's})(0.01613)(100)}{(\text{grams of sample})}$$

milliequivalent weight of zinc phosphide is 0.01613 or $\frac{(258.09)}{(16)(1000)}$

Reactions:

$$Zn_3P_2 + 3H_2SO_4 \longrightarrow 2PH_3\uparrow + 3ZnSO_4$$

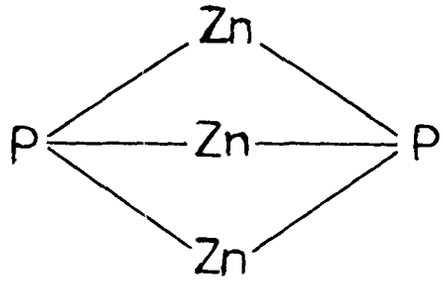
$$3PH_3 + 8KMnO_4 \longrightarrow 8MnO_2\downarrow + K_2HPO_4 + 2K_3PO_4 + 4H_2O$$

$$MnO_2 + (COOH)_2 + H_2SO_4 \longrightarrow MnSO_4 + 2CO_2\uparrow + 2H_2O$$

$$(COOH)_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10\ CO_2\uparrow + 8H_2O$$

Determination of Zinc Phosphide in Grain Baits by Gas-Liquid Chromatography (FPD)

Zinc phosphide is a registered rodenticide having the chemical structure:



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Stability: stable when dry but decomposes slowly in moist air; reacts violently with acids with decomposition to the spontaneously inflammable phosphine

Other names: Kilrat, Mous-con, Rumetan

Reagents:

1. Zinc phosphide standard of known % purity
2. Glucose, 100 mesh, dry powder
3. Toluene, pesticide or spectro grade
4. Sulfuric acid, 10% solution

Equipment:

1. Gas chromatograph with flame photometric detector (FPD) and phosphorus filter (526 nm emission band)
2. Column: 4' x 1/4" O.D. glass column packed with 5% QF-1 on 80/100 mesh Gas Chrom Q, conditioned isothermally at 40-50°C (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Electric sample mill or blender
5. Ultrasonic cleaner (aid to dispersion and dissolution of samples)
6. Usual laboratory glassware

Operating Conditions for FPD:

Column temperature:	40-50°C
Injection temperature:	200°C
Detector temperature:	140-150°C
Nitrogen carrier gas:	45-60 ml/min
Hydrogen to Detector:	50-150 ml/min
Air to Detector:	0-35 ml/min
Oxygen to Detector:	10-25 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

The linear detector response for phosphine should be determined at the concentrations of interest. Reference standards must be prepared each day as phosphine is not stable for prolonged periods. Analyses are referred to the reference standards rather than to a prepared standard curve.

Procedure:

Preparation of Standard:

Prepare a 1% mixture of zinc phosphide in glucose as follows: weigh 1.00 gram zinc phosphide (correcting for less than 100% purity) and make to 100 grams with dry, powdered glucose; mix thoroughly to insure a homogenous mixture.

Weigh 0.38 gram* of this diluted standard mixture into a 100 ml volumetric flask and fill to the mark with toluene. Add sufficient 10% sulfuric acid solution to bring the liquid level within 1 cm of the bottom of the glass stopper. Set aside for one hour, mixing occasionally by inverting several times and shaking for one minute.

Seal the top with tape to prevent loss of toluene and place in an ultrasonic bath for five minutes. Remove and let stand another hour. Optimum hydrolysis and absorption into the toluene may be achieved by allowing the hydrolyzed samples to stand overnight.

Standards and samples can be kept 24 hours if a toluene-to-glass seal is made by tilting the flask to cover the stopper.

(final conc approx 10 ppm PH_3 or 10 µg PH_3/ml)

*(0.3794 g of the 1% mixture will hydrolyze to 1 mg phosphine, which, dissolved in 100 ml toluene, gives a 10 µg/ml conc)

Preparation of Sample:

Chill a blender or an electric sample mill in a freezer until well chilled, add 30-40 grams of grain bait sample, and grind to a flour-like powder. Weigh 0.38 gram (for 1% formulation, 0.19 g for 2% formulation) into a 100 ml volumetric flask and follow the same procedure as above under preparation of standard. (final conc same as standard)

Determination:

Using a precision liquid syringe, inject 1 µl of standard solution and adjust attenuation to a 30-50% full scale response. Inject 1 µl of sample solution using the same conditions. When the peak heights for both the sample and standard are reproducible within ± 5%, make alternate injections of sample and standard. Measure the peak heights in mm of the standard and sample.

Calculation:

From the average peak heights of standard and sample, calculate the percent zinc phosphide as follows:

$$\% = \frac{(\text{pk. ht. sample})(\text{wt. std injected})(100)}{(\text{pk. ht. std})(\text{wt. sample injected})}$$

Any deficiencies found in formulations by this method should be checked by method EPA-1 (phosphine evolution method).

Method submitted by the Hawaiian Sugar Planters' Association, 1527 Keeaumoku Street, Honolulu, Hawaii 96822.

UPDATE 1

EPA MANUAL OF CHEMICAL METHODS FOR PESTICIDES AND DEVICES

Dear Subscriber:

Enclosed is the first update of the EPA Manual of Chemical Methods for Pesticides and Devices. This update includes:

1. Nineteen additional methods for the analysis of commercial pesticide formulations

2. One analytical method for the degradation product "ethylene-thiourea" in ethylenebisdithiocarbamate fungicide formulations

3. Pesticide Name Cross Reference Index to the above 20 methods

4. "Pen and ink" corrections to 59 methods

5. Special major correction to the Diphacinone EPA-1 method

A second update for this manual is tentatively scheduled for January 1978 and will include additional analytical methods, revisions, and corrections.

The Editorial Committee would appreciate written comments in relation to the following:

1. Corrections or modifications in data, analytical procedures, or calculations in the methods now in the manual

2. New methods or data for inclusion in future updates or revisions of this manual

3. Suggestions for additional methods, graphs, charts, data, or information (general or specific) that would increase the usefulness of this manual

Such comments may be made to members of the Editorial Committee or the AAPCO-EPA Review Committee as listed in the Preface (page 4) or sent to Jack B. Looker, Assistant Chairman, or Warren R. Bontoyan, Chairman, Editorial Committee.

Address: EPA, TSD
Room 101, Bldg. 306, ARC-East
Beltsville, Md. 20705

Warren R. Bontoyan
Chairman, Editorial Committee

Jack B Looker
Jack B. Looker
Asst. Chairman, Editorial Committee

Diphacinone EPA-1 - Special Correction

The method "Diphacinone EPA-1, Determination of Diphacinone in Baits by Ultraviolet Spectroscopy, November 1975" is no longer satisfactory for the analysis of diphacinone. Commercial bait formulations are more complex, including meat, fish, and apple flavors. This necessitates a more thorough extraction procedure such as in the following method.

Changes to be made are as follows:

(4-1) (1) Change November 1975 to: July 1977
(Revision of November 1975)

(4-1) (2) Add (tentative) to Diphacinone EPA-1

(4-1) (3) Replace pages 2 and 3 with the following method

Analytical Methods - First Supplement

July 1, 1977

Errors to be corrected:

4-Aminopyridine EPA-1 (tentative)
Pg 2 under UV Determination, 3rd and last lines
"302" should be "262"

Chlorophenoxy Herbicides EPA-1
The "second page 7 (containing Erbon data)" should be "page 8" and "page 8" should be "page 9" **

Chlorophenoxy Herbicides EPA-2
Pg 3 under UV Determination, middle of line 4
"286" should be "296" **

Norbormide EPA-1
Pg 2 and 3, top right corner
Change "EPA-2" to "EPA-1" **

Organotin Compounds EPA-1
Pg 5, calculation of % tin should be

$$\% \text{ tin} = \frac{(\text{ml } KIO_3)(\text{N } KIO_3)(0.05935)(100)}{(\text{grams sample})}$$

Pebulate EPA-1 (tentative)
Pg 3 under Note!
"iso-publate" should be "iso-pebulate" **

Phenols and Chlorophenols EPA-1
Pg 3, bottom line
"Chlorophene" should be "Clorophene" **

Pyrethrins EPA-2
Pg 1 under Equipment: 2.
column packing is 60-80 mesh **

Ronnel EPA-2
Pg 3 under Preparation of Standard:
"EPTC" should be "ronnel" **

Strychnine EPA-1
Pg 2 under Reagents: 1.
"ethanol" should be "ether"

** Manuals distributed by AOAC were corrected before publication.

49 GLC internal standard methods listed below
Under Calculation, the factor "(100)" should be deleted from the "% = - - - -" calculation.
This applies to the following methods:

(u-1) Alachlor EPA-1 (tentative)
Alachlor EPA-2 (tentative)
Anilazine EPA-2 (tentative)
Atrazine EPA-2 (tentative)
Benefin EPA-2 (tentative)
Bromacil EPA-1 (tentative)
Butylate EPA-4
Butylate EPA-5 (tentative)
Chlorophenoxy Herbicides EPA-4 (tentative)
Chlorophenoxy Herbicides EPA-5 (tentative)
Chloroxuron EPA-2 (tentative)
Coumaphos EPA-3 (tentative)
Crufomate EPA-2 (tentative)
Cycloate EPA-3
Deet EPA-2 (tentative)
Deet EPA-3 (tentative)
Diazinon EPA-4
p-Dichlorobenzene EPA-2 (tentative)
Disulfoton EPA-2 (tentative)
Endosulfan EPA-3 (tentative)
Endosulfan EPA-4 (tentative)
EPTC EPA-1 (tentative)
EPTC EPA-3
EPTC EPA-4 (tentative)
EPTC EPA-5 (tentative)
Ethoprop EPA-2 (tentative)
Ethoprop EPA-3 (tentative)
Ethyl Hexanediol EPA-2 (tentative)
Metaldehyde EPA-2 (tentative)
Methoxychlor EPA-2 (tentative)
Methyl Parathion EPA-4
Methyl Parathion EPA-5
Metobromuron EPA-3 (tentative)
Monocrotophos EPA-2
Parathion EPA-2 (tentative)
Pebulate EPA-2 (tentative)
Pebulate EPA-3 (tentative)
Phenols & Chlorophenols EPA-8 (tentative)
Piperonyl Butoxide EPA-2
Prometone EPA-1 (tentative)
Prometone EPA-2 (tentative)
Propargite EPA-2 (tentative)
u-1) Resmethrin EPA-3 (tentative)
u-1) Resmethrin EPA-5 (tentative)
u-1) Ronnel EPA-2
u-1) Terbutol EPA-2 (tentative)
u-1) Trifluralin EPA-1
u-1) Vernolate EPA-2
u-1) Vernolate EPA-3 (tentative)

The Editorial Staff of this manual would appreciate hearing of other errors so that they may be corrected in future updates.

ANALYTICAL METHODS - FIRST SUPPLEMENT

July 1, 1977

Antimycin A EPA-1 (tentative)

Asulam EPA-1 (tentative)

Bentazon EPA-1 (tentative)

Chlorobenzilate EPA-1 (tentative)

Chlorophacinone EPA-1 (tentative)

Crotoxyphos EPA-1 (tentative)

Dimethoate EPA-1 (tentative)

Dimethoate EPA-2 (tentative)

Ethylenethiourea EPA-1 (tentative)

Linuron EPA-3 (tentative)

Mercaptobenzothiazole EPA-1 (tentative)

Mercaptobenzothiazole EPA-2 (tentative)

Methidathion EPA-1 (tentative)

Monocrotophos EPA-3 (tentative)

Propylene Glycol EPA-1 (tentative)

Trichlorfon EPA-1 (tentative)

Trichlorfon EPA-2 (tentative)

Triethylene Glycol EPA-1 (tentative)

Vacor (trade name) EPA-1 (tentative)

Vacor (trade name) EPA-2 (tentative)

ANALYTICAL METHODS - FIRST SUPPLEMENT

July 1, 1977

Pesticide Name Cross Reference Index to the Methods

Acaraben	Chlorobenzilate EPA-1
Afalon	Linuron EPA-3
Akar	Chlorobenzilate EPA-1
Antimycin A EPA-1 (tentative)	UV
Asulam EPA-1 (tentative)	UV
Asulame	Asulam EPA-1
Asulox	Asulam EPA-1
Azodrin	Monocrotophos EPA-3
Bantex (zinc salt)	Mercaptobenzothiazole EPA-1 & 2
Basagran	Bentazon EPA-1
Bayer 15922	Trichlorfon EPA-1 & 2
Bayer L 13/59	Trichlorfon EPA-1 & 2
Bentazon EPA-1 (tentative)	UV
Benzilan	Chlorobenzilate EPA-1
C-23992	Chlorobenzilate EPA-1
Caid	Chlorophacinone EPA-1
Captax	Mercaptobenzothiazole EPA-1 & 2
Chlorobenzilate EPA-1 (tentative)	GLC-FID-IS
Chlorofos	Trichlorfon EPA-1 & 2
Chlorophacinone EPA-1 (tentative)	UV
2-[(p-chlorophenyl)phenylacetyl]-1,3-indandione	Chlorophacinone EPA-1

2-(2-p-chlorophenyl-2-phenylacetyl) indane-1,3-dione	Chlorophacinone EPA-1
Ciodrin	Crotoxyphos EPA-1
Crotoxyphos EPA-1 (tentative)	GLC-FID-IS
Cygon	Dimethoate EPA-1 & 2
Daphene	Dimethoate EPA-1 & 2
De-Fend	Dimethoate EPA-1 & 2
Dermacid	Mercaptobenzothiazole EPA-1 & 2
3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea	Linuron EPA-3
S-(2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl)dimethyl phosphorothiolothionate	Methidathion EPA-1
1,2-dihydroxypropane	Propylene Glycol EPA-1
Dimetate	Dimethoate EPA-1 & 2
Dimethoate EPA-1 (tentative)	GLC-TCD-IS
Dimethoate EPA-2 (tentative)	GLC-FID-IS
Dimethogen	Dimethoate EPA-1 & 2
cis-3-(dimethoxyphosphinyloxy)-N-methylcrotonamide	Monocrotophos EPA-3
dimethyl-2-(alpha-methylbenzocarbonyl)-1-methyl vinyl phosphate (E)	Crotoxyphos EPA-1
O, O-dimethyl S-[(methylcarbamoyl) methyl] phosphorodithioate	Dimethoate EPA-1 & 2
O, O-dimethyl-O-(2-methylcarbamoyl-1-methyl-vinyl)-phosphate	Monocrotophos EPA-3
dimethyl-1-methyl-2-methyl-carbamoyl-vinyl phosphate	Monocrotophos EPA-3
dimethyl cis-1-methyl-2-(1-phenylethoxycarbonyl)vinyl phosphate	Crotoxyphos EPA-1

dimethyl phosphate of alpha-methylbenzyl 3-hydroxy-cis-crotonate	Crotoxyphos EPA-1
dimethyl phosphate of 3-hydroxy-N-methyl-cis-crotonamide	Monocrotophos EPA-3
O,O-dimethyl phosphorodithioate S-ester with 4-(mercaptomethyl)-2-methoxy-delta 2-1,3,4-thiadiazolin-5-one	Methidathion EPA-1
dimethyl(2,2,2-trichloro-1-hydroxyethyl) phosphonate	Trichlorfon EPA-1 & 2
Dipterex	Trichlorfon EPA-1 & 2
dipterex	Trichlorfon EPA-1 & 2
Drat	Chlorophacinone EPA-1
Dylox	Trichlorfon EPA-1 & 2
E. I. 12,880	Dimethoate EPA-1 & 2
ethyl 4,4'-dichlorodiphenylglycollate	Chlorobenzilate EPA-1
ethyl 4,4'-dichlorobenzilate	Chlorobenzilate EPA-1
2,2'-ethylenedioxybis (ethanol)	Triethylene Glycol EPA-1
Ethylenethiourea EPA-1 (tentative)	GLC-FID & TCD
ETU	Ethylenethiourea EPA-1 (tentative)
Fintrol	Antimycin A EPA-1
Folbex	Chlorobenzilate EPA-1
Fostion MM	Dimethoate EPA-1 & 2
GS-13005	Methidathion EPA-1
HOE 2810	Linuron EPA-3
2-imidazolidinethione	Ethylenethiourea EPA-1
3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide	Bentazon EPA-1

Kop-Mite	Chlorobenzilate EPA-1
L 395	Dimethoate EPA-1 & 2
Linuron EPA-3 (tentative)	UV
Liphadione	Chlorophacinone EPA-1
Lorox	Linuron EPA-3
MB 9057	Asulam EPA-1
MBT	Mercaptobenzothiazole EPA-1 & 2
Mercaptobenzothiazole EPA-1 (tentative)	UV
Mercaptobenzothiazole EPA-2 (tentative)	potentiometric titration
2-mercaptobenzothiazole	Mercaptobenzothiazole EPA-1 & 2
Mertax	Mercaptobenzothiazole EPA-1 & 2
Methidathion EPA-1 (tentative)	GLC-FID-IS
S-[(5-methoxy-2-oxo-1,3,4-thiadiazol-3(2H)-yl)methyl] O,O-dimethyl phosphorodithioate	Methidathion EPA-1
methyl(4-aminobenzenesulphonyl) carbamate	Asulam EPA-1
1-methylbenzyl 3-(dimethoxyphosphinyloxy) -cis-crotonate	Crotoxyphos EPA-1
methylene glycol	Propylene Glycol EPA-1
methyl glycol	Propylene Glycol EPA-1
methyl sulfanilylcarbamate	Asulam EPA-1
metrifonate	Trichlorfon EPA-1 & 2
Monocron	Monocrotophos EPA-3
Monocrotophos EPA-3 (tentative)	GLC-FID-IS
Neguvon	Trichlorfon EPA-1 & 2
Niacides	Mercaptobenzothiazole EPA-1 & 2

Nuodex 84 (sodium salt)	Mercaptobenzothiazole EPA-1 & 2
Nuvacron	Monocrotophos EPA-3
Partox	Chlorophacinone EPA-1
Perfekthion	Dimethoate EPA-1 & 2
Poast	Bentazon EPA-1
1,2-propanediol	Propylene Glycol EPA-1
Propylene Glycol EPA-1 (tentative)	GLC-TCD-IS
N-3-pyridylmethyl-N'-p-nitrophenylurea	Vacor (trade name) EPA-1 & 2
Quick	Chlorophacinone EPA-1
Raviac	Chlorophacinone EPA-1
Rebelate	Dimethoate EPA-1 & 2
RH-787	Vacor (trade name) EPA-1 & 2
Rogor	Dimethoate EPA-1 & 2
Roxion	Dimethoate EPA-1 & 2
Rozol	Chlorophacinone EPA-1
Sarclex	Linuron EPA-3
SD 4294	Crotoxyphos EPA-1
Supracide	Methidathion EPA-1
Thiotax	Mercaptobenzothiazole EPA-1 & 2
Trichlorfon EPA-1 (tentative)	IR
Trichlorfon EPA-2 (tentative)	GLC-FID-IS
trichlorphon	Trichlorfon EPA-1 & 2
Triethylene Glycol EPA-1 (tentative)	GLC-TCD-IS

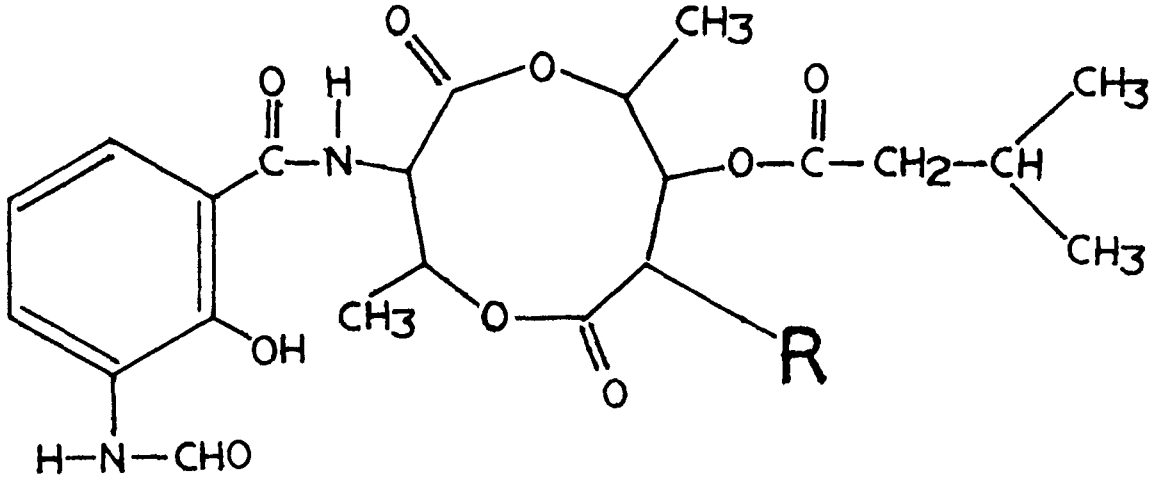
Trimetion	Dimethoate EPA-1 & 2
Tugon	Trichlorfon EPA-1 & 2
Ultracide	Methidathion EPA-1
Vacor	Vacor (trade name) EPA-1 & 2
Vacor (trade name) EPA-1 (tentative)	UV
Vacor (trade name) EPA-2 (tentative)	HPLC
Zetax (zinc salt)	Mercaptobenzothiazole EPA-1 & 2

Determination of Antimycin A by Ultraviolet Spectroscopy

Antimycin A is a registered piscicide, consisting of a mixture of antimycin A_1 and antimycin A_3 which have the following chemical names and structures:

antimycin A_1: Butanoic acid, 3-methyl-3-[[3-(formylamino)-2-hydroxybenzoyl]amino]-8-hexyl-2,6-dimethyl-4,9-dioxo-1,5-dioxonan-7-yl ester

antimycin A_3: 3-methylbutanoic acid 8-butyl-3-[[3-(formylamino)-2-hydroxybenzoyl]amino]-2,6-dimethyl-4,9-dioxo-1,5-dioxonan-7-yl ester



antimycin A_1 - R = hexyl $-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

antimycin A_3 - R = butyl $-CH_2-CH_2-CH_2-CH_3$

Molecular formula: $A_1 = C_{28}H_{40}N_2O_9$

$A_3 = C_{26}H_{36}N_2O_9$

Molecular weight: $A_1 = 548.62$

$A_3 = 520.56$

Melting point: $A_1 = 149\text{-}150^{\circ}C$

$A_3 = 170.5\text{-}171.5^{\circ}C$

Physical state, color, and odor: white solid

Solubility: practically insoluble in water; soluble in acetone, alcohol, chloroform, benzene; A_1 is very slightly soluble in benzene and carbon tetrachloride, but A_3 is freely soluble

Stability:

Other names: Fintrol

Reagents:

1. Antimycin A standard of known % purity
2. Methanol, spectro or pesticide grade

Equipment:

1. Ultraviolet spectrometer, double beam ratio recording with matched 1 cm silica cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.05 g antimycin A standard into a 100 ml volumetric flask, dissolve in, and make to volume with methanol. Pipet 2 ml into a second 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. (final conc 10 µg antimycin A/ml)

Preparation of Sample:

For liquids - weigh a portion of sample equivalent to 0.05 gram antimycin A into a small beaker. Heat on steam bath under a gentle stream of air to remove solvents present in the formulation (usually acetone). Cool, dissolve in 40-50 ml methanol, and quantitatively transfer to 100 ml volumetric flask, rinsing beaker several times with methanol. Make to volume with methanol and mix thoroughly. Pipet 2 ml to a second 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. (final conc 10 µg antimycin A/ml)

For wettable powders - weigh a portion of sample equivalent to 0.05 gram antimycin A into a 250 ml glass-stoppered flask or screw-cap bottle. Add 100 ml methanol by pipette, close tightly, and shake for one-half hour. Allow to settle; centrifuge or filter if necessary, taking precaution to prevent evaporation. Pipette 2 ml into a 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. (final conc 10 µg antimycin A/ml)

UV Determination:

With the UV spectrometer at the optimum quantitative settings, balance the pen for 0 and 100% transmission at 223 nm with methanol in each cell. Scan both sample and standard from 300 nm to 200 nm, using methanol in the reference cell. Measure the absorbance of both standard and sample at 223 nm, using the minimum at 280 nm as basepoint.

Calculation:

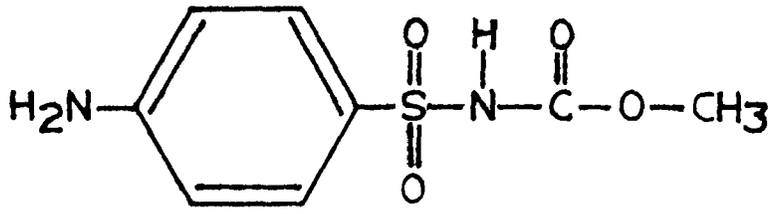
$$\% \text{ antimycin A} = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity of std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

Method submitted by Mark W. Law, EPA Beltsville Chemistry Laboratory, Beltsville, Md.

Any criticisms, suggestions, data, etc. on the use of this method will be appreciated.

Determination of Asulam by Ultraviolet Spectroscopy

Asulam is the accepted common name for methyl sulfanilylcarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_8H_{10}N_2O_4S$

Molecular weight: 230.0

Melting point: pure material - 143 to 144°C, technical material - 135°C, both with decomposition

Physical state, color, and odor: pure material - odorless white crystals; technical material - cream to buff powder

Solubility: about 0.5% in water, 34% in acetone, 28% in methanol, less than 2% in hydrocarbons and chlorinated hydrocarbons; sodium salt more than 40% in water

Stability: Asulam and its dry salts are very stable for years under ordinary storage conditions; aqueous solution of the sodium salt at pH 8.5 is very stable.

Other names: Asulox (May & Baker Ltd); MB 9057; methyl(4-aminobenzene-sulphonyl) carbamate; asulame (France)

Reagents:

1. Asulam standard of known % purity
2. Ethanol, 95%, ACS (or better grade)

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.06 gram asulam standard into a 100 ml volumetric flask. Dissolve in and make to volume with 95% ethanol. Mix thoroughly, pipette a 10 ml aliquot into a second 100 ml volumetric flask, make to volume with 95% ethanol, and mix thoroughly. Pipette a 10 ml aliquot into a third 100 ml volumetric flask, make to volume with 95% ethanol, and mix thoroughly. (final conc 6 µg asulam/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.06 gram asulam into a 250 ml Erlenmeyer flask, add by pipette 100 ml 95% ethanol, and shake on a mechanical shaker for 30 minutes. Allow to settle, filter if necessary, and pipette 10 ml into a 100 ml volumetric flask. Make to volume and mix thoroughly. Pipette 10 ml into another 100 ml volumetric flask, make to volume with 95% alcohol, and mix thoroughly. (final conc 6 µg asulam/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 263 nm with

95% ethanol in each cell. Scan both the standard and sample from 350 nm to 200 nm with 95% ethanol in the reference cell. Measure the absorbance of both standard and sample at 263 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent asulam as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

Method submitted by David Persch, EPA Product Analysis Laboratory, Region II, New York, N.Y.

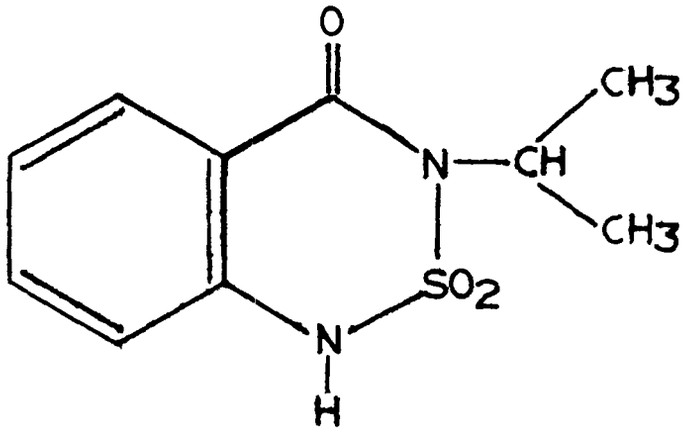
Any comments, criticisms, suggestions, data, etc. concerning the use of this method will be appreciated.

May 1977

Bentazon EPA-1
(tentative)

Determination of Bentazon and Its Sodium Salt by Ultraviolet Spectroscopy

Bentazon is the accepted common name for 3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_{12}N_2O_3S$

Molecular weight: 240.3

Melting point: 137 to 139°C

Physical state, color, and odor: odorless, white, crystalline solid

Solubility: solubility in grams per 100 grams solvent at 20°C: acetone 150.7, ethanol 86.1, ethyl acetate 65.0, ether 61.6, chloroform 18.0, benzene 3.3, water 0.05, cyclohexane 0.02

Stability: stable under ordinary conditions; non-corrosive; no degradation under visible light (400-600 nm) but 30% degradation under ultraviolet light (200-400 nm)

Other names: Basagran, Poast

Reagents:

1. Bentazon standard of known % purity
2. Sodium pyrophosphate, 1% aqueous solution - dissolve 5 grams of $Na_4P_2O_7.10H_2O$ in water and make to 500 ml.

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm silica cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.08 gram bentazon standard into a 100 ml volumetric flask; dissolve in and make to volume with 1% sodium pyrophosphate solution; mix thoroughly. Pipette 10 ml into a second 100 ml volumetric flask, make to volume with 1% sodium pyrophosphate solution, and mix thoroughly. Pipette 5 ml of this solution into a third 100 ml volumetric flask and make to volume with the pyrophosphate solution. Mix thoroughly. (final conc 4 µg bentazon/ml)

Preparation of Sample:

For wettable powders - weigh a portion of sample equivalent to 0.8 gram bentazon into a 250 ml glass-stoppered flask or screw-cap bottle. Add 100 ml of 1% sodium pyrophosphate solution, close tightly, and shake for 30 minutes. Allow to settle; centrifuge or filter if necessary. Proceed as in the third paragraph.

For liquid formulations - weigh a portion of sample equivalent to 0.8 gram bentazon into a 100 ml volumetric flask, make to volume with 1% sodium pyrophosphate solution, and mix thoroughly. Proceed as below.

Pipette 10 ml of either of the above sample solutions into a 100 ml volumetric flask, make to volume with 1% sodium pyrophosphate, and mix thoroughly. Pipette 10 ml of this solution into a 100 ml volumetric flask, make to volume with the pyrophosphate solution, and mix thoroughly. Pipette 5 ml of this solution into another 100 ml volumetric flask, make to volume with pyrophosphate solution, and mix thoroughly. (final conc 4 µg bentazon/ml)

UV Determination:

Balance pen for 0 and 100% transmission at 223 nm with 1% sodium pyrophosphate in each cell. Scan standard and sample from 280 nm to 150 nm with 1% sodium pyrophosphate solution in the reference cell. Measure absorbance of standard and sample at 223 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent bentazon as follows:

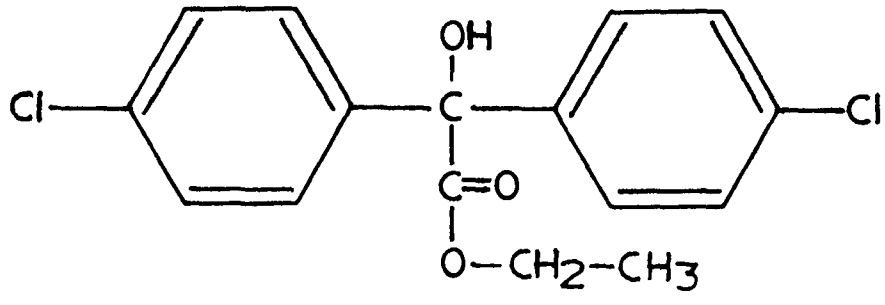
$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

Method submitted by Mark W. Law, EPA Beltsville Chemistry Laboratory, Beltsville, Md.

Any comments, criticisms, suggestions, data, etc. on the use of this method will be appreciated.

Determination of Chlorobenzilate by Gas Liquid Chromatography (FID - Internal Standard)

Chlorobenzilate is the common name for ethyl 4,4'-dichlorobenzilate, a registered acaricide having the chemical structure:



Molecular formula: $C_{16}H_{14}Cl_2O_3$

Molecular weight: 325.2

Melting point: 35-37°C for pure product

Boiling point: 156-158°C at 0.07 mm Hg

Physical state, color, and odor: pale yellow solid when pure; the technical product is a brownish liquid about 90% pure; characteristic odor

Solubility: practically insoluble in water; soluble in most organic solvents including petroleum oils

Stability: hydrolyzed by alkali and strong acids

Other names: C-23992, Akar, Folbex, Acaraben (Ciba-Geigy); ethyl 4,4'-dichlorodiphenylglycollate; Benzilan; Kop-Mite

Reagents:

1. Chlorobenzilate standard of known % purity
2. Heptachlor epoxide standard of known % purity
3. Acetone, pesticide or spectro grade

   Note: chloroform may also be used, but acetone is preferred.
4. Internal standard solution - weigh 1.0 gram heptachlor epoxide into a 100 ml volumetric flask; dissolve in and make to volume with acetone. Mix well. (conc 10 mg/ml or 10 µg/µl)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 1/4" glass column packed with 3.8% UC-V98 on 80/100 mesh diatoport S (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	230°C
Injection temperature:	260°C
Detector temperature:	260°C
Carrier gas:	Helium
Carrier gas pressure:	40 psi - 30 ml/min
Hydrogen pressure:	15 psi - 30 ml/min
Air pressure:	40 psi - 60 ml/min
Chart speed:	0.25"/min or 15"/hr

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram chlorobenzilate into a 100 ml volumetric flask, add 10 ml internal standard solution by pipette, make to volume with acetone, and mix well. (final conc 1 µg chlorobenzilate and 1 µg heptachlor epoxide/µl)

Preparation of Sample:

For liquids and emulsifiable concentrates - weigh a portion of sample equivalent to 0.1 gram chlorobenzilate into a 100 ml volumetric flask, add 10 ml internal standard solution, make to volume with acetone, and mix well.

For dusts and wettable powders - weigh a portion of sample equivalent to 0.2 gram chlorobenzilate into a 250 ml glass-stoppered flask or screw-cap bottle; add 100ml acetone by pipette. Close tightly and shake thoroughly to dissolve and extract the chlorobenzilate. Shake mechanically for 10-15 minutes or shake by hand intermittently for 25-30 minutes. Allow to settle; filter or centrifuge if necessary, taking precaution to avoid loss by evaporation. Pipette a 50 ml aliquot into a 100 ml volumetric flask, add 10 ml internal standard by pipette, make to volume with acetone, and mix thoroughly. (final conc 1 µg chlorobenzilate and 1 µg heptachlor epoxide/µl)

Determination:

Inject 3 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is heptachlor epoxide, then chlorobenzilate. Repeated injections should give the same peak ratios.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of chlorobenzilate and heptachlor epoxide from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

I.S. = internal standard = heptachlor epoxide

$$RF = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area chlorobenzilate})}{(\text{wt. chlorobenzilate})(\%\text{ purity chlorobenzilate})(\text{pk. ht. or area I.S.})}$$

Determine the percent chlorobenzilate for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area chlorobenzilate})}{(\text{wt. sample})(\text{pk. ht. or area I.S.})(RF)}$$

Method submitted by George B. Radan, EPA Product Analysis Laboratory, Region II, New York, N.Y.

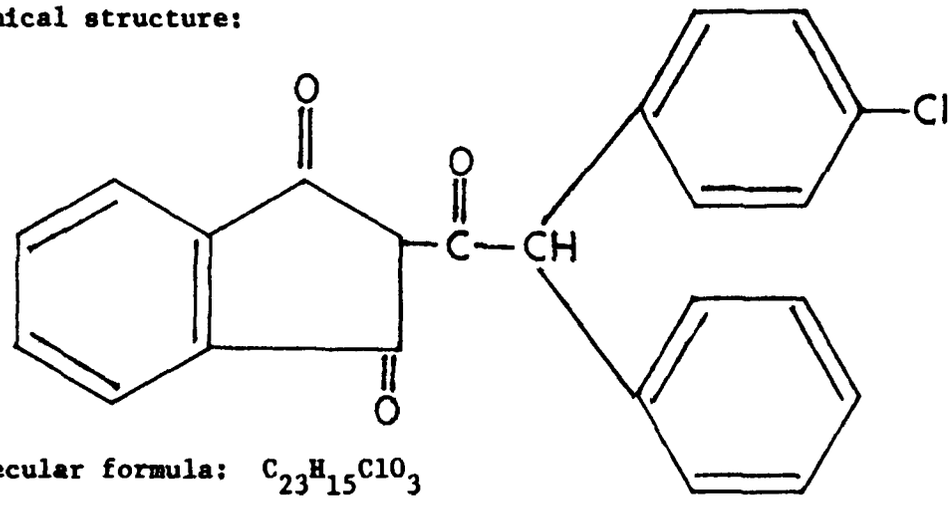
Any comments, criticism, suggestions, data, etc. concerning the use of this method will be appreciated.

May 1977

Chlorophacinone EPA-1
(tentative)

Determination of Chlorophacinone by Ultraviolet Spectroscopy

Chlorophacinone is the common name for 2-[(p-chlorophenyl) phenylacetyl]-1,3-indandione, a registered rodenticide having the chemical structure:



Molecular formula: $C_{23}H_{15}ClO_3$

Molecular weight: 374.6

Melting point: 140°C

Physical state, color, and odor: odorless, white crystalline solid

Solubility: sparingly soluble in water; soluble in organic solvents such as acetone, ethanol, ethyl acetate

Stability: stable and resistant to weathering; non-corrosive; compatible with cereals, fruits, roots, and other rodenticide baits; oxidized in bait formulations

Other names: Rozol (Chempar Chemical Co.); Caid, Liphadione, and Raviac (Lipha SA); Drat (May & Baker Ltd.); Quick (Rhône-Poulenc); Partox; 2-(2-p-chlorophenyl-2-phenylacetyl) indane-1,3-dione

Reagents:

1. Chlorophacinone standard of known % purity
2. Sodium pyrophosphate, 1% solution - dissolve 5 grams $Na_4P_2O_7.10H_2O$ in water and make to 500 ml.
3. Sodium pyrophosphate/dioxane mixture - add 10 ml dioxane to 200 ml of the 1% sodium pyrophosphate solution.

   (Dioxane is added to help dissolve the chlorophacinone.)
4. Ether-hexane mixture - extract 200 ml n-hexane (bp 60°-68°C) with three 20 ml portions of 1% pyrophosphate solution and add 50 ml ethyl ether making a 20% ether-80% hexane mixture.
5. Hydrochloric acid, 2.5N solution - 20.6 ml hydrochloric acid diluted to 100 ml

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm quartz cells
2. Centrifuge with 50 ml glass-stoppered tubes
3. Mechanical shaker
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.04 gram chlorophacinone standard into a 100 ml volumetric flask, dissolve in and make to volume with dioxane/sodium pyrophosphate mixture, mix thoroughly. Pipette 10 ml into a second 100 ml volumetric flask, make to volume with 1% pyrophosphate solution, and mix thoroughly. Pipette 10 ml of this solution into a 50 ml volumetric flask, make to volume with the 1% pyrophosphate solution, and mix thoroughly. (final conc 8 µg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.0008 gram chlorophacinone (0.4 gram for a 0.2% product) into a 250 ml glass-stoppered Erlenmeyer flask, add by pipette 100 ml dioxane/pyrophosphate mixture, close tightly, and shake on a mechanical shaker for one hour. Transfer 30-35 ml to a glass-stoppered centrifuge tube and centrifuge for 5 minutes. Pipette 25 ml of clear solution into a 125 ml glass-stoppered Erlenmeyer flask, add 5 ml 2.5N hydrochloric acid and 50 ml ether-hexane solution, stopper tightly, and shake for 5 minutes.

Pipette 20 ml of the ether layer into another centrifuge tube and add by pipette 10 ml 1% pyrophosphate solution. Shake for 2 minutes and remove the ether layer -- this is conveniently done by using a tube drawn into a fine tip and connected to a water aspirator. If the aqueous phase is not clear, centrifuge for a few minutes with the top off to remove any traces of the ether-hexane phase. (final conc 8 μg chlorophacinone/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings, balance the pen for 0 and 100% transmission at 285 nm with 1% pyrophosphate solution in each cell. Scan both standard and sample from 360 nm to 240 nm, using 1% pyrophosphate solution in the reference cell. Measure the absorbance of both standard and sample at 285 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent chlorophacinone as follows:

$$\% = \frac{(\text{abs. sample})(\text{wt. std.})(\% \text{ purity std.})}{(\text{abs. std.})(\text{wt. sample})}$$

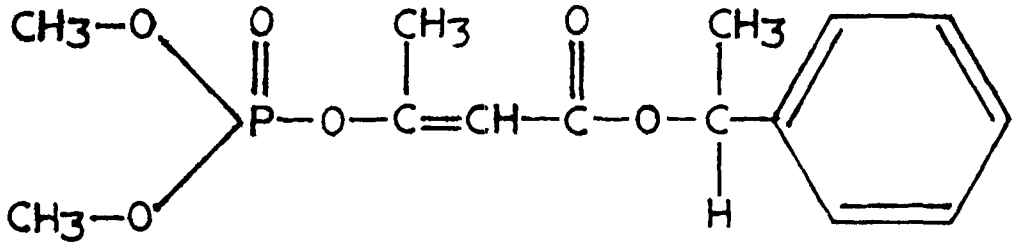
Method submitted by Mark W. Law, EPA Beltsville Chemistry Laboratory, Beltsville, Md.

April 1977

Crotoxyphos EPA-1
(tentative)

Determination of Crotoxyphos by Gas Liquid Chromatography FID - Internal Standard

Crotoxyphos is the common name (ISO and BSI) for dimethyl phosphate of alpha-methylbenzyl 3-hydroxy-cis-crotonate, a registered insecticide having the chemical structure:



Molecular formula: $C_{14}H_{19}O_6P$

Molecular weight: 314.3

Boiling point: 135°C at 0.03 mm Hg (technical grade)

Physical state, odor, and color: light straw-colored liquid with a mild ester odor

Solubility: 0.1% in water at room temperature; slightly soluble in kerosene and saturated hydrocarbons; soluble in acetone, chloroform, ethanol, isopropanol, and highly chlorinated hydrocarbons; miscible with xylene

Stability: stable in hydrocarbon solvents, but hydrolyzed by water; decomposes in acidic or basic solution; slightly corrosive to mild steel, copper, lead, zinc, and tin; non-corrosive to stainless steel 316, monel, aluminum 3003; will not attack rigid PVC, fiber glass, reinforced polyester or the usual lacquers used for lining drums; formulations made with common pesticide carriers are not stable for

Other names: Ciodrin (Shell), SD 4294, dimethyl-2-(alpha-methyl-benzocarbonyl)-1-methyl vinyl phosphate(E), 1-methyl-benzyl 3-(dimethoxyphosphinyloxy)-cis-crotonate, dimethyl cis-1-methyl-2-(1-phenylethoxycarbonyl) vinyl phosphate

Note! This method was developed and is used by the EPA Beltsville Chemistry Laboratory. The Kentucky Division of Regulatory Services uses a very similar method--data is given for their method following this EPA method.

Reagents:

1. Crotoxyphos standard of known % purity
2. Dipentyl phthalate standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 1.0 gram dipentyl phthalate standard into a 50 ml volumetric flask; dissolve in and make to volume with acetone. (conc 20 mg dipentyl phthalate/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 2 mm ID glass column packed with 5% SE-30 on Chromosorb W DMCS AW (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	205°C
Injection temperature:	250°C
Detector temperature:	250°C
Carrier gas:	Nitrogen or helium
Carrier gas pressure:	30 psi (adjusted for specific GC)
Hydrogen pressure:	20 psi (adjusted for specific GC)
Air pressure:	30 psi (adjusted for specific GC)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram crotoxyphos standard into a 25 ml volumetric flask. Add by pipette 5 ml of the internal standard solution, make to volume with acetone, and shake thoroughly. (final conc 4 mg crotoxyphos and 4 mg dipentyl phthalate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram crotoxyphos into a 25 ml volumetric flask. Add by pipette 5 ml of the internal standard solution. Dissolve and make to volume with acetone. (final conc 4 mg crotoxyphos and 4 mg dipentyl phthalate/ml)

Determination:

Inject 5 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is crotoxyphos, then dipentyl phthalate.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of crotoxyphos and dipentyl phthalate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

I.S. = internal standard = dipentyl phthalate

$$RF = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area crotoxyphos})}{(\text{wt. crotoxyphos})(\%\text{ purity crotoxyphos})(\text{pk. ht. or area I.S.})}$$

Determine the percent crotoxyphos for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area crotoxyphos})}{(\text{wt. sample})(\text{pk. ht. or area I.S.})(RF)}$$

Method submitted by Mark W. Law, EPA Beltsville Chemistry Laboratory, Beltsville, Maryland.

A very similar method, differing as noted below, was submitted by the Division of Regulatory Services, Kentucky Agricultural Experiment Station, University of Kentucky, Lexington, Kentucky 40506.

Column: 6' x 2 mm ID glass column packed with 3% OV-1 on 60/80 mesh Gas Chrom Q

Internal Standard: dibutyl phthalate

Conc. of crotoxyphos: 10 mg/ml in both standard and sample solutions

Conc. of internal standard: 2.5 mg/ml in both standard and sample solutions

Volume injected: 1.5 µl

Column temperature: 230°C

Injection temperature: 300°C

Detector temperature: 300°C

Carrier gas: Nitrogen - 60 psi or 13.3 ml/min

Hydrogen: 34 psi or 30 ml/min

Air: 28 psi or 300 ml/min

Instrument: Perkin Elmer 900 or Varian 2700

The above conditions should be adjusted to give optimum results with the particular GC used.

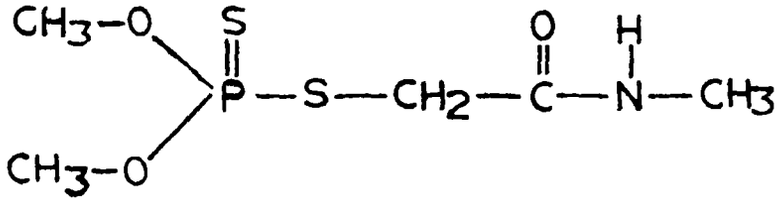
Note: These methods have been designated as tentative. Any comments, criticisms, suggestions, data, etc. concerning these methods will be appreciated, especially as related to analysis of different crotoxyphos formulations.

June 1977

Dimethoate EPA-1
(tentative)

Determination of Dimethoate by Gas Liquid Chromatography (TCD - Internal Standard)

Dimethoate is the accepted common name for O,O-dimethyl S-[(methylcarbamoyl) methyl] phosphorodithioate, a registered insecticide having the chemical structure:



Molecular formula: $C_5H_{12}NO_3PS_2$

Molecular weight: 229.1

Melting point: pure compound - 51 to 52°C; technical - 43 to 50°C

Physical state, color, and odor: pure compound forms colorless crystals and has a camphor-like odor; technical compound has a mercaptan odor

Solubility: 2-3% in water; most soluble in polar solvents such as alcohols and ketones (acetone and cyclohexanone); lower solubility in non-polar solvents such as xylene and hexane

Stability: stable in aqueous solutions; hydrolyzed by aqueous alkali; heating converts dimethoate to the $-SCH_3$ isomer; incompatible with alkaline pesticides

Other names: E.I. 12,880, Cygon, Dimetate (American Cyanamid); L395, Fostion MM, Rogor (Montecatini); Roxion (Cela); Perfekthion (BASF); Daphene, De-Fend, Dimethogen, Rebelate, Trimetion

Reagents:

1. Dimethoate standard of known % purity
2. Heptachlor standard of known % purity
3. Chloroform, pesticide or spectro grade
4. Internal Standard solution - weigh 1 gram heptachlor standard into a 25 ml volumetric flask; dissolve in and make to volume with chloroform; mix well. (conc 40 mg heptachlor/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 4' x 1/4" I.D. glass, packed with 5% SE-30 on Diatoport S or equivalent column (such as 4' x 1/4" I.D. glass, packed with 5% SP-2100 on 80/100 Chromosorb 750)
3. Precision liquid syringe: 10 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	165°C
Injection temperature:	200°C
Detector temperature:	200°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas pressure:	40 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

For use with emulsifiable concentrates and liquid formulations - weigh 0.1 gram dimethoate standard into a 10 ml volumetric flask; add 5 ml internal standard solution by pipette, make to volume with chloroform, and mix well. (final conc 10 mg dimethoate and 20 mg heptachlor/ml)

For use with dusts, granules, and wettable powders - weigh 0.1 gram dimethoate standard into a small glass-stoppered flask or screw-cap bottle, add by pipette 5 ml of internal standard solution and 5 ml chloroform, close tightly and shake well to dissolve the dimethoate. (final conc 10 mg dimethoate and 20 mg heptachlor/ml)

Preparation of Sample:

For emulsifiable concentrates and liquid formulations - weigh a portion of sample equivalent to 0.1 gram dimethoate into a 10 ml volumetric flask; add 5 ml of internal standard solution by pipette, make to volume with chloroform, and mix well. (final conc 10 mg dimethoate and 20 mg heptachlor/ml)

For dusts, granules, and wettable powders - weigh a portion of sample equivalent to 0.1 gram dimethoate into a small glass-stoppered flask or screw-cap bottle; add by pipette 5 ml internal standard and 5 ml of chloroform, close tightly, and shake on a mechanical shaker for 10-15 minutes or shake by hand intermittently for 25-30 minutes. (final conc 10 mg dimethoate and 20 mg heptachlor/ml)

Determination:

Inject 2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is dimethoate, then heptachlor.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of dimethoate and heptachlor from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{\text{(wt. heptachlor)(\% purity heptachlor)(pk. ht. or area dimethoate)}}{\text{(wt. dimethoate)(\% purity dimethoate)(pk. ht. or area heptachlor)}}$$

Determine the percent dimethoate for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{\text{(wt. heptachlor)(\% purity heptachlor)(pk. ht. or area dimethoate)}}{\text{(wt. sample)(pk. ht. or area heptachlor)(RF)}}$$

Method submitted by Stelios Gerazounis, EPA Product Analysis Lab, Region II, New York, N.Y. (experimental method May 1970)

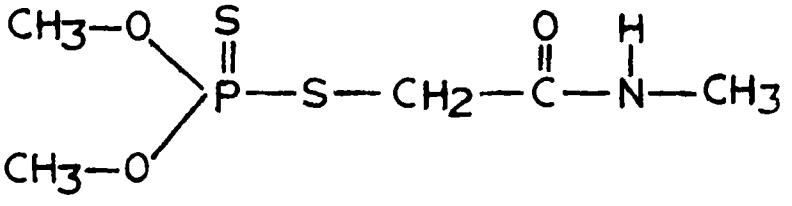
Any comments, criticisms, suggestions, data, etc. concerning this method or its use will be appreciated.

June 1977

Dimethoate EPA-2
(tentative)

Determination of Dimethoate by Gas Liquid Chromatography (FID - Internal Standard)

Dimethoate is the accepted common name for O,O-dimethyl S-[(methylcarbamoyl) methyl]phosphorodithioate, a registered insecticide having the chemical structure:



Molecular formula: $C_5H_{12}NO_3PS_2$

Molecular weight: 229.1

Melting point: pure compound - 51 to 52°C; technical - 43 to 50°C

Physical state, color, and odor: pure compound forms colorless crystals and has a camphor-like odor; technical compound has a mercaptan odor

Solubility: 2-3% in water; most soluble in polar solvents such as alcohols and ketones (acetone and cyclohexanone); lower solubility in non-polar solvents such as xylene and hexane

Stability: stable in aqueous solutions; hydrolyzed by aqueous alkali; heating converts dimethoate to the $-SCH_3$ isomer; incompatible with alkaline pesticides

Other names: E.I. 12,880, Cygon, Dimetate (American Cyanamid); L395, Fostion MM, Rogor (Montecatini); Roxion (Cela); Perfekthion (BASF); Daphene, De-Fend, Dimethogen, Rebelate, Trimetion

Reagents:

1. Dimethoate standard of known % purity
2. Dibutyl phthalate standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 1.5 gram dibutyl phthalate into a 200 ml volumetric flask; dissolve in and make to volume with acetone; mix well. (conc 7.5 mg dibutyl phthalate/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm glass column packed with 5% SE-30 on 80/100 Chromosorb W HP (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Usual laboratory glassware*

* Virginia laboratories place their weighed samples in 25 mm x 200 mm screw-top culture tubes, add solvent by pipette, and seal tightly with teflon-faced rubber-lined screw caps.

These tubes are rotated end over end at about 40-50 RPM on a standard Patterson-Kelley twin shell blender that has been modified by replacing the blending shell with a box to hold a 24-tube rubber-covered rack.

Operating Conditions for FID:

Column temperature: 170°C

Injection temperature: 220°C

Detector temperature: 220°C

Carrier gas: Nitrogen

Carrier gas pressure: 60 psi (adjusted as necessary)

Hydrogen pressure: 20 psi (adjusted as necessary)

Air pressure: 30 psi (adjusted as necessary)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram dimethoate standard into a 50 ml volumetric flask, add 10 ml internal standard solution by pipette, make to volume with acetone, and shake to dissolve. (final conc 2 mg dimethoate and 1.5 mg dibutyl phthalate/ml)

Preparation of Sample:

For emulsifiable concentrates and liquid formulations - weigh a portion of sample equivalent to 0.1 gram dimethoate into a 50 ml volumetric flask; add 10 ml internal standard solution, make to volume with acetone, and mix well. (final conc 2 mg dimethoate and 1.5 mg dibutyl phthalate/ml)

For dusts, granules, and wettable powders - weigh a portion of sample equivalent to 0.1 gram dimethoate into a glass-stoppered flask or screw-cap bottle; add by pipette 10 ml internal standard solution and 40 ml acetone, close tightly, and shake on a mechanical shaker for 10-15 minutes or shake by hand intermittently for 25-30 minutes. (final conc 2 mg dimethoate and 1.5 mg dibutyl phthalate/ml)

Determination:

Inject 1-2 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is dimethoate, then dibutyl phthalate.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of dimethoate and dibutyl phthalate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

DBP = dibutyl phthalate

$$RF = \frac{(\text{wt. DBP})(\%\text{ purity DBP})(\text{pk. ht. or area dimethoate})}{(\text{wt. dimethoate})(\%\text{ purity dimethoate})(\text{pk. ht. or area DBP})}$$

Determine the percent dimethoate for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. DBP})(\%\text{ purity DBP})(\text{pk. ht. or area dimethoate})}{(\text{wt. sample})(\text{pk. ht. or area DBP})(\text{RF})}$$

This method was submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, Va. 23219.

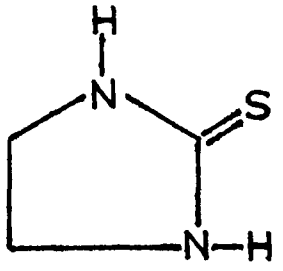
This method has been designated as tentative since it is a Va. Exp. method and because some of the data has been suggested by EPA's Beltsville Chemistry Lab. Any comments, criticism, suggestion, data, etc. concerning this method will be appreciated.

Determination of Ethylenethiourea in Ethylenebisdithiocarbamate Fungicides by Gas Liquid Chromatography (FID and TCD)

Ethylenethiourea (ETU) is a degradation product of ethylene-bisdithiocarbamates (EBDC). It may be formed during manufacture, storage, or use of EBDC fungicide formulations.

The following methods are not residue methods in the sense of measuring ETU in raw crops, processed foods, soil, or water. However, these methods will show the presence of ETU in formulated EBDC fungicide products.

Chemically, ETU is 2-imidazolidinethione and has the structure:



Molecular formula: $C_3H_6N_2S$

Molecular weight: 102.17

Melting point: 203-204°C (technical: 199-204°C)

Physical state, color, and odor: white to pale green crystals, faint amine odor

Solubility: solubility in 100 ml water - 2 g at 30°, 9 g at 60°, 44 g at 90°; moderately soluble at room temperature in methanol, ethanol, ethylene glycol, pyridine, acetic acid, and naphtha; insoluble in acetone, ether, chloroform, benzene, and ligroin

Stability: dry crystals are stable under usual laboratory storage conditions; solutions in water or methanol are reasonably stable for 6 months to 1 year; somewhat affected by ultraviolet light; reported to be unstable as residue on crops or upon cooking

Other names: ETU

The method includes a procedure for using either a flame ionization detector (FID) or a thermal conductivity detector (TCD). The FID with its higher sensitivity is more useful for determining small amounts of ETU. However, since the TCD is non-destructive, it permits collection of ETU and other eluted components for Infrared or Mass Spectrometry confirmation.

Reagents:

1. ETU standard of known % purity
2. Methanol, pesticide or spectro grade -- add about 10 grams anhydrous sodium sulfate per 100 ml to minimize the effect on any water present in the alcohol.
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Gas chromatograph with flame ionization detector and/or thermal conductivity detector
2. TCD column: 3' x 1/4" OD stainless steel packed with 2% Carbowax 20M on Chromosorb W AW DMCS (or equivalent column -- see note below)
3. FID column: 6' x 2 mm ID glass packed with 2% SP-1000 on Chromosorb 750 (or equivalent column -- see note below)

4. Precision liquid syringe: 50 µl (TCD) and/or 10 µl (FID)
5. Screw-cap test tubes: 16 mm x 150 mm
6. Centrifuge (for above tubes)

Note! Carbowax 20M and SP-1000 are equally effective (very similar McReynolds Constants) in the determination of ETU. OV-225 and XE-60 have also been used. OV-225 produces less tailing with methanol and ETU.

Supelcoport, Chromosorb W AW DMCS, Chromosorb W HP, and Chromosorb 750 all have been used and are satisfactory solid supports.

Any combination of these or other stationary phases and solid supports may be used if the ETU peak is reasonably symmetrical and well separated from the solvent tail.

Determination using Thermal Conductivity Detector:

Operating Conditions:

Column temperature:	220°C
Injection temperature:	270°C
Detector temperature:	250°C
Filament current:	250 ma
Carrier gas:	Helium
Carrier gas pressure:	40 psi (adjusted for specific GC)
Carrier gas flow:	100 ml/min (adjusted for specific GC)

Operating conditions for filament current, column temperature, or gas flow should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.2 gram ETU standard into a 100 ml volumetric flask; dissolve in and make to volume with methanol (conc 2 µg ETU/µl)

Preparation of Sample:

Weigh 1 gram of the ethylenebisdithiocarbamate fungicide sample into a 16 mm x 150 mm screw-cap test tube and add approximately 1 gram anhydrous sodium sulfate. Add 5 ml methanol by pipette, close tightly, and shake intermittently over a period of one hour. Centrifuge until a clear liquid layer is obtained. (The sides of the tube may be washed down with the clear layer and the tube re-centrifuged for final clarification of the liquid layer.)

One gram of sample in 5 ml methanol gives a sample concentration of 200 µg/µl which is equivalent to a concentration of 2 µg ETU/µl at the 1% ETU level or of 0.2 µg ETU/µl at the 0.1% ETU level. For higher concentrations, 10 or 15 ml of methanol may be used instead of only 5 ml with 1 gram of sample, or a smaller sample size may be used.

Determination:

Using a precision liquid syringe, alternately inject three 5-80 µl portions each of standard and sample solutions depending on the amount needed to give a measurable size peak. Measure the peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks, especially with samples containing very small amounts of ETU. The amount injected is limited by the size of the methanol peak.

Using a Beckman GC-2A gas chromatograph (no longer used) on which the injection port, column, and detector were all at the same temperature, the standardization curve using peak area vs. µl of ETU standard was linear from 10 to 160 µg. Other gas chromatographs where the injection port and detector can be at a higher temperature than the column will give a better response, as will a more sensitive detector. Under these conditions the linearity may be extended down to 5 µg or less.

Calculation:

From the average peak area calculate the percent ETU as follows:

$$\% = \frac{(\text{pk. area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. area standard})(\text{wt. sample injected})}$$

Collection of ETU for Infrared and Mass Spectrometry:

The exhaust port of the thermal conductivity detector is modified by attaching a piece of 1/8" stainless steel tubing covered with Teflon tubing. The exact length depends on the configuration needed for the particular detector. The Teflon tubing should extend about one inch past the end of the stainless steel tubing to allow insertion of about 1" of a 6-inch piece of 3 mm glass tubing. The entire length of Teflon tubing is wound with a flexible heating tape attached to a variac. It is convenient to include a thermometer (preferably dial type with stainless steel shaft also covered by Teflon) placed along the side of the heated tube. The variac should be set so that the temperature is the same as the detector or about 10°C higher.

The ETU is condensed in the glass tube, usually within a one-inch length of the air-cooled tube just outside of the heated portion. No special cooling is needed.

For IR identification, the ETU is washed from the glass tube with 4 or 5 50 µl portions of methanol into a small (1 or 2 ml) Mini-Vial (small vial with cone-shaped interior) containing a few milligrams of potassium bromide. The KBr and methanol solution is stirred with a small glass rod drawn into a long fine tip. Gentle heat is applied until the methanol evaporates completely. The KBr (with ETU) is then placed into a micro-pellet press, formed into a disk, and scanned on an IR spectrophotometer from 4000 cm^{-1} to 250 cm^{-1} (2.5 µ to 40 µ). A similar pellet is made from a portion of ETU standard solution and the IR scans compared.

For mass spectrometer identification, the ETU is washed from the glass tube into a 1 ml Kuderna-Danish concentrator tube, evaporated to a convenient workable volume, and injected into a GC-MS.

Determination using Flame Ionization Detector:

Operating Conditions:

Column temperature:	180°C
Injection temperature:	270°C
Detector temperature:	270°C
Carrier gas:	Helium

Operating conditions for column temperature, carrier gas flow, or hydrogen/air flow rates should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.2 gram ETU standard into a 100 ml volumetric flask; dissolve and make to volume with methanol (final conc 2 mg ETU/µl)

Preparation of Sample:

Weigh 1 gram of the ethylenebisdithiocarbamate fungicide sample into a 16 x 150 mm screw-cap test tube and add approximately 1 gram of anhydrous sodium sulfate. Add 5 ml methanol by pipette, close tightly, and shake intermittently over a period of one hour. Centrifuge until a clear liquid layer is obtained. (The sides of the tube may be washed down with the clear layer and the tube re-centrifuged for final clarification of the liquid layer.)

One gram of sample in 5 ml methanol gives a sample concentration of 200 µg/µl which is equivalent to a concentration of 2 µg ETU/µl at the 1% ETU level or of 0.2 µg ETU/µl at the 0.1% ETU level. For higher concentrations of ETU, 10 or 15 ml of methanol may be used instead of only 5 ml with 1 gram of sample, or a smaller sample size may be used.

Determination:

Using a precision liquid syringe, alternately inject three 2-3 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent ETU as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

This method (including both TCD and FID) has been used by EPA Beltsville Chemistry Lab for the last six years. The collection technique has been developed by Jack Looker.

The method is designated as tentative since several different columns and gas chromatographs have been used throughout these six years.

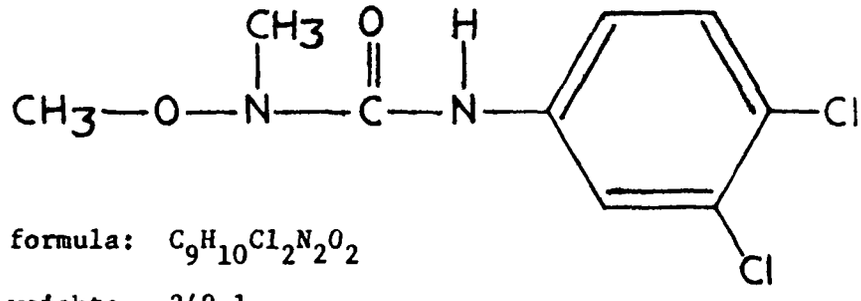
Any comments, criticism, suggestions, or data concerning the use of this method will be greatly appreciated.

April 1977

Linuron EPA-3
(tentative)

Determination of Linuron by Ultraviolet Spectroscopy

Linuron is the common name for 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{10}Cl_2N_2O_2$

Molecular weight: 249.1

Melting point: 93 to 94°C

Physical state, color, and odor: odorless, white, crystalline solid

Solubility: 75 ppm in water at 25°C; slightly soluble in aliphatic hydrocarbons, moderately soluble in ethanol and common aromatic solvents, soluble in acetone

Stability: stable at its m.p. and in solution; slowly decomposed by acids and bases in moist soil; non-corrosive

Other names: Lorox (DuPont), Afalon, Sarclex, HOE 2810

Reagents:

1. Linuron standard of known % purity
2. Methanol, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram linuron standard into a 100 ml volumetric flask. Dissolve in and make to volume with methanol; mix thoroughly. Pipette a 10 ml aliquot into a second 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette a 5 ml aliquot into a third 100 ml volumetric flask, make to volume with methanol, and again mix thoroughly. (final conc 5 µg linuron/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram of linuron into a 250 ml Erlenmeyer glass-stoppered flask. Add 100 ml methanol by pipette and shake on a mechanical shaker for 30 minutes. Allow to settle; filter or centrifuge if necessary, taking precautions to avoid evaporation. Pipette 10 ml into a 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette 5 ml into another 100 ml volumetric flask, make to volume with methanol, and again mix thoroughly. (final conc 5 µg linuron/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 246 nm with methanol in each cell. Scan both the standard and sample from 350 nm to 200 nm with methanol in the reference cell. Measure the absorbance of both standard and sample at 246 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent linuron as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

Beer's Law is followed from 1 to 10 µg/ml.

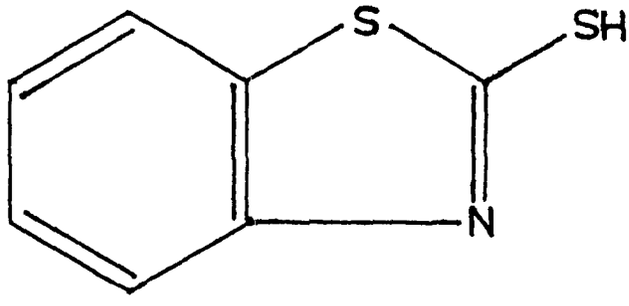
Method submitted by David Persch, EPA Product Analysis Lab, Region II, New York, N. Y.

April 1977

Mercaptobenzothiazole EPA-1
(tentative)

Determination of 2-Mercaptobenzothiazole (Sodium Salt) by Ultraviolet Spectroscopy

2-mercaptobenzothiazole is a registered fungicide having the chemical structure:



Molecular formula: $C_7H_5NS_2$

Molecular weight: 167.25

Melting point: 180.2 to 181.7°C (technical product - 170° to 175°C)

Physical state, color, and odor: pale yellow, monoclinic needles or leaflets; disagreeable odor

Solubility: practically insoluble in water; solubility at 25°C - 2% in alcohol, 1% in ether, 10% in acetone, 1% in benzene, $<$0.2% in carbon tetrachloride, $<$0.5% in naphtha; moderately soluble in glacial acetic acid; soluble in alkalies and alkali carbonate solutions

Stability:

Other names: 2-benzothiazolethiol, MBT, Captax, Dermacid, Mertax, Thiotax, Nuodex 84 (sodium salt), Bantex and Zetax (zinc salts), Niacides (mixtures with carbamate fungicides)

Reagents:

1. 2-mercaptobenzothiazole standard of known % purity
2. Sodium hydroxide - 0.5% solution in water

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.09 gram 2-mercaptobenzothiazole standard into a 500 ml volumetric flask, dissolve in and make to volume with 0.5% sodium hydroxide solution, and mix thoroughly. Pipette a 25 ml aliquot into a 100 ml volumetric flask, make to volume with 0.5% sodium hydroxide solution, and mix thoroughly. Pipette 10 ml of this solution into another 100 ml volumetric flask, again make to volume with 0.5% sodium hydroxide solution, and mix thoroughly. (final conc 4.5 µg 2-mercaptobenzothiazole/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.09 gram 2-mercapto-benzothiazole into a 500 ml volumetric flask, dissolve in and make to volume with 0.5% sodium hydroxide solution, and mix thoroughly. Pipette a 25 ml aliquot into a 100 ml volumetric flask, make to volume with 0.5% sodium hydroxide solution, and mix thoroughly. Pipette 10 ml of this solution into another 100 ml volumetric flask, again make to volume with 0.5% sodium hydroxide solution, and mix thoroughly. (final conc 4.5 µg 2-mercaptobenzothiazole/ml)

Note: Samples in paste form have been successfully extracted by one hour shaking.

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 308 nm with 0.5% sodium hydroxide solution in each cell. Scan both the standard and sample from 360 nm to 250 nm with 0.5% sodium hydroxide solution in the reference cell. Measure the absorbance of both standard and sample at 308 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent 2-mercaptobenzothiazole as follows:

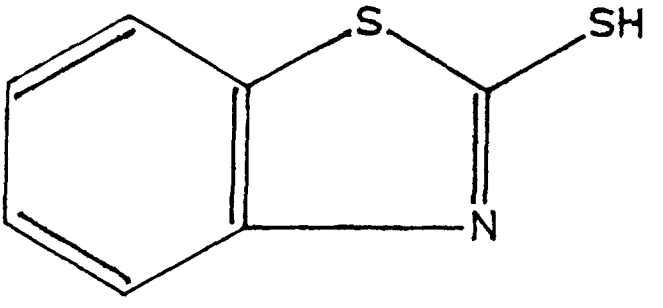
$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

% 2-mercaptobenzothiazole, sodium salt = 1.131 x 2-mercaptobenzothiazole

Method submitted by Edward Yager, EPA Product Analysis Laboratory, Region II, New York, N.Y.

Determination of 2-Mercaptobenzothiazole (40% Solution of Sodium Salt) by Potentiometric Titration

2-mercaptobenzothiazole is a registered fungicide having the chemical structure:



Molecular formula: $C_7H_5NS_2$

Molecular weight: 167.25

Melting point: 180.2 to 181.7°C (technical product - 170° to 175°C)

Physical state, color, and odor: pale yellow, monoclinic needles or leaflets; disagreeable odor

Solubility: practically insoluble in water; solubility at 25°C - 2% in alcohol, 1% in ether, 10% in acetone, 1% in benzene, <0.2% in carbon tetrachloride, <0.5% in naphtha; moderately soluble in glacial acetic acid; soluble in alkalies and alkali carbonate solutions

Stability:

Other names: 2-benzothiazolethiol, MBT, Captax, Dermacid, Mertax, Thiotax, Nuodex 84 (sodium salt), Bantex and Zetax (zinc salts), Niacides (mixtures with carbamate fungicides)

Reagents:

1. 2-mercaptobenzothiazole, sodium salt standard of known % purity (see note under Procedure: Calibration of Instrument:)
2. Hydrochloric acid, 0.1 N solution
3. Buffer solutions, pH 4.00 and 7.00

Equipment:

1. pH meter or titrimeter
2. Magnetic stirrer with 1" stirring bar
3. Usual laboratory glassware

Procedure:

Calibration of Instrument:

Calibrate the pH meter or titrimeter at pH 4.00 and pH 7.00.

Note: Each time the instrumentation for this method is changed (new pH meter, new electrode, repairs, etc.) or at least once a year, it is desirable to titrate a known standard to verify proper instrument response and to locate the inflection point on the titration curve where the 2-mercaptobenzothiazole will be determined.

Preparation of Sample:

Weigh a portion of sample equivalent to 0.4-0.5 gram 2-mercaptobenzothiazole (for a 21-26 ml (net) titration) into a 250 ml beaker; add 100 ml distilled water and a 1" magnetic stirring bar. Place the beaker on a magnetic stirrer, insert the electrodes, and stir.

Titration:

Titrate with 0.1 N hydrochloric acid solution in small increments, recording the milliliters added and the corresponding pH after each addition. On either side of pH 9.5 and pH 5, add the hydrochloric acid in increasingly smaller amounts, finally adding the acid drop by drop to obtain a detailed change in the slope of the titration curve at both inflection points.

Calculation:

Plot the milliliters of hydrochloric acid on the abscissa and the corresponding pH values on the ordinate. Draw a smooth curve through these points. Two inflection points indicate free sodium hydroxide and the sodium salt of 2-mercaptobenzothiazole.

The first endpoint is taken as the mid-point of the inflection near pH 9.5 and is the milliliters of 0.1 N hydrochloric acid used to titrate any free sodium hydroxide according to the reaction:

$$NaOH + HCl \rightarrow NaCl + H_2O$$

The second endpoint is taken as the mid-point of the inflection near pH 5 and is the total milliliters of 0.1 N hydrochloric acid used to titrate any free sodium hydroxide plus the sodium salt of 2-mercaptobenzothiazole (RSNa) according to the reaction:

$$RSNa + HCl \rightarrow RSH + NaCl$$

The percent sodium salt of 2-mercaptobenzothiazole is determined as follows:

$$\% = \frac{(B-A)(N)(0.18924)(100)}{(\text{weight of sample})} ,$$

where:

B = mls 0.1 N hydrochloric acid at second endpoint

A = mls 0.1 N hydrochloric acid at first endpoint

N = actual N of hydrochloric acid

0.18924 = meq. wt. of sodium salt of 2-mercaptobenzothiazole

Method submitted by Stelios Gerazounis, EPA Product Analysis Laboratory, Region II, New York, N.Y.

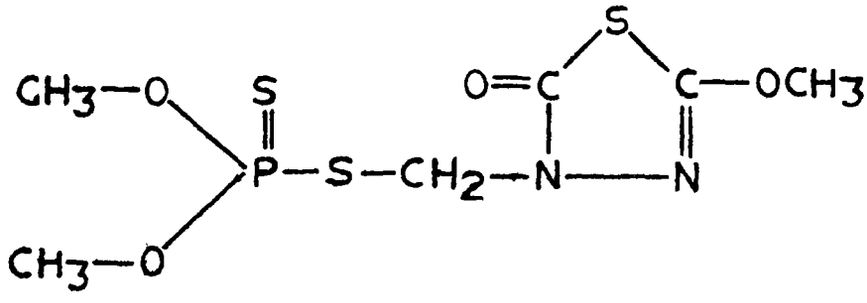
Any comments, criticisms, suggestions, data, etc. concerning this method will be appreciated, especially as related to any other formulation analysis.

June 1977

Methidathion EPA-1
(tentative)

Determination of Methidathion by Gas Liquid Chromatography (FID - Internal Standard)

Methidathion is the accepted common name for O,O-dimethyl phosphorodithioate S-ester with 4-(mercaptomethyl)-2-methoxy-delta 2-1,3,4-thiadiazolin-5-one, a registered insecticide and acaricide having the chemical structure:



Molecular formula: $C_6H_{11}N_2O_4PS_3$

Molecular weight: 302.3

Melting point: 39 to 40°C

Physical state, color, and odor: colorless crystals, characteristic odor of organophosphates

Solubility: 240 ppm in water at 25°C; readily soluble in acetone, benzene, methanol

Stability: stable in neutral and weakly acid media but much less stable in alkali. Compatible with captan, thiram, zineb, and acaricides.

Other names: GS-13005, Supracide, Ultracide (Ciba-Geigy); S-(2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl) dimethyl phosphorothiolothionate; S-[(5-methoxy-2-oxo-1,3,4-thiadiazol-3(2H)-yl)methyl] O,O-dimethyl phosphorodithioate

Reagents:

1. Methidathion standard of known % purity
2. Aldrin standard of known HHDN content
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh a portion of aldrin standard equivalent to 0.1 gram HHDN into a 100 ml volumetric flask; dissolve in and make to volume with acetone; mix well. (conc 1 mg HHDN/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 4 mm glass column packed with 3% OV-1 on 60/80 Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Usual laboratory glassware

Operating Conditions for FID:

Column temperature: 185°C

Injection temperature: 215°C

Detector temperature: 240°C

Carrier gas: Nitrogen

Carrier gas pressure: 60 psi (adjusted as necessary)

Hydrogen pressure: 20 psi (adjusted as necessary)

Air pressure: 20 psi (adjusted as necessary)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram methidathion standard into a small glass-stoppered flask or screw-cap bottle. Add by pipette 25 ml of the internal standard solution and shake to dissolve. (final conc 4 mg methidathion and 1 mg HHDN/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram methidathion into a small glass-stoppered flask or screw-cap bottle. Add by pipette 25 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the methidathion. For coarse or granular materials, shake mechanically for 10-15 minutes or shake by hand intermittently for 25-30 minutes. (final conc 4 mg methidathion and 1 mg HHDN/ml)

Determination:

Inject 2-3 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is HHDN, then methidathion.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of methidathion and HHDN from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. HHDN})(\text{pk. ht. or area methidathion})}{(\text{wt. methidathion})(\%\ \text{purity methidathion})(\text{pk. ht. or area HHDN})}$$

Determine the percent methidathion for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. HHDN})(\text{pk. ht. or area methidathion})}{(\text{wt. sample})(\text{pk. ht. or area HHDN})(RF)}$$

Method submitted by Division of Regulatory Services, Kentucky Agricultural Experiment Station, University of Kentucky, Lexington, Ky. 40506.

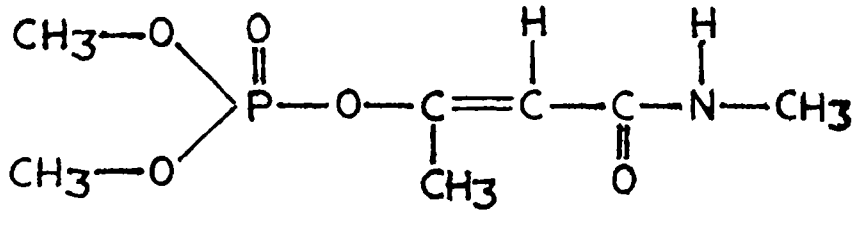
Any comments, criticism, suggestions, data, etc. concerning this method or its use will be appreciated.

April 1977

Monocrotophos EPA-3
(tentative)

Determination of Monocrotophos in Liquid Formulations by Gas Liquid Chromatography (FID - Internal Standard)

Monocrotophos is the common name for dimethyl phosphate of 3-hydroxy-N-methyl-cis-crotonamide, a registered insecticide having the chemical structure:



Molecular formula: $C_7H_{14}NO_5P$

Molecular weight: 223

Melting point: 54 to 55°C (technical material 25 to 30°C)

Physical state, color, and odor: colorless to white crystalline material with a mild ester odor. The technical product is a reddish brown semi-solid.

Solubility: miscible with water; soluble in acetone and ethanol; sparingly soluble in xylene but almost insoluble in diesel oils and kerosene

Stability: unstable in lower but stable in higher alcohols and glycols, stable in ketones; hydrolyzes slowly at pH 1 to 7, rapidly above pH 7; corrosive to black iron, drum steel, brass, SS 304, but does not attack glass, aluminum, or SS 316; incompatible with alkaline pesticides

Other names: Azodrin (Shell); Nuvacron (Ciba); Monocron; dimethyl-1-methyl-2-methyl carbamoyl vinyl phosphate; cis-3-(dimethoxyphosphinyloxy)-N-methylcrotonamide; O,O-dimethyl-O-(2-methylcarbamoyl-1-methyl vinyl)-phosphate

Reagents:

1. Monocrotophos standard of known % purity
2. Benzyl benzoate standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.45 gram benzyl benzoate into a 100 ml volumetric flask; dissolve in; and make to volume with acetone. (conc 4.5 mg benzyl benzoate/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 1/4" glass column packed with 3.8% UC-W98 on 80/100 diatoport S (or equivalent column such as SP-2100 on Chromosorb 750)
3. Precision liquid syringe: 5 or 10 µl
4. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	175°C
Injection temperature:	200°C (225° may be used)
Detector temperature:	240°C
Carrier gas:	Helium (nitrogen may be used)
Carrier gas flow rate:	30 ml/min - 40 PSI
Hydrogen flow rate:	30 ml/min - 12 PSI
Air flow rate:	55 ml/min - 40 PSI

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.13 gram monocrotophos standard into a 50 ml volumetric flask. Add (by pipette) 10 ml of the internal standard solution, swirl to dissolve, and make to volume with acetone. Mix thoroughly. (final conc 2.6 mg monocrotophos and 0.9 mg benzyl benzoate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.13 gram monocrotophos into a 50 ml volumetric flask. Add (by pipette) 10 ml of the internal standard solution; make to volume with acetone and mix thoroughly. (final conc 2.6 mg monocrotophos and 0.9 mg benzyl benzoate/ml)

Determination:

Inject 2-4 µl of standard solution and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is monocrotophos, then benzyl benzoate.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of monocrotophos and benzyl benzoate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

I.S. = internal standard = benzyl benzoate

$$RF = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area monocrotophos})}{(\text{wt. monocrotophos})(\%\text{ purity monocrotophos})(\text{pk. ht. or area I.S.})}$$

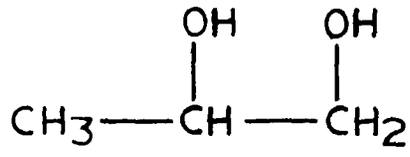
Determine the percent monocrotophos for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area monocrotophos})}{(\text{wt. sample})(\text{pk. ht. or area I.S.})(RF)}$$

Method submitted by George B. Radan, EPA Product Analysis Laboratory, Region II, New York, N. Y.

Determination of Propylene Glycol by Gas Liquid Chromatography (TCD - Internal Standard)

Propylene glycol is the common name for 1,2-dihydroxypropane, a registered disinfectant having the chemical structure:



Molecular formula: $C_3H_8O_2$

Molecular weight: 76.09

Boiling point: 188.2° at 760 mm Hg; freezes at -59°C

Physical state, color, and odor: colorless, viscous, hygroscopic liquid; slight odor; slightly acrid taste

Solubility: miscible with water, acetone, alcohols, chloroform, and many organic solvents; will dissolve many essential oils but is immiscible with fixed oils

Stability: stable under ordinary conditions; will oxidize at high temperatures giving such products as propionaldehyde, lactic acid, pyruvic acid, and acetic acid

Other names: 1,2-propanediol; methyl glycol; methylene glycol

Reagents:

1. Propylene glycol standard of known % purity
2. Octyl alcohol standard of known % purity

Reagents (cont'd):

3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 4 grams octyl alcohol standard into a 100 ml volumetric flask and make to volume with acetone; mix well. (conc 40 mg octyl alcohol/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 4' x 1/4" glass packed with 3% XE-60 on 60/80 Chromosorb G AW DMCS (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	80°C
Injection temperature:	150°C
Detector temperature:	230°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas flow:	30 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.3 gram propylene glycol standard into a 25 ml volumetric flask, add 10 ml internal standard solution by pipette,

Preparation of Standard (cont'd):

and make to volume with acetone; mix well. (final conc 12 µg propylene glycol and 16 µg octyl alcohol/µl)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.3 gram propylene glycol into a 25 ml volumetric flask, add 10 ml internal standard solution, and make to volume with acetone; mix well. (final conc 12 µg propylene glycol and 16 µg octyl alcohol/µl)

Determination:

Inject 2-3 µl of standard-internal standard solution and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights from 1/2 to 3/4 full scale. The peak heights of propylene glycol and octyl alcohol should be nearly the same (definitely within 25% of each other); if not, concentrations should be adjusted accordingly. The elution order is propylene glycol, then octyl alcohol. If the sample contains triethylene glycol, time should be allowed for this component to be eluted before the next injection is made.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of propylene glycol and octyl alcohol from both the standard-internal standard solution and the sample-internal standard solution.

Calculation (cont'd):

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

IS = internal standard = octyl alcohol

PG = propylene glycol

$$RF = \frac{(\text{wt. IS})(\%\text{ purity IS})(\text{pk. ht. or area PG})}{(\text{wt. PG})(\%\text{ purity PG})(\text{pk. ht. or area IS})}$$

Determine the percent propylene glycol for each injection of sample-internal standard solution as follows and calculate the average:

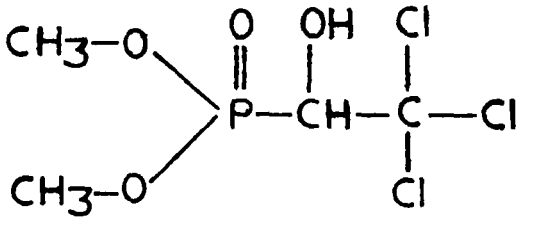
$$\% = \frac{(\text{wt. IS})(\%\text{ purity IS})(\text{pk. ht. or area PG})}{(\text{wt. sample})(\text{pk. ht. or area IS})(RF)}$$

Method submitted by Stelios Gerazounis, EPA Product Analysis Laboratory, Region II, New York, N.Y.

Any comments, criticisms, suggestions, data, etc. concerning the use of this method will be appreciated.

Determination of Trichlorfon by Infrared Spectroscopy

Trichlorfon is the common name (approved by ISO) for dimethyl (2,2,2-trichloro-1-hydroxyethyl) phosphonate, a registered insecticide having the chemical structure:



Molecular formula: $C_4H_8Cl_3O_4P$

Molecular weight: 257.5

Melting point: 83-84°C

Physical state, color, and odor: white crystalline solid

Solubility: 15.4 g/100 ml water at 25°C; soluble in benzene, ether, ethanol, and most chlorinated solvents; slightly soluble in petroleum oils, and in carbon tetrachloride

Stability: stable at room temperature, but is decomposed by water at higher temperatures and at pH 5.5 to form dichlorovos

Other names: trichlorphon (Great Britain), chlorofos (USSR), dipterex (Turkey), metrifonate (WHO), Neguvon (veterinary use), Dipterex, Tugon, Dylox, Bayer L 13/59, Bayer 15922

Reagents:

1. Trichlorfon standard of known % purity
2. Chloroform, pesticide or spectro grade preferred
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording, with matched 0.2 mm NaCl or KBr cells
2. Mechanical shaker
3. Filtration apparatus or centrifuge
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.250 gram trichlorfon standard into a 25 ml volumetric flask; dissolve and make to volume with chloroform. Add a small amount of granular anhydrous sodium sulfate to insure dryness. (final conc 10 mg trichlorfon/ml)

Preparation of Sample:

For dusts, granules, and wettable powders - weigh a portion of sample equivalent to 0.5 gram trichlorfon into a 125 ml glass-stoppered or screw-cap Erlenmeyer flask. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly, shake on a mechanical shaker for 1 hour, allow to settle; filter or centrifuge if necessary, taking precaution to avoid evaporation. (final conc 10 mg trichlorfon/ml)

For liquids - weigh sample equivalent to 0.5 gram trichlorfon into a 50 ml volumetric flask and make to volume with chloroform. Add a small amount of anhydrous sodium sulfate to insure dryness.

IR Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 1150 cm^{-1} to 900 cm^{-1} (8.7 μ to 11.1 μ).

Determine the absorbance of standard and sample using the peak at 1040 cm^{-1} (9.6 μ) and baseline from 1135 cm^{-1} to 950 cm^{-1} (8.8 μ to 10.53 μ).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent trichlorfon as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Method submitted by Mark W. Law, EPA Beltsville Chemistry Laboratory, Beltsville, Md.

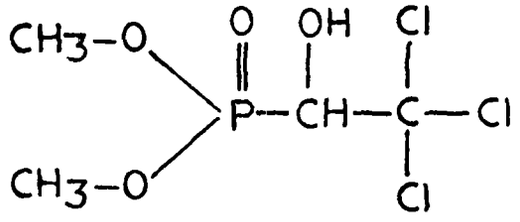
Any criticisms, suggestions, data, etc. on the use of this method will be appreciated.

April 1977

Trichlorfon EPA-2
(tentative)

Determination of Trichlorfon by Gas Liquid Chromatography (FID - Internal Standard)

Trichlorfon is the common name (approved by ISO) for dimethyl (2,2,2-trichloro-1-hydroxyethyl) phosphonate, a registered insecticide having the chemical structure:



Molecular formula: $C_4H_8Cl_3O_4P$

Molecular weight: 257.5

Melting point: 83-84°C

Physical state, color, and odor: white crystalline solid

Solubility: 15.4 g/100 ml water at 25°C; soluble in benzene, ether, ethanol, and most chlorinated solvents; slightly soluble in petroleum oils, and in carbon tetrachloride

Stability: stable at room temperature, but is decomposed by water at higher temperatures and at pH 5.5 to form dichlorovos

Other names: trichlorphon (Great Britain), chlorofos (USSR), dipterex (Turkey), metrifonate (WHO), Neguvon (veterinary use), Dipterex, Tugon, Dylox, Bayer L 13/59, Bayer 15922

Reagents:

1. Trichlorfon standard of known % purity
2. Diethyl phthalate standard of known % purity

3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 0.5 gram diethyl phthalate standard into a 50 ml volumetric flask; dissolve in and make to volume with acetone. (conc 10 mg diethyl phthalate/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 2 mm ID glass column packed with 5% SE-30 on Chromosorb W DMCS 80/100 mesh (or equivalent column)
3. Precision liquid syringe: 5 or 10 µl
4. Mechanical shaker
5. Centrifuge
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	135°C
Injection temperature:	200°C
Detector temperature:	200°C
Carrier gas:	Nitrogen or Helium
Carrier gas flow:	30 ml/min (adjusted for specific GC)
Hydrogen pressure:	20 psi (adjusted for specific GC)
Air pressure:	30 psi (adjusted for specific GC)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.2 gram trichlorfon standard into a 50 ml volumetric flask. Add by pipette 5 ml of the internal standard solution, make to volume with acetone, and shake thoroughly. (final conc 4 mg trichlorfon and 1 mg diethyl phthalate/ml)

Preparation of Sample:

For dusts, granules, and wettable powders - weigh a portion of sample equivalent to 0.2 gram trichlorfon into a small glass-stoppered flask or screw-cap bottle. Add by pipette 5 ml of the internal standard solution and 45 ml acetone. Close tightly and shake 1 hr. on shaking machine. (final conc 4 mg trichlorfon and 1 mg diethyl phthalate/ml)

For liquids - weigh a portion of sample equivalent to 0.2 gram trichlorfon into a 50 ml volumetric flask. Add 5 ml internal standard solution, and make to volume with acetone. (final conc 4 mg trichlorfon and 1 mg diethyl phthalate/ml)

Determination:

Inject 5 µl of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is trichlorfon, then diethyl phthalate.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of trichlorfon and diethyl phthalate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

I.S. = internal standard = diethyl phthalate

$$RF = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area trichlorfon})}{(\text{wt. trichlorfon})(\%\text{ purity trichlorfon})(\text{pk. ht. or area I.S.})}$$

Determine the percent trichlorfon for each injection of the sample-internal standard solution as follows and calculate the average:

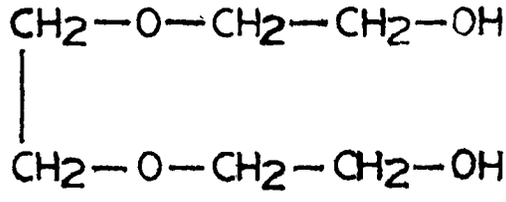
$$\% = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area trichlorfon})}{(\text{wt. sample})(\text{pk. ht. or area I.S.})(\text{RF})}$$

Method submitted by Mark W. Law, EPA Beltsville Chemistry Laboratory, Beltsville, Md.

Any criticisms, suggestions, data, etc. on this method will be appreciated.

Determination of Triethylene Glycol by Gas Liquid Chromatography (TCD - Internal Standard)

Triethylene glycol is a registered disinfectant having the chemical structure:



Molecular formula: $C_6H_{14}O_4$

Molecular weight: 150.17

Boiling point: 285-287°C

Physical state, color, and odor: colorless, hygroscopic, practically odorless liquid

Solubility: miscible with water, alcohol, benzene, toluene; sparingly soluble in ether; practically insoluble in petroleum ether

Stability: stable; hygroscopic

Other names: 2,2'-ethylenedioxybis(ethanol)

Reagents:

1. Triethylene glycol standard of known % purity
2. Ethyl hexanediol standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 3.5 grams ethyl hexanediol standard into a 100 ml volumetric flask and make to volume with acetone; mix well. (conc 35 mg ethyl hexanediol/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 4' x 1/4" glass packed with 3% XE-60 on 60/80 Chromosorb G AW DMCS (or equivalent column)
3. Precision liquid syringe: 10 µl
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	140°C
Injection temperature:	185°C
Detector temperature:	230°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas flow:	30 ml/min

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.5 gram triethylene glycol standard into a 25 ml volumetric flask, add 10 ml internal standard solution by pipette, and make to volume with acetone; mix well. (final conc 20 µg triethylene glycol and 14 µg ethyl hexanediol/µl)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.5 gram triethylene glycol into a 25 ml volumetric flask, add 10 ml internal standard solution, and make to volume with acetone; mix well. (final conc 20 µg propylene glycol and 14 µg ethyl hexanediol/µl)

Determination:

Inject 2-3 µl of standard-internal standard solution and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights from 1/2 to 3/4 full scale. The peak heights of triethylene glycol and ethyl hexanediol should be nearly the same (definitely within 25% of each other); if not, concentrations should be adjusted accordingly. The elution order is ethyl hexanediol, then triethylene glycol.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of triethylene glycol and ethyl hexanediol from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

IS = internal standard = ethyl hexanediol

TEG = triethylene glycol

$$RF = \frac{(\text{wt. IS})(\%\text{ purity IS})(\text{pk. ht. or area TEG})}{(\text{wt. TEG})(\%\text{ purity TEG})(\text{pk. ht. or area IS})}$$

Determine the percent triethylene glycol for each injection of sample-internal standard solution as follows and calculate the average:

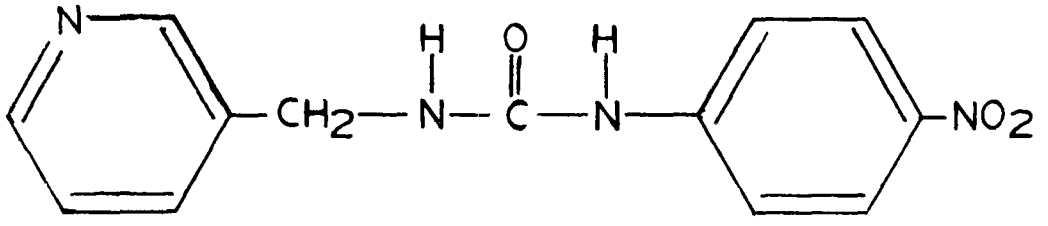
$$\% = \frac{(\text{wt. IS})(\% \text{ purity IS})(\text{pk. ht. or area TEG})}{(\text{wt. sample})(\text{pk. ht. or area IS})(\text{RF})}$$

Method submitted by Stelios Gerazounis, EPA Product Analysis Laboratory, Region II, New York, N.Y.

Any comments, criticisms, suggestions, data, etc. concerning the use of this method will be appreciated.

Determination of Vacor (trade name) by Ultraviolet Spectroscopy

Vacor is the trade name (a common name has not yet been approved) for N-3-pyridylmethyl-N'-p-nitrophenylurea, a registered rodenticide having the chemical structure:



Molecular formula: $C_{13}H_{12}N_4O_3$

Molecular weight: 272.27

Melting point: 223-225°C with decomposition

Physical state, color, and odor: odorless, light yellow powder

Solubility: extremely low in water; slightly soluble in pyridine and dimethylformamide at 25°C; soluble in pyridine, dimethylformamide, methyl cellosolve, and dimethyl sulfoxide at 80°C; insoluble in acetone, methanol, ethanol, isopropanol, ethyl acetate, butyl acetate, butyl cellosolve, acetonitrile, chlorobenzene, and toluene

Stability:

Other names: Vacor and RH-787 (Rohm & Haas)

Reagents:

1. Vacor standard of known % purity
2. Methanol, spectro or pesticide grade

(Note! 95% ethanol may also be used.)

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm silica cells
2. Mechanical shaker
3. Filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.05 gram Vacor standard into a 50 ml volumetric flask, make to volume with methanol, and shake to dissolve. If available, an ultrasonic shaker will aid solution of the Vacor. (Note! Even though under Solubility, Vacor is listed as insoluble in methanol, it has been found that 0.1 gram will dissolve in 50 ml.) Pipette 10 ml into a 100 ml volumetric flask, make to volume, and mix thoroughly. Pipette 10 ml of this solution into another 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. (final conc 10 µg Vacor/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram Vacor into a 250 ml glass-stoppered flask or screw-cap bottle, add 100 ml methanol by pipette, close tightly, and shake on a mechanical shaker for one hour. (Note! For a 2% meal-type sample, one hour is more

than adequate.) Allow to settle; filter or centrifuge if necessary, taking care to prevent loss due to evaporation. Pipette 10 ml into a 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette 10 ml of this solution into another 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. (final conc 10 µg Vacor/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 328 nm with methanol in each cell. Scan both the standard and sample from 360 nm to 260 nm with methanol in the reference cell. Measure the absorbance of both standard and sample at 328 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent Vacor as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in } \mu g/ml)(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in } \mu g/ml)}$$

Method submitted by George B. Radan, EPA Product Analysis Laboratory, Region II, New York, N.Y.

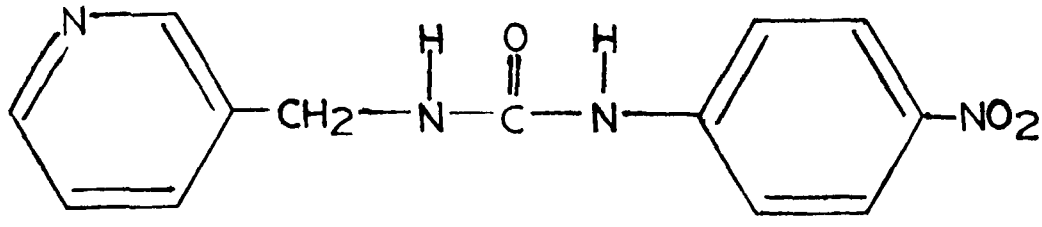
Any comments, criticism, suggestions, data, etc. concerning the use of this method will be appreciated.

May 1977

Vacor (trade name) EPA-2
(tentative)

Determination of Vacor by High Pressure Liquid Chromatography

Vacor is the trade name (a common name has not yet been approved) for N-3-pyridylmethyl-N'-p-nitrophenylurea, a registered rodenticide having the chemical structure:



Molecular formula: $C_{13}H_{12}N_4O_3$

Molecular weight: 272.27

Melting point: 223-225°C with decomposition

Physical state, color, and odor: odorless, light yellow powder

Solubility: extremely low in water; slightly soluble in pyridine and dimethylformamide at 25°C; soluble in pyridine, dimethylformamide, methyl cellosolve, and dimethyl sulfoxide at 80°C; insoluble in acetone, methanol, ethanol, isopropanol, ethyl acetate, butyl acetate, butyl cellosolve, acetonitrile, chlorobenzene, and toluene

Stability:

Other names: Vacor and RH-787 (Rohm & Haas)

Reagents:

1. Vacor standard of known % purity
2. Dimethylformamide, spectro or pesticide grade

Equipment:

1. High pressure liquid chromatograph with variable wavelength UV detector (for 327 nm)
2. Suitable column such as: DuPont Permaphase ETH, 0.5 meter x 2.1 mm I.D.

   (Permaphase ETH is an ether stationary phase chemically bonded to the surface of "Zipax." Permaphase ETH is a polar bonded packing by means of a Si-O-Si bond. The support contains approx. 1% stationary phase by weight.)
3. 5 µl high pressure liquid syringe or sample injection loop
4. Mechanical shaker
5. Centrifuge
6. 5 micron millipore filter
7. Usual laboratory glassware

Operating Conditions:

Mobile phase:	15% methanol + 85% water
Column temperature:	ambient
Flow rate:	0.75 to 1.0 ml/min
Chart speed:	12'/hr
Amount injected:	5 µl

Conditions may have to be adjusted for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.05 gram Vacor into a 50 ml volumetric flask; dissolve in and make to volume with dimethylformamide; mix thoroughly. (final conc 1 mg Vacor/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram Vacor into a 250 ml glass-stoppered flask or screw-cap bottle, add 100 ml dimethylformamide by pipette, close tightly, and shake for one hour on a mechanical shaker. Allow to settle; if not crystal clear, centrifuge a portion for 5 minutes. If still not crystal clear, filter through a 5 micron millipore filter. Take precaution to prevent evaporation. (final conc 1 mg Vacor/ml)

Determination:

Alternately inject three 5 µl portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent Vacor as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Elmer H. Hayes, EPA Beltsville Chemistry Laboratory, Beltsville, Md.

Any comments, criticism, suggestions, data, etc. concerning the use of this method will be appreciated.

Analytical Methods - Second Supplement

May 1, 1979

1. Bendiocarb EPA-1 (tentative)
2. Bendiocarb EPA-2 (tentative)
3. Butylate EPA-6 (tentative)
4. Carboxin EPA-2 (tentative)
5. Chlorothalonil EPA-2 (tentative)
6. Chlorpyrifos EPA-1 (tentative)
7. Chlorpyrifos EPA-2 (tentative)
8. Chlorpyrifos EPA-3 (tentative)
9. Chlorpyrifos EPA-4 (tentative)
10. Deet EPA-4 (tentative)
11. Diphacinone EPA-2 (tentative)
12. Diphenylamine EPA-1 (tentative)
13. Endosulfan EPA-5 (tentative)
14. EPTC EPA-6 (tentative)
15. Ethofumesate EPA-4 (tentative)
16. Flammability Test EPA-1 (Flame Projection)
17. Flammability Test EPA-2 (Drum Test)
18. Fluometuron EPA-2 (tentative)
19. Methomyl EPA-1 (tentative)
20. Methoxychlor EPA-3 (tentative)
21. Mexacarbate EPA-1 (tentative)
22. Mixed Pesticides EPA-1 (Warfarin & Sulfaquinoxaline)
23. Oryzalin EPA-1 (tentative)
24. Parathion EPA-3 (tentative)
25. Parathion EPA-4 (tentative)
26. Pirimicarb EPA-1 (tentative)
27. Pyrazon EPA-1 (tentative)
28. Strychnine EPA-3 (tentative)
29. Vernolate EPA-4 (tentative)
30. TLC Identification EPA-2

Analytical Methods - Second Supplement

May 1, 1979

Pesticide Name Cross Reference Index to the Methods

4-amino-N-2-quinoxalinylbenzene-sulfonamide	Mixed Pesticides EPA-1 (see sulfaquinoxaline)
Bendiocarb EPA-1 (tentative)	IR
Bendiocarb EPA-2 (tentative)	UV
Big Dipper	Diphenylamine EPA-1 (tentative)
Butylate EPA-6 (tentative)	HPLC - reversed phase
Carboxin EPA-2 (tentative)	UV
Chlorothalonil EPA-2 (tentative)	GLC-FID-IS
Chlorpyrifos EPA-1 (tentative)	IR
Chlorpyrifos EPA-2 (tentative)	UV
Chlorpyrifos EPA-3 (tentative)	GLC-TCD-IS
Chlorpyrifos EPA-4 (tentative)	HPLC
Compound 3-120	Mixed Pesticides EPA-1 (see sulfaquinoxaline)
Deet EPA-4 (tentative)	HPLC - normal phase
2-dimethylamino-5,6-dimethyl-pyrimidin-4-yl-dimethylcarbamate	Pirimicarb EPA-1 (tentative)
4-dimethylamino-3,5-xylyl N-methylcarbamate	Mexacarbate EPA-1 (tentative)
2,2-dimethyl-1,3-benzodioxol-4-yl-N-methylcarbamate	Bendiocarb EPA-1 (tentative)
5,6-dimethyl-2-dimethylamino-4-pyrimidinyl dimethylcarbamate	Pirimicarb EPA-1 (tentative)
Diphacinone EPA-2 (tentative)	HPLC-PIC
Diphenylamine EPA-1 (tentative)	GLC-TCD
Dirimal	Oryzalin EPA-1 (tentative)

Dowco 139	Mexacarbate EPA-1 (tentative)
Dowco 179	Chlorpyrifos EPA-1, 2, 3, 4
Dursban (mosquito control)	Chlorpyrifos EPA-1, 2, 3, 4
EL-119	Oryzalin EPA-1 (tentative)
Endosulfan EPA-5 (tentative)	GLC-FID-IS
EPTC EPA-6 (tentative)	HPLC - reversed phase
Ethofumesate EPA-1 (tentative)	GLC-FID-IS
Ficam	Bendiocarb EPA-1 (tentative)
Flammability Test EPA-1	Flame Projection
Flammability Test EPA-2	Closed Drum
Fluometuron EPA-2 (tentative)	UV
Garvox	Bendiocarb EPA-1 (tentative)
H 119	Pyrazon EPA-1 (tentative)
2,3-isopropylidenedioxyphenyl methylcarbamate	Bendiocarb EPA-1 (tentative)
Lannate	Methomyl EPA-1 (tentative)
Lorsban (agricultural use)	Chlorpyrifos EPA-1, 2, 3, 4
Methomyl EPA-1 (tentative)	HPLC
Methoxychlor EPA-3 (tentative)	HPLC - normal phase
Methylcarbamic acid 4-(dimethylamino)-3,5-xylyl ester	Mexacarbate EPA-1 (tentative)
Mexacarbate EPA-1 (tentative)	GLC-TCD-IS
Mixed Pesticides EPA-1 (Warfarin & sulfaquinoxaline)	HPLC-PIC
Multimet	Bendiocarb EPA-1 (tentative)
NC 6897	Bendiocarb EPA-1 (tentative)
Nortron	Ethofumesate EPA-1 (tentative)

Nudrin	Methomyl EPA-1 (tentative)
Oryzalin EPA-1 (tentative)	Visible (colorimetric) spectroscopy
Parathion EPA-3 (tentative)	GLC-FID-IS
Parathion EPA-4 (tentative)	HPLC - reversed phase
PCA	Pyrazon EPA-1 (tentative)
N-phenylbenzeneamine	Diphenylamine EPA-1 (tentative)
Pirimicarb EPA-1 (tentative)	UV
Pirimor	Pirimicarb EPA-1 (tentative)
PP062	Pirimicarb EPA-1 (tentative)
Pyramin	Pyrazon EPA-1 (tentative)
Pyrazon EPA-1 (tentative)	UV
Ryzelan	Oryzalin EPA-1 (tentative)
Scaldip	Diphenylamine EPA-2 (tentative)
Strychnine EPA-3 (tentative)	HPLC - reversed phase
Sulfabenzpyrazine	Mixed Pesticides EPA-1 (see sulfaquinoxaline)
Sulfacox	Mixed Pesticides EPA-1 (see sulfaquinoxaline)
Sulfaline	Mixed Pesticides EPA-1 (see sulfaquinoxaline)
2-sulfanilamidoquinoxaline	Mixed Pesticides EPA-1 (see sulfaquinoxaline)
Sulfa-Q	Mixed Pesticides EPA-1 (see sulfaquinoxaline)
Sulfaquinoxaline (with Warfarin)	Mixed Pesticides EPA-1
Sulquin	Mixed Pesticides EPA-1 (see sulfaquinoxaline)
Surflan	Oryzalin EPA-1 (tentative)

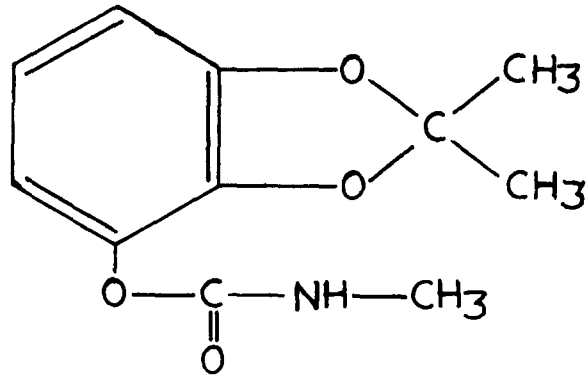
TLC Identification EPA-2	TLC
Trichloropyrphos	Chlorpyrifos EPA-1, 2, 3, 4
Vernolate EPA-4 (tentative)	HPLC - reversed phase
Warfarin (with sulfaquinoxaline)	Mixed Pesticides EPA-1
Zectran	Mexacarbate EPA-1 (tentative)

March 1978

Bendiocarb EPA-1
(tentative)

The Determination of Bendiocarb in Wettable Powder Formulations by Infrared Spectroscopy

Bendiocarb is the common name for 2,2-dimethyl-1,3-benzodioxol-4-yl N-methylcarbamate, a registered insecticide having the chemical structure:



Molecular formula: $C_{11}H_{13}NO_4$

Molecular weight: 223.23

Melting point: 129-130°C

Physical state, color, and odor: white crystalline solid

Solubility: at 25°C is: 0.004% in water, 0.03% in kerosene, 1.0% in o-xylene, 4% in ethanol and benzene, and 20% in acetone, dichloromethane, dioxan and chloroform

Stability: the hydrolysis (to the phenol) half-life in solution in 0.01M aqueous sodium phosphate buffer at pH 7 and 25°C is 20 days.

Other names: Ficam (Fisons Ltd., Great Britain); NC 6897; Garvox; Multimet; 2,3-isopropylidenedioxyphenyl methylcarbamate

Reagents:

1. Bendiocarb standard of known % purity
2. Chloroform, spectro or pesticide grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording with matched 0.5 mm NaCl or KBr cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Hypodermic syringe (1-2 ml, for filling IR cells)

Procedure:

Preparation of Standard:

Weigh 0.1 gram bendiocarb standard into a small glass-stoppered flask or screw-cap bottle, add 25 ml chloroform by pipette, and shake to dissolve. Add a small amount of anhydrous sodium sulfate to insure dryness. (conc 4 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.2 gram bendiocarb into a 125 ml glass-stoppered flask or screw-cap bottle. Add 50 ml chloroform by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly and shake on a mechanical shaker for 30 minutes. Allow to settle, centrifuge or filter if necessary, taking precaution to prevent evaporation. (final conc 4 mg/ml)

IR Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular infrared spectrophotometer being used, scan the standard and sample from 2000 cm^{-1} to 1538 cm^{-1} (5.0 u to 6.5 u).

Determine the absorbance of standard and sample using the peak at 1761 cm^{-1} (5.68 u) and a baseline from 1961 cm^{-1} to 1703 cm^{-1} (5.10 u to 5.87 u).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent bendiocarb as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity of std})}{(\text{abs. standard})(\text{conc. sample in mg/ml})}$$

Method submitted by Stelios Gerazounis, EPA Chemistry Laboratory, Region II, New York.

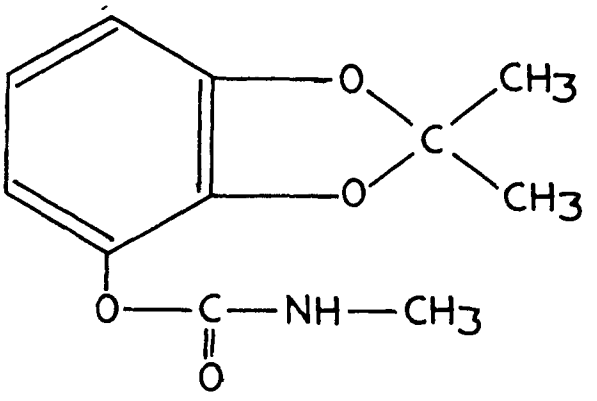
Any comments, criticism, suggestion, data, etc. concerning the use of this method will be appreciated.

June 1978

Bendiocarb EPA-2
(tentative)

The Determination of Bendiocarb in Wettable Powder Formulations by Ultraviolet Spectrometry

Bendiocarb is the common name for 2,2-dimethyl-1,3-benzodioxol-4-yl N-methylcarbamate, a registered insecticide having the chemical structure:



Molecular formula: $C_{11}H_{13}NO_4$

Molecular weight: 223.23

Melting point: 129-130°C

Physical state, color, and odor: white crystalline solid

Solubility: at 25°C is: 0.004% in water, 0.03% in kerosene, 1.0% in o-xylene, 4% in ethanol and benzene, and 20% in acetone, dichloromethane, dioxan and chloroform

Stability: the hydrolysis (to the phenol) half-life in solution in 0.01M aqueous sodium phosphate buffer at pH 7 and 25°C is 20 days.

Other names: Ficam (Fisons Ltd., Great Britain); NC 6897; Garvox; Multimet; 2,3-isopropylidenedioxyphenyl methylcarbamate

Reagents:

1. Bendiocarb standard of known % purity
2. Methanol, spectro or pesticide grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm silica cells
2. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram bendiocarb standard into a 100 ml volumetric flask. Dissolve in, make to volume with methanol, and mix thoroughly. Pipette 5 ml into a second 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. (conc 50 ug/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram bendiocarb into a 100 ml volumetric flask. Make to volume with methanol and mix thoroughly. Pipette 5 ml into a second 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. (final conc 50 ug/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 278 nm with methanol in each cell. Scan both the standard and sample from 310 nm to 240 nm with methanol in the reference cell. Measure the absorbance of both standard and sample at 278 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent bendiocarb as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. standard in ug/ml})(\% \text{ purity standard})}{(\text{abs. standard})(\text{conc. sample in ug/ml})}$$

Note! This method is linear from 0 to 250 ug/ml final concentration.

Method submitted by George B. Radan, EPA Chemistry Laboratory, Region II, New York.

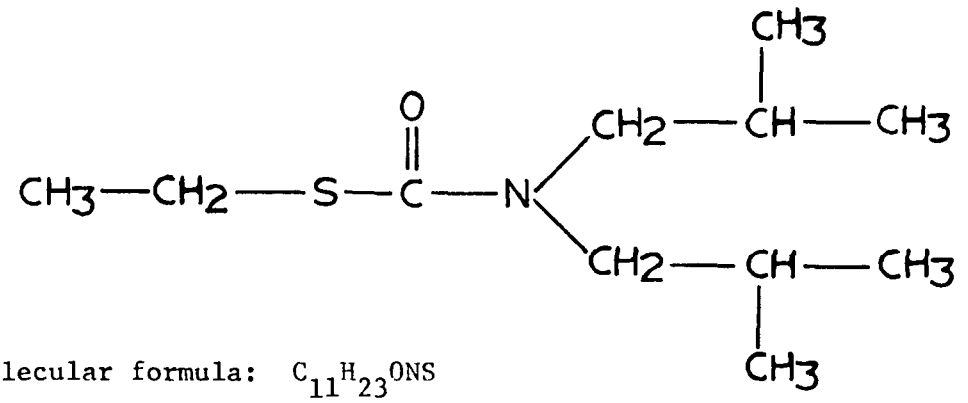
Any criticism, data, or suggestions concerning this method will be appreciated.

March 1978

Butylate EPA-6
(tentative)

Determination of Butylate by High Pressure Liquid Chromatography (Reverse Phase)

Butylate is the common name for S-ethyl diisobutylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{11}H_{23}ONS$

Molecular weight: 217.4

Boiling point: 71° at 10 mm

Physical state and color: Amber liquid

Solubility: 45 ppm in water at room temperature; miscible with kerosene, acetone, methyl isobutyl ketone, ethanol, xylene

Stability: stable under ordinary conditions; non-corrosive

Other names: Sutan (Stauffer), R1910

Reagents:

1. Butylate standard of known % purity
2. Dioxane, pesticide or spectro grade

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm. If a variable wavelength UV detector is available, other wavelengths may be used to increase sensitivity or to eliminate interference; 230 nm is very good for butylate.
2. Suitable column such as:
   a. Dupont ODS Permaphase, 1 meter x 2.1 mm ID
   b. Perkin-Elmer ODS Sil-X-II RP, (two) 0.5 meter x 2.6 mm ID
3. High pressure liquid syringe or sample injection loop
4. Usual laboratory glassware

Operating Conditions:

Mobile phase:	25% acetonitrile + 75% water
Column temperature:	30°C
Chart speed:	12"/hr
Flow rate:	0.5 to 1.5 ml/min (Perkin-Elmer 1 meter column)
Pressure:	1800-2000 psi (Dupont 1 meter column)
Attenuation:	Adjusted

Conditions may have to be varied by the analyst for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram butylate standard into a 50 ml volumetric flask, make to volume with dioxane, and mix thoroughly. (conc 2 mg/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.1 gram butylate into a 50 ml volumetric flask, make to volume with dioxane, and mix thoroughly. (conc 2 mg butylate/ml)

Determination:

Alternately, inject three 5 ul portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent butylate as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Note: Generally, butylate can be easily separated on a reverse phase HPLC system if the right solvent polarity is used. Acetonitrile and methanol are good primary solvents. They have similar dielectric constants but have different hydrogen bondings. Since butylate's molecular weight is high, acetonitrile would be the solvent of choice because of its low polarity. This would give a short retention time with good resolution. If more separation is desired, methanol should be used, but some loss of resolution would be expected.

Method submitted by Elmer H. Hayes, EPA Beltsville Chemistry Laboratory, Beltsville, Maryland.

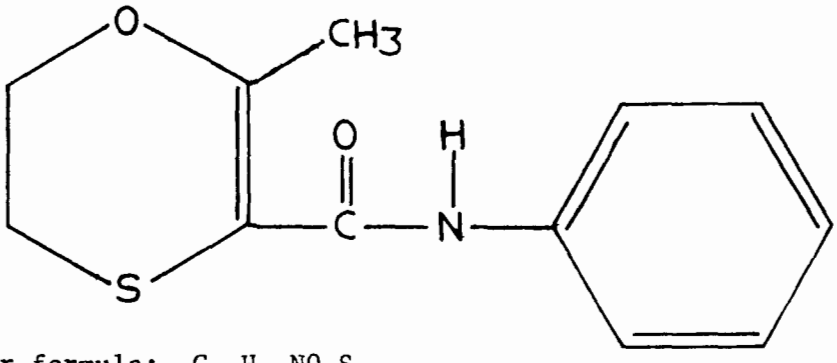
Any criticism, data, or suggestions concerning the use of this method will be appreciated.

March 1978

Carboxin EPA-2
(tentative)

Determination of Carboxin in Dusts and Powders by Ultraviolet Spectroscopy

Carboxin is the common name for 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide, a registered fungicide having the chemical structure:



Molecular formula: $C_{12}H_{13}NO_2S$

Molecular weight: 235

Melting point: 91.5 to 92.5°C; a dimorphic form has a m.p. of 98 to 100°C

Physical state, color, and odor: odorless, white, crystalline solid (The technical product is at least 97% pure.)

Solubility: 170 ppm in water at 25°C; soluble in acetone, benzene, dimethyl sulfoxide, ethanol, methanol

Stability: compatible with all except highly alkaline or acidic pesticides

Other names: Vitavax, D735 (Uniroyal); DCMO

Reagents:

1. Carboxin standard of known % purity
2. Methanol, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram carboxin standard into a 100 ml volumetric flask. Dissolve in, make to volume with methanol, and mix thoroughly. Pipette a 10 ml aliquot into a second 100 ml volumetric flask and make to volume with methanol. Mix thoroughly and pipette a 10 ml aliquot into a third 100 ml volumetric flask. Make to volume with methanol and again mix thoroughly. (conc 10 ug/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram of carboxin into a 250 ml Erlenmeyer glass-stoppered flask. Add 100 ml methanol by pipette and shake on a mechanical shaker for one hour. Allow to settle; filter if necessary. Pipette 10 ml of the clear filtrate into a 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette 10 ml into another 100 ml volumetric flask, make to volume with methanol, and again mix thoroughly. (final conc 10 ug carboxin/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 248 nm with methanol in each cell. Scan both the standard and sample from 300 nm to 200 nm with methanol in the reference cell. Measure the absorbance of both standard and sample at 248 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent carboxin as follows:

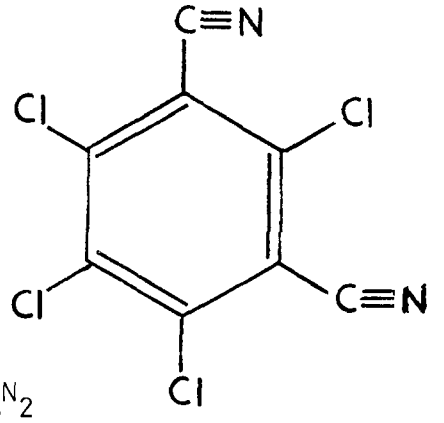
$$\% = \frac{(\text{abs. sample})(\text{conc. std in ug/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in ug/ml})}$$

Method submitted by Edward Zager, EPA Product Analysis Laboratory, Region II, New York, NY.

Any criticism, data, or suggestions concerning the use of this method will be appreciated.

Determination of Chlorothalonil by Gas Liquid Chromatography (FID - Internal Standard)

Chlorothalonil is the common name for tetrachloroisophthalonitrile, a registered fungicide having the chemical structure:



Molecular formula: $C_8Cl_4N_2$

Molecular weight: 266

Melting point: 250 to 251°C

Physical state, color, and odor: white crystalline solid, odorless in pure form; the technical product (about 98% pure) has a slightly pungent odor.

Solubility: insoluble in water (0.6 ppm); slightly soluble in acetone (2% w/w), cyclohexanone (3% w/w), methyl ethyl ketone (2% w/w), xylene (8% w/w), and kerosene less than 1%

Stability: stable to ultraviolet radiation and to moderately alkaline and acid aqueous media; thermally stable under normal storage conditions; non-corrosive

Other names: Daconil 2787 (Diamond Shamrock Chem. Co.); Bravo; Termil; 2,4,5,6-tetrachloro-1,3-dicyanobenzene; 2,4,5,6-tetrachloro-3-cyanobenzonitrile

Reagents:

1. Chlorothalonil standard of known % purity
2. Aldrin standard of known HHDN content
3. Xylene, pesticide or spectro grade preferred, ACS ok
   Note: large injections of xylene may dirty the detector.
4. Internal standard solution - weigh 0.15 gram aldrin into a 100 ml volumetric flask, dissolve in and make to volume with xylene. Mix well. (conc 1.5 mg/ml or 1.5 ug/ul)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm ID glass column packed with 1% XE-60 on 80/100 mesh Chromosorb G (or equivalent column)
3. Precision liquid syringe: 1 or 5 ul
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	170°C
Injection temperature:	300°C
Detector temperature:	300°C
Carrier gas:	Nitrogen
Carrier gas pressure:	Adjust for optimum performance (0.9 Kg/cm^2)
Hydrogen pressure:	Adjust for optimum performance (0.7 Kg/cm^2)
Air pressure:	Adjust for optimum performance (1.3 Kg/cm^2)
Chart speed:	0.25"/min or 15"/hr

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram chlorothalonil standard into a small glass-stoppered flask or screw-cap tube. Add by pipette 20 ml of the internal standard solution and shake to dissolve. (final conc 5 mg chlorothalonil and 1.5 mg aldrin/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram chlorothalonil into a small glass-stoppered flask or screw-cap tube. Add by pipette 20 ml of the internal standard solution. Close tightly and shake on a mechanical shaker to dissolve. Filter if necessary. (final conc 5 mg chlorothalonil and 1.5 mg aldrin/ml)

Determination:

Inject 0.5-1 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is aldrin, then chlorothalonil.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of chlorothalonil and aldrin from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

chlor. = chlorothalonil

$$RF = \frac{(\text{wt. aldrin})(\%\text{ purity aldrin})(\text{pk. ht. or area chlor.})}{(\text{wt. chlor.})(\%\text{ purity chlor.})(\text{pk. ht. or area aldrin})}$$

Determine the percent chlorothalonil for each injection of the sample-internal standard solution as follows and calculate the average:

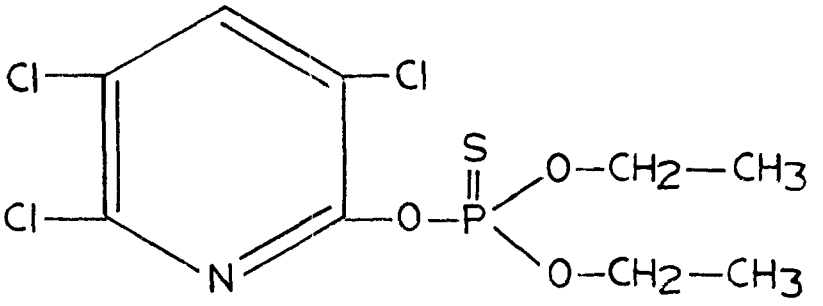
$$\% = \frac{(\text{wt. aldrin})(\%\text{ purity aldrin})(\text{pk. ht. or area chlor.})}{(\text{wt. sample})(\text{pk. ht. or area aldrin})(RF)}$$

Method submitted by Dr. Gabriele Tartari, Agrochemical Dept., Control Laboratory, CIBA-GEIGY S.p.A., C.P. 88, I-21047 Saronno (VA), ITALY.

Any criticism, data or suggestions concerning the use of this method will be appreciated.

Determination of Chlorpyrifos by Infrared Spectroscopy

Chlorpyrifos is the accepted (ANSI, ISO, BSI) common name for O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)-phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_9H_{11}Cl_3NO_3PS$

Molecular weight: 350.5

Physical state, color, and odor: white crystals with a mild mercaptan odor

Melting point: 41 to 43°C

Solubility: 2 ppm in water at 25°C; 79% in isooctane w/w, 43% in methanol w/w; readily soluble in most other organic solvents

Stability: stable under normal storage conditions; compatible with non-alkaline pesticides but is corrosive to copper and brass; half-life in aqueous methanolic solution 1930 days at pH 6.0, 7.2 days at pH 9.96

Other names: Dursban (for mosquito control); Lorsban (for agricultural use); Dowco 179 (Dow Chemical); trichlorpyrphos

Reagents:

1. Chlorpyrifos standard of known % purity
2. Carbon disulfide, pesticide or spectro grade preferred
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam ratio recording, with matched 0.5 mm NaCl or KBr cells
2. Mechanical shaker
3. Filtration apparatus or centrifuge
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.125 gram chlorpyrifos standard into a 25 ml volumetric flask, dissolve in and make to volume with carbon disulfide; mix thoroughly. Add a small amount of granular anhydrous sodium sulfate to insure dryness. (final conc 5 mg chlorpyrifos/ml)

Preparation of Sample:

For dusts, granules, and wettable powders - weigh a portion of sample equivalent to 0.25 gram chlorpyrifos into a 125 ml glass-stoppered or screw-cap Erlenmeyer flask. Add 50 ml carbon disulfide by pipette and 1-2 grams anhydrous sodium sulfate. Close tightly, shake on a mechanical shaker for 1 hour, allow to settle, filter or centrifuge if necessary taking precaution to avoid evaporation. (final conc 5 mg chlorpyrifos/ml)

For liquids - weigh sample equivalent to 0.25 gram chlorpyrifos into a 50 ml volumetric flask and make to volume with carbon disulfide. Add a small amount of anhydrous sodium sulfate to insure dryness. (final conc 5 mg chlorpyrifos/ml)

IR Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample from 990 cm^{-1} to 900 cm^{-1} (10.1 u to 11.1 u).

Determine the absorbance of standard and sample using the peak at 960 cm^{-1} (10.4 u) and a horizontal baseline from 930 cm^{-1} (10.75 u).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent chlorpyrifos as follows:

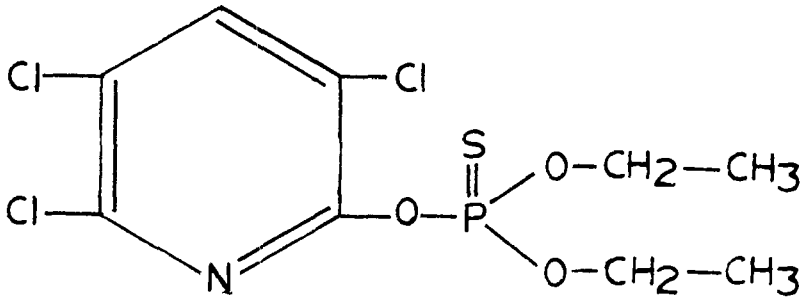
$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Method submitted by Mississippi State Chemistry Laboratory, Box CR, Mississippi State, Mississippi 39762.

Any criticisms, suggestions, data, etc. on the use of this method will be appreciated.

Determination of Chlorpyrifos by Ultraviolet Spectroscopy

Chlorpyrifos is the accepted (ANSI, ISO, BSI) common name for O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)-phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_9H_{11}Cl_3NO_3PS$

Molecular weight: 350.5

Physical state, color, and odor: white crystals with a mild mercaptan odor

Melting point: 41 to 43°C

Solubility: 2 ppm in water at 25°C; 79% in isooctane w/w, 43% in methanol w/w; readily soluble in most other organic solvents

Stability: stable under normal storage conditions; compatible with non-alkaline pesticides but is corrosive to copper and brass; half-life in aqueous methanolic solution 1930 days at pH 6.0, 7.2 days at pH 9.96

Other names: Dursban (for mosquito control); Lorsban (for agricultural use); Dowco 179 (Dow Chemical); trichlorpyrphos

Reagents:

1. Chlorpyrifos standard of known % purity
2. Methanol, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm silica cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram chlorpyrifos standard into a 100 ml volumetric flask, dissolve in and make to volume with methanol; mix thoroughly. Pipette 10 ml into a second 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette 20 ml of this solution into a third 100 ml volumetric flask and make to volume with methanol. Mix thoroughly. (final conc 20 ug chlorpyrifos/ml)

Preparation of Sample:

For wettable powders - weigh a portion of sample equivalent to 0.1 gram chlorpyrifos into a 250 ml glass-stoppered flask or screw-cap bottle. Add 100 ml of methanol, close tightly, and shake for 30 minutes. Allow to settle, centrifuge or filter if necessary. Proceed as in the third paragraph beginning "Pipette 10 ml - - -."

For liquid formulations - weigh a portion of sample equivalent to 0.1 gram chlorpyrifos into a 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Proceed as below.

Pipette 10 ml of either of the above sample solutions into a 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette 20 ml of this solution into a 100 ml volumetric flask, make to volume with the methanol, and mix thoroughly. (final conc 20 ug chlorpyrifos/ml)

UV Determination:

Balance pen for 0 and 100% transmission at 285 nm with methanol in each cell. Scan standard and sample from 330 nm to 230 nm with methanol in the reference cell. Measure absorbance of standard and sample at 285 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent chlorpyrifos as follows:

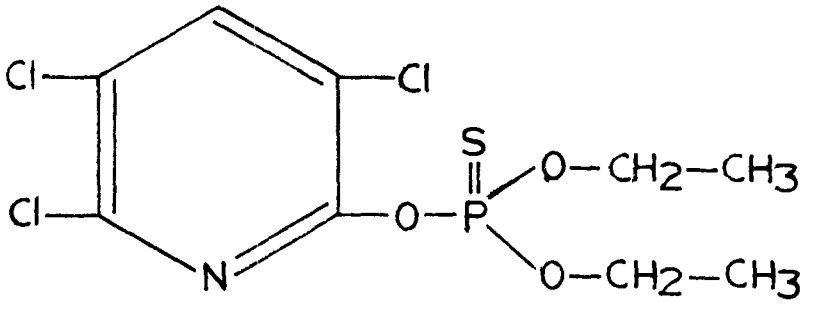
$$\% = \frac{(\text{abs. sample})(\text{conc. std in ug/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in ug/ml})}$$

Method submitted by David Persch, EPA Product Analysis Laboratory, Region II, New York, NY.

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Chlorpyrifos by Gas Liquid Chromatography (TCD - Internal Standard)

Chlorpyrifos is the accepted (ANSI, ISO, BSI) common name for O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)-phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_9H_{11}Cl_3NO_3PS$

Molecular weight: 350.5

Physical state, color, and odor: white crystals with a mild mercaptan odor

Melting point: 41 to 43°C

Solubility: 2 ppm in water at 25°C; 79% in isooctane w/w, 43% in methanol w/w; readily soluble in most other organic solvents

Stability: stable under normal storage conditions; compatible with non-alkaline pesticides but is corrosive to copper and brass; half-life in aqueous methanolic solution 1930 days at pH 6.0, 7.2 days at pH 9.96

Other names: Dursban (for mosquito control); Lorsban (for agricultural use); Dowco 179 (Dow Chemical); trichlorpyrphos

Reagents:

1. Chlorpyrifos standard of known % purity
2. Benzyl benzoate standard of known % purity
3. Chloroform, pesticide or spectro grade
4. Internal Standard solution - weigh 1.3 gram benzyl benzoate standard into a 100 ml volumetric flask, dissolve in and make to volume with chloroform; mix well. (conc 13 mg benzyl benzoate/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 4' x 1/4" ID glass, packed with 4% SE-30 on 80/100 Diatoport S or equivalent column (such as 4' x 1/4" ID glass, packed with 4% SP-2100 on 80/100 Chromosorb 750)
3. Precision liquid syringe: 10 ul
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	180°C
Injection temperature:	215°C
Detector temperature:	230°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas pressure:	40 psi (20 ml/min)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

For use with emulsifiable concentrates and liquid formulations - weigh 0.15 gram chlorpyrifos standard into a 25 ml volumetric flask; add 5 ml internal standard solution by pipette, make to volume with chloroform, and mix well. (final conc 6 mg chlorpyrifos and 2.6 mg benzyl benzoate/ml)

For use with dusts, granules, and wettable powders - weigh 0.15 gram chlorpyrifos standard into a small glass-stoppered flask or screw-cap bottle, add by pipette 5 ml of internal standard solution and 25 ml chloroform, close tightly and shake well to dissolve the chlorpyrifos. (final conc 6 mg chlorpyrifos and 2.6 mg benzyl benzoate/ml)

Preparation of Sample:

For emulsifiable concentrates and liquid formulations - weigh a portion of sample equivalent to 0.15 gram chlorpyrifos into a 25 ml volumetric flask; add 5 ml of internal standard solution by pipette, make to volume with chloroform, and mix well. (final conc 6 mg chlorpyrifos and 2.6 mg benzyl benzoate/ml)

For dusts, granules, and wettable powders - weigh a portion of sample equivalent to 0.15 gram chlorpyrifos into a small glass-stoppered flask or screw-cap bottle; add by pipette 5 ml internal standard and 25 ml of chloroform, close tightly and shake on a mechanical shaker for 10-15 minutes or shake by hand intermittently for 25-30 minutes. (final conc 6 mg chlorpyrifos and 2.6 mg benzyl benzoate/ml)

Determination:

Inject 2 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is benzyl benzoate, then chlorpyrifos.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of chlorpyrifos and benzyl benzoate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

(I.S. = benzyl benzoate)

$$RF = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area chlorpyrifos})}{(\text{wt. chlorpyrifos})(\%\text{ purity chlorpyrifos})(\text{pk. ht. or area I.S.})}$$

Determine the percent chlorpyrifos for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. I.S.})(\%\text{ purity I.S.})(\text{pk. ht. or area chlorpyrifos})}{(\text{wt. sample})(\text{pk. ht. or area I.S.})(RF)}$$

Method submitted by Stelios Gerazounis, EPA Product Analysis Lab, Region II, New York, NY. (also from experimental #17 method May 1970)

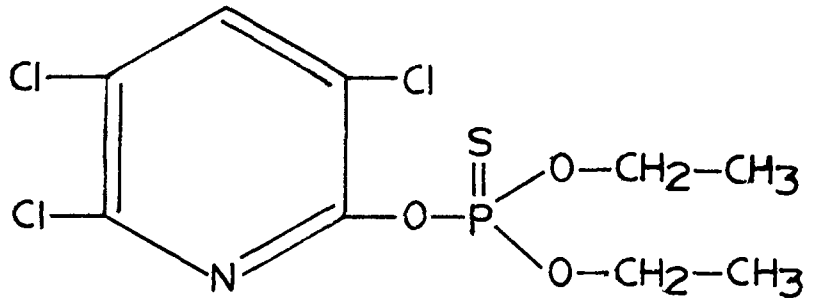
Any criticisms, suggestions, or data concerning this method or its use will be appreciated.

April 1979

Chlorpyrifos EPA-4
(tentative)

Determination of Chlorpyrifos by High Pressure Liquid Chromatography

Chlorpyrifos is the accepted (ANSI, ISO, BSI) common name for O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)-phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_9H_{11}Cl_3NO_3PS$

Molecular weight: 350.5

Physical state, color, and odor: white crystals with a mild mercaptan odor

Melting point: 41 to 43°C

Solubility: 2 ppm in water at 25°C; 79% in isooctane w/w, 43% in methanol w/w; readily soluble in most other organic solvents

Stability: stable under normal storage conditions; compatible with non-alkaline pesticides but is corrosive to copper and brass; half-life in aqueous methanolic solution 1930 days at pH 6.0, 7.2 days at pH 9.96

Other names: Dursban (for mosquito control); Lorsban (for agricultural use); Dowco 179 (Dow Chemical); trichlorpyrphos

Reagents:

1. Chlorpyrifos standard of known % purity
2. Methanol, spectro or pesticide grade

Equipment:

1. High pressure liquid chromatograph with variable wavelength UV detector (for 289 nm)
2. Suitable column such as: Partisil 10 ODS 25 cm x 4.6 mm ID
3. 10 ul high-pressure syringe or sample injection loop
4. Solvent and sample clarification kit (Millipore)
5. Usual laboratory apparatus

Operating Conditions:

Mobile phase:	75% methanol + 25% water
Column temperature:	Ambient
Flow rate:	1.5 ml/min
Chart speed:	0.5 in/min (or adjusted)
Amount injected:	10 ul

Conditions may have to be adjusted for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.125 gram chlorpyrifos standard into a 50 ml glass-stoppered Erlenmeyer flask or 2 oz screw-capped bottle, add by pipette 25 ml methanol, close tightly and shake to dissolve. (conc 5 mg chlorpyrifos/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.125 gram chlorpyrifos into a 50 ml glass-stoppered Erlenmeyer flask or 2 oz screw-capped bottle, add by pipette 25 ml methanol, shake to extract and dissolve the chlorpyrifos. Filter through a millipore clarification filter. (final conc 5 mg chlorpyrifos/ml)

Determination:

Alternately inject three 10 ul portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent chlorpyrifos as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by State of California, Department of Food and Agriculture, Chemistry Laboratory Services, Sacramento, CA.

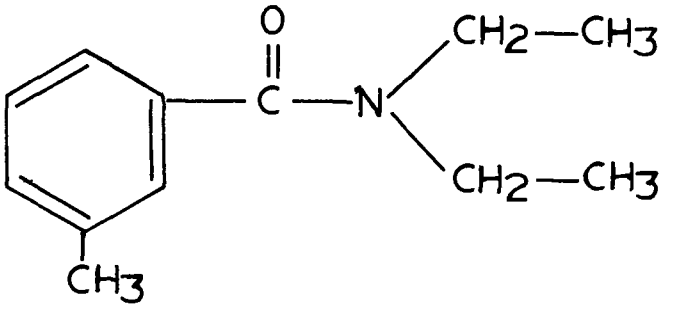
Any criticism, suggestions, or data concerning the use of this method will be appreciated.

March 1978

Deet EPA-4
(tentative)

Determination of Deet by High Pressure Liquid Chromatography (Normal Phase)

Deet is the common name for N,N-diethyl-m-toluamide, a registered insect repellent having the chemical formula:



Molecular formula: $C_{12}H_{17}NO$

Molecular weight: 191.3

Boiling point: 111°C at 1 mm Hg

Physical state and color: colorless to amber liquid, nearly odorless; the technical product contains 85-95% m isomer; the o and p isomers are highly repellent but less effective than the m isomer

Solubility: practically insoluble in water; miscible with ethanol, isopropanol, propylene glycol, cottonseed oil, ether, benzene

Stability: stable under normal conditions; non-corrosive to most metals

Other names: Metadelphene (Hercules), Delphene, Detamide, Off

Reagents:

1. Deet standard of known % purity
2. Chloroform, pesticide or spectro grade

Equipment:

1. High pressure liquid chromatograph with ultraviolet detector at 254 nm
2. Liquid chromatography column: 30 cm x 4 mm ID, micro Porasil or equivalent silica column
3. High pressure liquid syringe or sample injection loop

Operating Conditions:

Mobile phase:	60% chloroform + 40% iso-octane
Column temperature:	Ambient
Column pressure:	1000 psi (observed)
Flow rate:	1 ml/min

Operating Conditions (cont'd):

Detector: 254 nm
Chart speed: Adjusted
Injection: 5 ul

Conditions may have to be adjusted for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram deet standard into a 50 ml volumetric flask, make to volume with chloroform, and mix thoroughly. (conc 2 ug/ul)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.1 gram deet into a 50 ml volumetric flask, make to volume with chloroform, and mix thoroughly. (conc 2 ug deet/ul)

Determination:

Using a high pressure liquid syringe or a sample injection loop, alternately inject three 10 ul portions each of the standard and sample solutions. Measure the peak height or area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area, calculate the percent deet as follows:

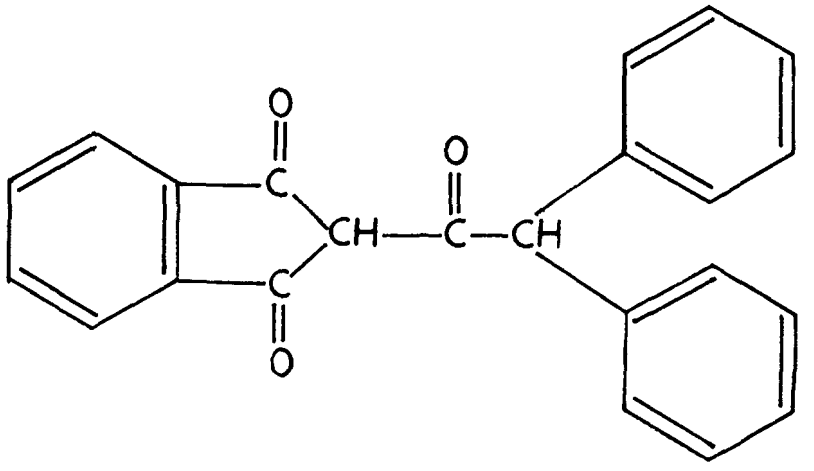
$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Elmer H. Hayes, EPA Beltsville Chemistry Laboratory, Beltsville, Md.

Any criticism, data, or suggestions concerning the use of this method will be appreciated.

Determination of Diphacinone by High Pressure Liquid Chromatography Using Paired Ion Chromatography

Diphacinone is the accepted common name for 2-(diphenylacetyl)-1,3-indandione, a registered rodenticide having the chemical structure:



Molecular formula: $C_{23}H_{16}O_3$

Molecular weight: 340.4

Melting point: 145°C

Physical state, color, and odor: yellow, odorless crystals

Solubility: slightly soluble in water and benzene; soluble in acetone and acetic acid. Forms a sodium salt which is sparingly soluble in water.

Stability: resists hydrolysis; stable toward mild oxidants; non-corrosive

Other names: Diphacin (Velsicol Chem. Corp.), diphacin (Turkey), Ramik, diphenadione

Reagents:

1. Diphacinone standard of known % purity
2. Dioxane, ACS
3. Paired Ion Chromatography (PIC) Reagent A - Add one bottle of PIC Reagent A to 1000 ml distilled water, stir for 5 minutes, and filter through a 0.45 micron filter.

   Each bottle of PIC Reagent A (tetrabutylammonium phosphate for separation of acids) contains sufficient PIC A to make one liter of mobile solvent. This solution is filtered through the 0.45 micron filter to remove any suspended particulate material increasing the useful life of the PIC solution, and to prevent clogging of the column.

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm. If a variable wavelength UV detector is available, other wavelengths may be used to increase sensitivity or to eliminate interference (280 nm is very good for diphacinone).
2. 30 cm x 2.0 mm ID Waters C_{18} Bondapak or equivalent column
3. High pressure liquid syringe or sample injection loop
4. Usual laboratory glassware

Operating Conditions:

Mobile phase:	90% methanol + 10% aqueous PIC Reagent A
Column temperature:	Ambient
Chart speed:	5 min/inch or equivalent
Flow rate:	0.5 to 1.5 ml/min
Pressure:	1000-1200 psi
Attenuation:	Adjusted

Conditions may have to be varied by the analyst for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram standard diphacinone into a 100 ml volumetric flask, dissolve in, and make to volume with dioxane. Mix thoroughly. Pipet 10 ml into a second 100 ml volumetric flask, make to volume with dioxane, and mix thoroughly. Pipet 10 ml into a third 100 ml volumetric flask, make to volume with dioxane, and again mix thoroughly. (conc 10 ug/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.00025 gram diphacinone (5 grams for a 0.005% formulation) into a small glass-stoppered flask or screw-cap bottle. Add 25 ml dioxane and shake on a mechanical shaker for one hour. Allow any solid matter to settle and filter through a 0.45 micron filter. (conc 10 ug diphacinone/ml)

Determination:

Alternately inject three 10 ul portions each of standard and sample solutions. Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Calculation:

From the average peak height or peak area calculate the percent diphacinone as follows:

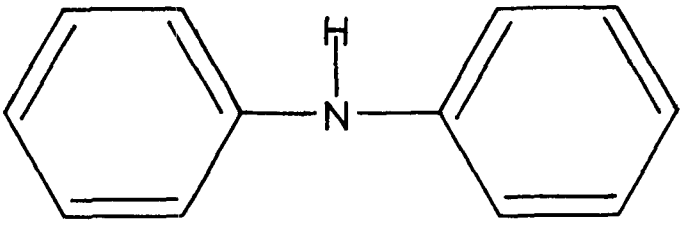
$$\% = \frac{(\text{pk. ht. or area sample})(\text{conc. std in ug/ml})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{conc. sample in ug/ml})}$$

Method submitted by Elmer H. Hayes and Mark W. Law, EPA Beltsville Chemistry Laboratory, Beltsville, Md.

Any criticism, data, or suggestions concerning this method will be appreciated.

Determination of Diphenylamine by Gas Liquid Chromatography (TCD)

Diphenylamine is a registered insecticide having the chemical structure:



Molecular formula: $C_{12}H_{11}N$

Molecular weight: 169.2

Melting point: 53-54°C; boiling point: 302°C

Physical state, color, and odor: white crystalline solid, floral odor

Solubility: insoluble in water; one gram dissolves in 2.2 ml alcohol, 4.5 ml propyl alcohol; freely soluble in benzene, ether, glacial acetic acid, and carbon disulfide

Stability: discolors in light; forms salts with strong acids

Other names: N-phenylbenzeneamine, Big Dipper, Scaldip

Reagents:

1. Diphenylamine standard of known % purity
2. Benzene, pesticide or spectro grade

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 4' x 1/4" glass column packed with 3.8% SE-30 on Diatoport S 80/100 mesh (or equivalent column)
3. Precision liquid syringe: 10 ul
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	155°C
Injection temperature:	200°C
Detector temperature:	200°C
Filament current:	200 ma
Carrier gas:	Helium
Attenuation:	1
Flow rate:	100 ml/min

Operating conditions for filament current, column temperature, or gas flow should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.15 gram diphenylamine standard into a 25 ml volumetric flask, make to volume with benzene, and mix thoroughly. (conc 6 ug/ul)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.15 gram diphenylamine into a 25 ml volumetric flask, make to volume with benzene, and mix thoroughly. (conc 6 ug diphenylamine/ul)

Determination:

Using a precision liquid syringe, alternately inject three 4 ul portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent diphenylamine as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Stelios Gerazounis, EPA Pesticide Chemistry Laboratory, Region II, New York, NY.

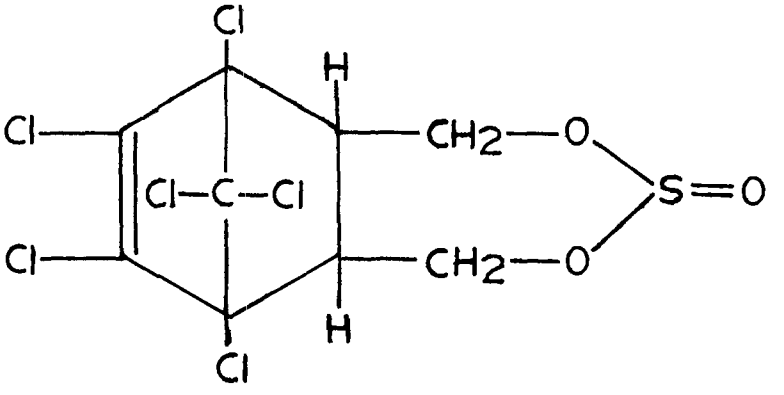
Any comments, data, or suggestions concerning the use of this method will be appreciated.

March 1978

Endosulfan EPA-5
(tentative)

Determination of Endosulfan by Gas Liquid Chromatography (FID - Internal Standard)

Endosulfan is the accepted common name for Hexachlorohexahydro-methano-2,4,3-benzodioxathiepin-3-oxide, a registered pesticide having the chemical structure:



Molecular formula: $C_9H_6Cl_6O_3S$

Molecular weight: 406.9

Melting point: (see below)

Physical state, color, and odor: endosulfan is an odorless white crystalline solid mixture of two isomers with mp's of 106°C and 212°C; the technical product is a brownish crystalline solid, mp 70-100°C, with a 4:1 ratio of the above isomers. Both isomers are insecticidally active.

Solubility: practically insoluble in water, but soluble in most organic solvents

Stability: generally quite stable; decomposition catalyzed by iron; slowly hydrolyzed by water; sensitive to acid and bases; compatible with non-alkaline pesticides

Other names: Thiodan (Farwerke Hoechst), Beosit, Chlorthiepin, Cyclodan, Insectophene, Kop-Thiodan, Malix, Thifor, Thimul, Thionex, HOE 2671, NIA 5462, FMC 5462

The following method (from N.C. Dept. of Agr.) determines the two isomers of endosulfan. The ratio of endosulfan I isomer to endosulfan II isomer in samples ranges from about 4:1 to 2:1. The procedure as written matches a 2-2/3:1 ratio. Linearity and precision by area (electronic integration) are very good. Peak height measurements were not calculated; therefore, should not be used unless a linearity and precision determination is made. This method is applicable to formulations containing malathion and parathion. Both of these will elute before endosulfan I and are completely resolved from it.

Reagents:

1. Endosulfan I isomer of known % purity
2. Endosulfan II isomer of known % purity
3. p-terphenyl, reagent grade
4. Chloroform, pesticide or spectro grade
5. Internal Standard solution - weigh 0.15 gram p-terphenyl into a 100 ml volumetric flask, make to volume with chloroform, and mix thoroughly. (conc 1.5 ug/ul)

Equipment:

1. Gas chromatograph with flame ionization detector (FID) and electronic integrator
2. Column: 6' x 4 mm ID glass column packed with 3% OV-17 on 100/120 mesh Gas Chrom Q (or equivalent column)
3. Precision liquid syringe: 5 or 10 ul
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	205°
Injection temperature:	225°
Detector temperature:	240°
Carrier gas:	Nitrogen, 80 cc/min
Carrier gas pressure:	40 psi
Hydrogen pressure:	20 psi
Air pressure:	40 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.08 gram endosulfan I and 0.03 gram endosulfan II standards (vary wt. of endosulfan II to match sample more appropriately if necessary) into a small glass-stoppered flask or screw-cap bottle. Add by pipet 20 ml of the internal standard solution and shake to dissolve. (final conc 5.5 ug total endosulfan and 1.5 ug p-terphenyl/ul)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.11 gram endosulfan into a small glass-stoppered flask or screw-cap bottle. Add by pipette 20 ml of the internal standard solution. Close tightly and shake thoroughly to dissolve and extract the endosulfan. For coarse or granular materials, shake mechanically for 30 minutes or shake by hand intermittently for one hour. (final conc 5.5 ug total endosulfan and 1.5 ug p-terphenyl/ul)

Determination:

Inject 2 ul of standard and, if necessary, adjust the instrument parameters to give a complete separation and an elution time of 6-9 minutes for endosulfan II. The elution order is endosulfan I, p-terphenyl, then endosulfan II.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak areas of endosulfan I, endosulfan II and p-terphenyl from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$\text{RF endosulfan I} = \frac{(\text{peak area endosulfan I})}{(\text{wt. endosulfan I})(\text{peak area p-terphanyl})}$$

$$\text{RF endosulfan II} = \frac{(\text{peak area endosulfan II})}{(\text{wt. endosulfan II})(\text{peak area p-terphanyl})}$$

(Weights of endosulfan standards should be adjusted according to % purity.)

Determine the percent endosulfan I and endosulfan II for each injection of the sample-internal standard solution as follows and calculate the average:

$$\%\ \text{endosulfan I} = \frac{(\text{peak area endosulfan I})(100)}{(\text{wt. sample})(\text{peak area p-terphenyl})(\text{RF endosulfan I})}$$

$$\%\ \text{endosulfan II} = \frac{(\text{peak area endosulfan II})(100)}{(\text{wt. sample})(\text{peak area p-terphenyl})(\text{RF endosulfan II})}$$

$$\%\ \text{total endosulfan} = \%\ \text{endosulfan I} + \%\ \text{endosulfan II}$$

Method submitted by North Carolina Department of Agriculture, Pesticide Section, Raleigh, N.C.

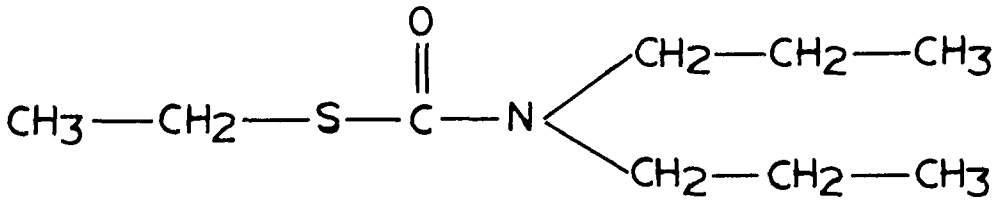
Any criticisms, data, or suggestions concerning the use of this method will be appreciated.

March 1978

EPTC EPA-6
(tentative)

Determination of EPTC by High Pressure Liquid Chromatography (Reverse Phase)

EPTC is the common name for S-ethyl dipropylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{19}NOS$

Molecular weight: 189.3

Boiling point: 127°C at 20 mm Hg (235°C by extrapolation)

Physical state, color, and odor: Light yellow-colored liquid with an amine odor

Solubility: 365 ppm in water at 20°C; miscible with acetone, benzene, ethanol, isopropanol, kerosene, methanol, methyl isobutyl ketone, toluene, and xylene

Stability: stable, non-corrosive

Other names: Eptam (Stauffer), Eradicane, Knoxweed

Reagents:

1. EPTC standard of known % purity
2. Dioxane, pesticide or spectro grade
3. Methanol, pesticide or spectro grade

Equipment:

1. High pressure liquid chromatograph with variable ultraviolet detector adjustable to 230 nm (254 nm may be used but sensitivity is less)
2. Liquid chromatographic column, two 1/2 m x 2.0 mm I.D. Permaphase ODS or equivalent silica column
3. High pressure liquid syringe or 5 ul sample injection loop

Operating Conditions for Perkin-Elmer HPLC:

Mobile phase:	25% methanol + 75% water
Column temperature:	Ambient
Column pressure:	2600 psi (observed)
Flow rate:	0.75 ml/min
Detector:	Variable wavelength 230 nm
Chart speed:	Adjusted
Injection:	5 ul

Procedure:

Preparation of Standard:

Weigh 0.1 gram EPTC standard into a 50 ml volumetric flask, make to volume with dioxane, and mix thoroughly. (conc 2 ug/ul)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.1 gram EPTC into a 50 ml volumetric flask. For emulsifiable concentrates make to volume with dioxane; for dusts or granules add 50 ml of dioxane by pipette. Shake thoroughly to dissolve or extract the EPTC. (conc 2 ug EPTC/ul)

Determination:

Using a high pressure liquid syringe or 5 ul injection loop, alternately inject three 5 ul portions each of the standard and sample solutions. Measure the peak height or area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent EPTC as follows:

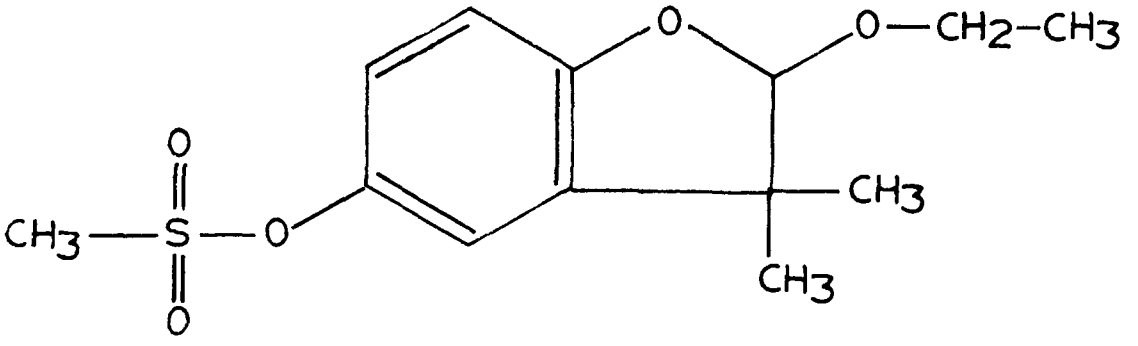
$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Elmer H. Hayes, EPA Beltsville Chemistry Laboratory, Beltsville, Md.

Any criticism, data, or suggestions concerning the use of this method will be appreciated.

Determination of Ethofumesate by Gas Liquid Chromatography (FID - Internal Standard)

Ethofumesate is the common name (ISO, BSI, and ANSI pending) for 2-ethoxy-2,3-dihydro-3,3-dimethyl-5-benzofuranyl methanesulphonate, a registered herbicide having the chemical structure:



Molecular formula: $C_{13}H_{18}O_5S$

Molecular weight: 286.34

Melting point: 70-72°C

Physical state and color: white, crystalline solid

Solubility: 110 ppm in water; 10% in ethanol; 25% in glycerol; 40% in acetone, benzene, chloroform, and dioxan; 0.4% in hexane

Stability: stable to hydrolysis in water at pH 7

Other names: Nortron* (Fisons Ltd., Great Britain), NC 8438

*Note: The name "Nortron" was previously used by Fisons Limited for "6-chloro-2-trifluoromethyl-3-H-imidazo-(4,5,6) pyridine" with the proposed ISO name "fluoromidine." This compound was discontinued and the name "Nortron" was then used for ethofumesate, the compound described in this method.

Reagents:

1. Ethofumesate standard of known % purity
2. Dipentyl phthalate standard of known % purity
3. Methylene chloride, pesticide or spectro grade
4. Internal Standard solution - weigh 0.75 gram dipentyl phthalate standard into a 50 ml volumetric flask, dissolve in, and make to volume with methylene chloride. (conc 15 mg/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 2 mm ID glass column packed with 5% SE-30 on Chromosorb W HP 80-100 mesh (or equivalent column)
3. Precision liquid syringe: 5 or 10 ul
4. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	200°C
Injection temperature:	220°C
Detector temperature:	240°C
Carrier gas:	Helium or Nitrogen
Carrier gas flow:	30 ml/min (adjusted for specific GC)
Hydrogen pressure:	20 psi (adjusted for specific GC)
Air pressure:	30 psi (adjusted for specific GC)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.075 gram ethofumesate standard into a 25 ml volumetric flask. Add 5 ml of internal standard solution by pipette and shake to dissolve the ethofumesate. Make to volume with methylene chloride and mix thoroughly. (final conc 3 mg ethofumesate and 3 mg dipentyl phthalate/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.075 gram ethofumesate into a 25 ml volumetric flask. Add 5 ml of internal standard by pipette and shake to dissolve the ethofumesate in the sample. Make to volume with methylene chloride and mix thoroughly. (final conc 3 mg ethofumesate and 3 mg dipentyl phthalate/ml)

Determination:

Inject 5 ul of the standard-internal standard solution and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and to give peak heights of from 1/2 to 3/4 full scale. The elution order is dipentyl phthalate, then ethofumesate.

Proceed with the determination, making at least three injections each of standard-internal standard and sample-internal standard solutions in random order.

Calculation:

Measure the peak heights or areas of ethofumesate and dipentyl phthalate from both the standard-internal standard and the sample-internal standard solutions.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

(DPP = dipentyl phthalate = internal standard)

$$RF = \frac{(\text{wt. DPP})(\%\text{ purity DPP})(\text{pk. ht. or area ethofumesate})}{(\text{wt. ethofumesate})(\%\text{ purity ethofumesate})(\text{pk. ht. or area DPP})}$$

Determine the percent ethofumesate for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. DPP})(\%\text{ purity DPP})(\text{pk. ht. or area ethofumesate})}{(\text{wt. sample})(\text{pk. ht. or area DPP})(RF)}$$

Method submitted by Mark W. Law, EPA Beltsville Chemistry Laboratory, Beltsville, Md.

Any criticism, data, or suggestion concerning the use of this method will be appreciated.

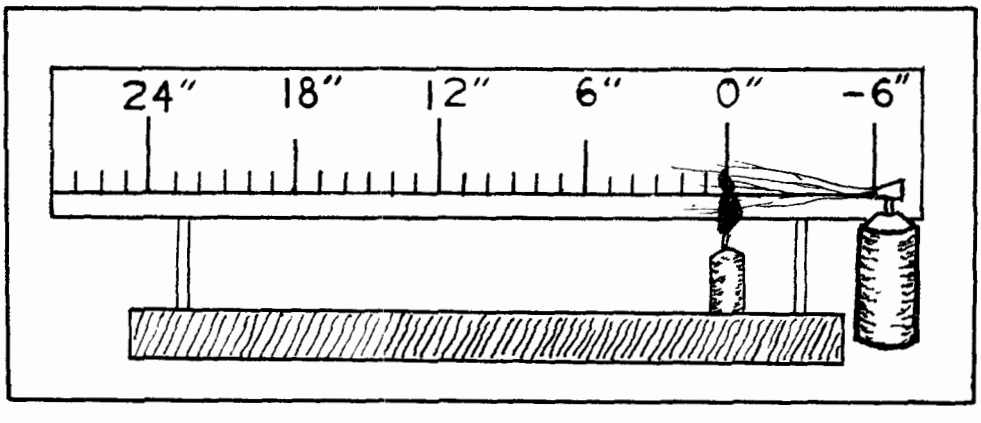
Flame Projection Flammability Test for Self-Pressurized Aerosol Dispensers

This test indicates the flammability hazard of aerosol formulations by measuring the length of flame that occurs when an aerosol (self-pressurized dispenser) is sprayed across a burning candle. Under the standardized conditions of this test, a flame 18 inches or longer is considered flammable.

The Flammability Test EPA-2 (Closed Drum) should also be used for the same aerosol formulation because the two tests together give a better indication of the flammability hazard than either test alone.

Equipment:

The test equipment consists of a wooden base 8-10 inches wide and 30 inches long. A two-foot scale marked at 1-inch intervals is mounted horizontally along one side six inches above the base. The zero point of the scale starts six inches from the end. A small candle is placed at this zero point at such a height that the top third of the flame is even with the scale. The flame should be about 2 inches high.



Procedure:

The test equipment should be placed in a draft-free area that can be ventilated to clear the atmosphere after each test.

Place the aerosol at a distance of 6 inches from the flame or at the end of the test equipment (really minus 6 inches from the ruled scale). Spray the dispenser so that the spray passes through the top third of the flame at a right angle to it. Spray for several seconds while an observer notes the length of flame. The normal bending of the flame is about 2 inches and is considered part of the flame length. Take three readings for each aerosol and average the results.

Self-pressurized dispensers should be classed as flammable:

(1) when the length of flame at full valve opening is 18 inches or more,

(2) if there is a flash-back to the container at any degree of valve opening.

Closed Drum Flammability Test for Self-Pressurized Aerosol Dispensers

This test indicates the hazard that results from spraying different aerosol formulations in a closed space in which there is a flame. The amount of time it takes for a positive result to occur indicates the hazard from various degrees of dilution with air (longer spraying time equals higher concentration of the formulation in the atmosphere in the drum).

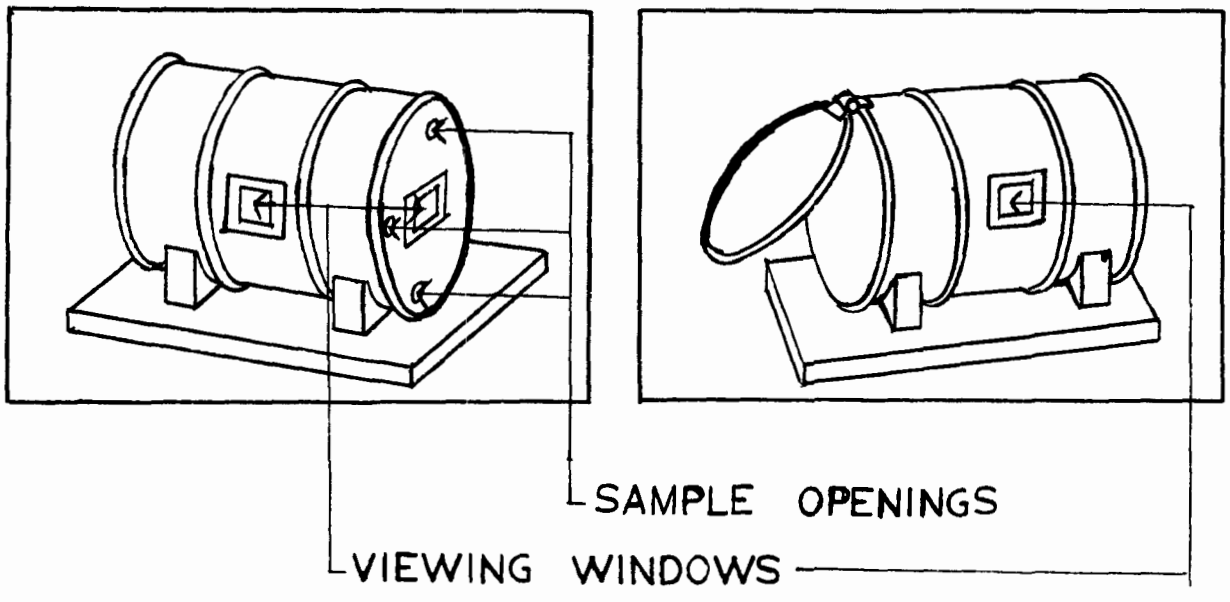
The Flammability Test EPA-1 (Flame Projection) should also be used for the same aerosol formulation because the two tests together give a better indication of the flammability hazard than either test alone.

Equipment:

A 55-gallon open-head drum or similar container is fitted with a hinged (at the top) cover arranged so that it will readily swing open at a pressure of five pounds. The cover does not have to be "airtight" but should adequately close the end of the drum.

The opposite end of the drum is equipped with three shuttered openings--top, side, and bottom--each two inches from the drum's edge and each one inch in diameter. The end is also fitted with a six-inch-square observation window covered with safety glass. A side observation window is optional.

A small candle is placed inside the drum (as it lies on its side) on the bottom midway between the ends.



Procedure:

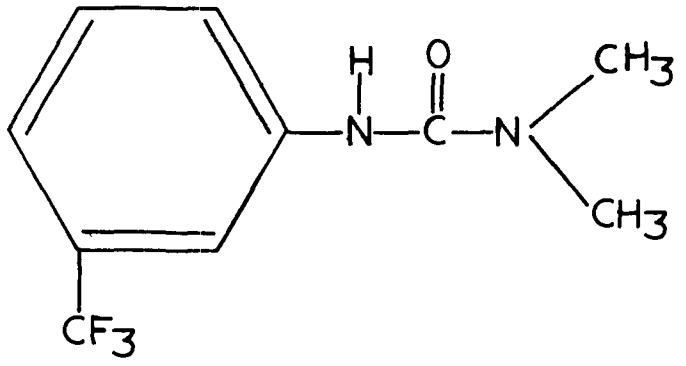
The drum should be used out of doors when the temperature is between 60-80°F. If this is not possible, place the drum in a working area that is properly ventilated.

Open one of the shutters and spray the aerosol (valve fully opened) into the drum for one minute. Clear the atmosphere in the drum and repeat with each of the other two openings.

Any rapid burning or explosion of the vapor-air mixture sufficient to cause the hinged cover to move is considered a positive test and is enough to class the unit being tested as flammable.

Determination of Fluometuron by Ultraviolet Spectroscopy

Fluometuron is the accepted common name for 1,1-dimethyl-3-(a,a,a-trifluoro-m-tolyl) urea, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_{11}F_3N_2O$

Molecular weight: 232.2

Melting point: 163 to 164.5°C (the technical product is about 96% pure and has a m.p. of about 155°C)

Physical state, color, and odor: odorless, white, crystalline solid

Solubility: 90 ppm in water at 25°C; soluble in acetone, ethanol, isopropanol

Stability: stable, non-corrosive, compatible with other herbicides

Other names: Cotoran (CIBA-Geigy), Lanex (Nor-Am), C-2059, CIBA-2059

Reagents:

1. Fluometuron standard of known % purity
2. Methanol, pesticide or spectro grade
   (Other suitable organic solvents such as 95% methanol, isopropylanol, or chloroform may be used.)

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm silica cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram fluometuron standard into a 100 ml volumetric flask. Dissolve in, make to volume with methanol, and mix thoroughly. Pipette 10 ml into a second 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette 5 ml of this solution into a third 100 ml volumetric flask, and make to volume with methanol. Mix thoroughly. (conc 5 ug/ml)

Preparation of Sample:

For wettable powders - weigh a portion of sample equivalent to 0.1 gram fluometuron into a 250 ml glass-stoppered flask or screw-cap bottle. Add 100 ml methanol, close tightly, and shake for one hour. Allow to settle, centrifuge or filter if necessary. Proceed as in the third paragraph beginning "Pipette 10 ml - - -."

For concentrates or high percent formulations (above 90% fluometuron), weigh a portion of sample equivalent to 0.1 gram fluometuron into a 100 ml volumetric flask, make to volume with methanol, and mix thoroughly.

Pipette 10 ml of either of the above sample solutions into a 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette 5 ml of this solution into another 100 ml volumetric flask, make to volume with the methanol, and mix thoroughly. (final conc 5 ug fluometuron/ml)

UV Determination:

Balance pen for 0 and 100% transmission at 243 nm with methanol in each cell. Scan standard and sample from 300 nm to 200 nm with methanol solution in the reference cell. Measure absorbance of standard and sample at 243 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent fluometuron as follows:

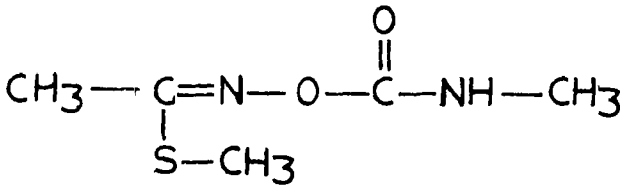
$$\% = \frac{(\text{abs. sample})(\text{conc. std in ug/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in ug/ml})}$$

Method submitted by George Radan, EPA Product Analysis Laboratory, New York, NY.

Any criticisms, data, or suggestions concerning the use of this method will be appreciated.

Determination of Methomyl by High Pressure Liquid Chromatography

Methomyl is the accepted (ANSI, BSI) common name for S-methyl N-[(methylcarbamoyl)oxy] thioacetimidate, a registered insecticide and nematocide having the chemical structure:



Molecular formula: $C_5H_{10}N_2O_2S$

Molecular weight: 162.2

Physical state, color, and odor: white crystalline solid with a slight sulfurous odor

Melting point: 78-79°C

Solubility: solubility at 25°C w/w is 5.8 in water, 73 in acetone, 42 in ethanol, 22 in isopropanol, 100 in methanol, 3 in toluene

Stability: stable in solid form and in aqueous solutions under normal conditions; subject to decomposition under moist conditions in soil; aqueous solution is non-corrosive

Other names: Lannate (duPont), Nudrin (Shell)

Reagents:

1. Methomyl standard of known % purity
2. Methanol, spectro or pesticide grade

Equipment:

1. High pressure liquid chromatograph with variable wavelength UV detector for 233 nm
2. Suitable column such as: Partisil 10 ODS 25 cm x 4.6 mm ID
3. High pressure 10 ul liquid syringe (or suitable sample injection loop)
4. Mechanical shaker
5. Solvent and sample clarification kit (obtainable from Millipore)
6. Usual laboratory glassware

Operating Conditions:

Mobile phase:	75% methanol + 25% water
Column temperature:	ambient
Flow rate:	1.3-1.5 ml/min
Chart speed:	0.5 cm/min

Conditions may have to be adjusted for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.125 gram methomyl standard into a small screw-cap bottle, add by pipette 25 ml methanol, shake to dissolve and to mix thoroughly. (final conc 5 mg methomyl/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.125 gram methomyl into a small screw-cap bottle, add by pipette 25 ml methanol, close tightly and shake for 15-30 minutes on a mechanical shaker. Allow to settle and if not clear, centrifuge a portion for a few minutes, then filter through a millipore filter. Take precaution to prevent evaporation. (final conc 5 mg methomyl/ml)

Determination:

Alternately inject three 5 ul portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent methomyl as follows:

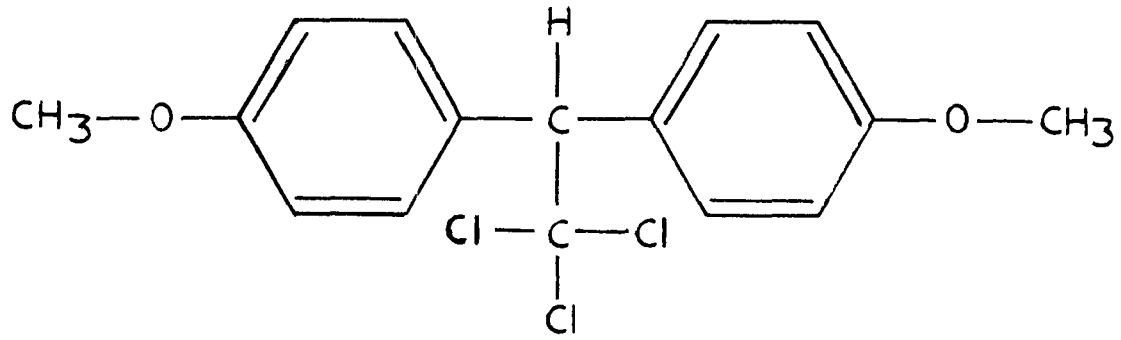
$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by the Sacramento Pesticide Laboratory, Dept. of Food and Agriculture, State of California, 1220 N Street, Sacramento, CA 95814.

Any criticism, suggestions, or data concerning the use of this method will be appreciated.

Determination of Methoxychlor by High Pressure Liquid Chromatography (Normal phase)

Methoxychlor, technical is the official name for 2,2-bis (p-methoxyphenyl)-1,1,1-trichloroethane 88% and related compounds 12%; it is a registered insecticide having the chemical structure:



Molecular formula: $C_{16}H_{15}Cl_3O_2$

Molecular weight: 345.5

Physical state, color, and odor: pure p,p' isomer forms colorless crystals; technical product is a gray flaky powder containing 88% p,p' isomer with the bulk of the remainder being the o,p isomer

Melting point: pure p,p' isomer 89°C; technical 70 to 85°C

Solubility: practically insoluble in water; moderately soluble in ethanol and petroleum oils; readily soluble in most aromatic solvents

Stability: resistant to heat and oxidation; susceptible to dehydrochlorination by alcoholic alkali and heavy metal catalyst

Other names: Marlate (DuPont), Moxie, 1,1,1-trichloro-2,2-bis(p-methoxyphenyl) ethane

Reagents:

1. Methoxychlor standard of known % purity
2. Petroleum ether, spectro or pesticide grade
3. Dichloromethane, spectro or pesticide grade

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm
2. Suitable column such as: 4 mm ID x 25 cm packed with Partisil (10 micron)(or equivalent column)
3. 10 ul high pressure liquid syringe or sample injection loop
4. Mechanical shaker
5. Centrifuge
6. Millipore sample clarification kit
7. Usual laboratory glassware

Operating Conditions:

Mobile phase:	80% petroleum ether + 20% dichloromethane
Column temperature:	ambient
Flow rate:	2 ml/min
Chart speed:	0.5 in/min
Amount injected:	10 ul

Conditions may have to be adjusted for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram methoxychlor into a 125 ml glass-stoppered flask or screw-cap bottle, add (by pipette) 50 ml dichloromethane, dissolve, and mix thoroughly. (final conc 2 mg methoxychlor/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram methoxychlor into a 125 ml glass-stoppered flask or screw-cap bottle, add 50 ml dichloromethane by pipette, close tightly, and shake for 30 minutes on a mechanical shaker. Allow to settle; if not clear, centrifuge a portion a few minutes. Filter a portion through a 5 micron millipore filter. Take precaution to prevent evaporation. (final conc 2 mg methoxychlor/ml)

Determination:

Alternately inject three 10 ul portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent methoxychlor as follows:

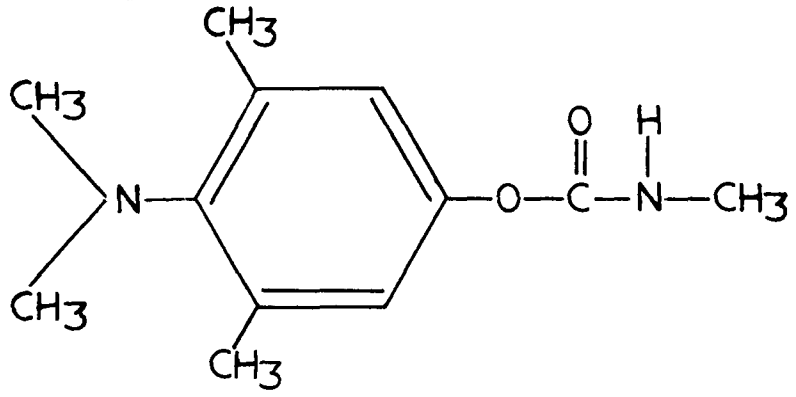
$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Elmer H. Hayes, EPA Beltsville Chemistry Laboratory, Beltsville, Md.

Any criticism, suggestions, or data concerning the use of this method will be appreciated.

Determination of Mexacarbate by Gas Liquid Chromatography (TCD - Internal Standard)

Mexacarbate is the accepted common name for 4-dimethylamino-3,5-xylyl methylcarbamate, a registered insecticide and acaricide having the chemical structure:



Molecular formula: $C_{12}H_{18}N_2O_2$

Molecular weight: 222.3

Melting point: 85°C

Physical state, color, and odor: white, odorless, crystalline solid

Solubility: 0.01% in water at 25°C; sparingly soluble in petroleum solvents; very soluble in benzene, ethanol, chloroform, methylene chloride, acetonitrile, and acetone

Stability: decomposed in highly alkaline media; stable under normal storage conditions; compatible with most other pesticides

Other names: Zectran (Dow Chem. Co.), Dowco 139, 4-dimethylamino-3,5-xylyl N-methylcarbamate, methylcarbamic acid 4-(dimethylamino)-3,5-xylyl ester

Reagents:

1. Mexacarbate standard of known % purity
2. Deet standard of known % purity
3. Acetone, pesticide or spectro grade
4. Internal Standard solution - weigh 7.0 grams deet standard into a 50 ml volumetric flask, dissolve in and make to volume with acetone; mix thoroughly. (conc 140 mg deet/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 4' x 1/4" I.D. glass, packed with 3.8% SE-30 on 80/100 Diatoport S or equivalent column (such as 4' x 1/4" I.D. glass, packed with 4% SP-2100 on 80/100 Chromosorb 750)
3. Precision liquid syringe: 10 ul
4. Usual laboratory glassware

Operating Conditions for TCD:

Column temperature:	135°C
Injection temperature:	200°C
Detector temperature:	200°C
Filament current:	200 ma
Carrier gas:	Helium
Carrier gas pressure:	40 psi

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Note: Mexacarbate shows a small peak approximately 12 minutes after injection at above parameters, most possibly due to the decomposition of carbamate at relatively elevated temperatures. On standing for several days the small peak increased significantly, while the main peak decreased (by about 50%). EPA's New York Chemistry Lab states: "the method given here is rapid enough and the temperature is relatively low to give reproducible results (obtained 95-97% of claimed active ingredient). This method has been used in our lab for two years."

Procedure:

Preparation of Standard:

For emulsifiable concentrates and liquid formulations - weigh 0.6 gram mexacarbate standard into a 10 ml volumetric flask; add 5 ml internal standard solution by pipette, make to volume with acetone, and mix thoroughly. (conc 60 mg mexacarbate and 70 mg deet/ml)

For dusts, granules, and wettable powders - weigh 0.6 gram mexacarbate standard into a small glass-stoppered flask or screw-cap bottle, add by pipette 5 ml of internal standard solution and 5 ml acetone, close tightly and mix thoroughly. (conc 60 mg mexacarbate and 70 mg deet/ml)

Preparation of Sample:

For emulsifiable concentrates and liquid formulations - weigh a portion of sample equivalent to 0.6 gram mexacarbate into a 10 ml volumetric flask; add 5 ml of internal standard solution by pipette, make to volume with acetone, and mix thoroughly. (final conc 60 mg mexacarbate and 70 mg deet/ml)

For dusts, granules, and wettable powders - weigh a portion of sample equivalent to 0.6 gram mexacarbate into a small glass-stoppered flask or screw-cap bottle; add by pipette 5 ml internal standard and 5 ml of acetone, close tightly and shake on a mechanical shaker for 10-15 minutes or shake by hand intermittently for 25-30 minutes. (final conc 60 mg mexacarbate and 70 mg deet/ml)

Determination:

Inject 1-2 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is mexacarbate, then deet.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of mexacarbate and deet from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. deet})(\%\text{ purity deet})(\text{pk. ht. or area mexacarbate})}{(\text{wt. mexacarbate})(\%\text{ purity mexacarbate})(\text{pk. ht. or area deet})}$$

Determine the percent mexacarbate for each injection of the sample-internal standard solution as follows and calculate the average:

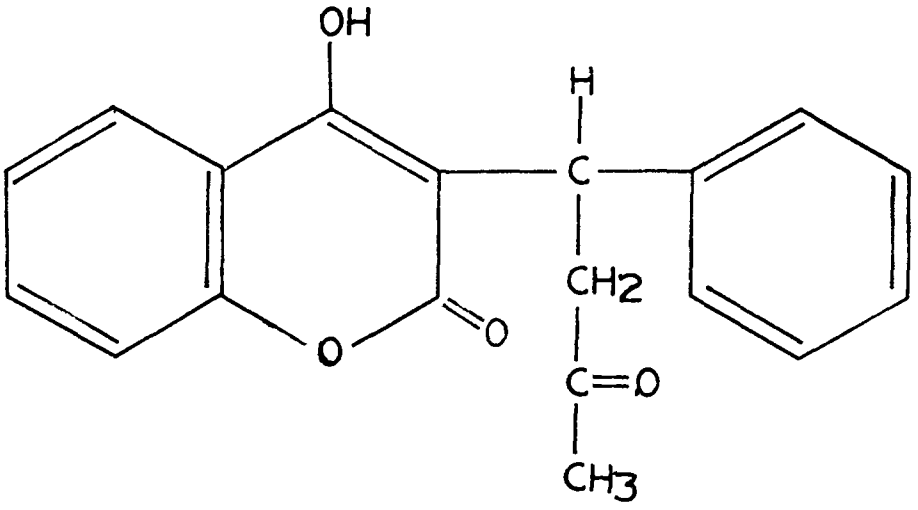
$$\% = \frac{(\text{wt. deet})(\%\text{ purity deet})(\text{pk. ht. or area mexacarbate})}{(\text{wt. sample})(\text{pk. ht. or area deet})(RF)}$$

Method submitted by George Radan, EPA Product Analysis Lab, Region II, New York, NY.

Any criticisms, data, or suggestions concerning this method or its use will be appreciated.

Determination of Warfarin and Sulfaquinoxaline in Bait Formulations by HPLC-PIC

Warfarin is the official common name for 3-(alpha-acetonylbenzyl)-4-hydroxycoumarin, a registered rodenticide having the chemical structure:



Molecular formula: $C_{19}H_{16}O_4$

Molecular weight: 308.3

Melting point: (dl form) 159 to 161°C

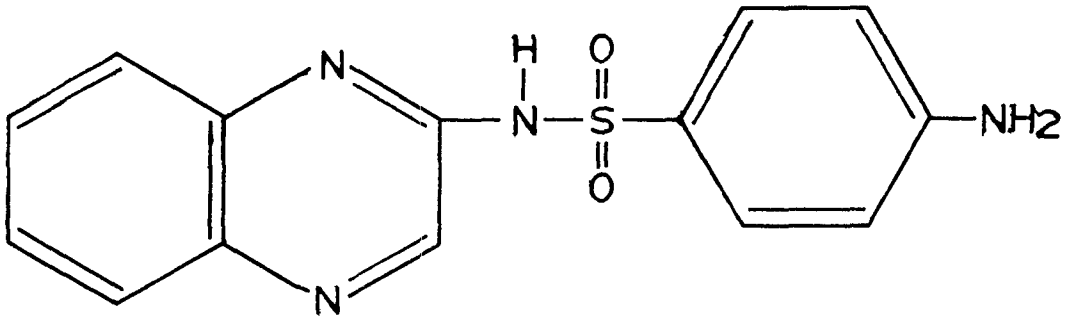
Physical state, color, odor, taste: (dl form) colorless, tasteless, odorless crystals

Solubility: practically insoluble in water and benzene, moderately soluble in alcohols, readily soluble in acetone and dioxane; forms water-soluble salts with sodium

Stability: stable under normal conditions

Other names: WARF (Wisconsin Alumni Research Foundation), coumafene (France), zoocoumarin (Netherlands, USSR), Kypfarin

Sulfaquinoxaline is the common name for N'-(2-quinoxalinyl) sulfanilamide, a warfarin additive (when added to warfarin formulations it inhibits the vitamin K producing bacteria in the digestive system of rats and mice, thereby rendering these rodents more susceptible to the warfarin). It has the chemical structure:



Molecular formula: $C_{14}H_{12}N_4O_2S$

Molecular weight: 300.33

Melting point: 247-248°C

Physical state, color, and odor: minute crystals

Solubility: solubility in water at pH 7: 0.75 mg/100 ml; in 95% alcohol: 73 mg/100 ml; in acetone: 430 mg/100 ml. Soluble in aqueous Na_2CO_3 and NaOH solutions

Stability: The amorphous salt is deliquescent and absorbs CO_2 which liberates the practically insoluble sulfaquinoxaline.

Other names: 4-amino-N-2-quinoxalinylbenzenesulfonamide; 2-sulfanilamido-quinoxaline; sulfabenzpyrazine; Compound 3-120; sulquin; sulfacox; sulfaline; sulfa-Q

Reagents:

1. Warfarin standard of known % purity
2. Sulfaquinoxaline standard of known % purity
3. Methanol, pesticide or spectro grade
4. Dioxane, pesticide or spectro grade
5. Water - PIC Reagent A (see note below)
6. Methanol - PIC Reagent A (see note below)

Note: Each bottle of PIC (paired ion chromatography) Reagent A (tetrabutyl ammonium phosphate for separation of acids) contains sufficient PIC A to make one liter of mobile solvent. Add one bottle of PIC A to 1000 ml of water and one bottle PIC A to 1000 ml of methanol, stir for about 5 minutes, and filter through a 0.45 micron filter. These solutions are filtered to remove any suspended particulate material increasing the useful life of the PIC solution, and to prevent clogging of the column.

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm. If a variable wavelength UV detector is available, other wavelengths may be useful to increase sensitivity or eliminate interference. Warfarin is more easily determined at 308 nm.
2. Suitable column such as Waters Bondapak C_{18} 30 cm x 2.1 mm ID
3. High pressure liquid syringe or sample injection loop
4. Millipore filter apparatus (0.045 micron)
5. Usual laboratory glassware

Operating Conditions:

Mobile phase:	55% methanol-PIC A Reagent + 45% water-PIC A reagent
Column temperature:	Ambient
Chart speed:	5 min/inch or equivalent
Flow rate:	0.5 to .75 ml/min
Pressure:	1000-1400 psi
Attenuation:	Adjusted

Conditions may have to be varied by the analyst for the specific instrument being used, column variations, sample composition, etc. to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Warfarin - weigh 0.05 gram warfarin standard into a 50 ml volumetric flask, dissolve in, and make to volume with dioxane. Mix thoroughly, pipette 5 ml into a second 50 ml volumetric flask, make to volume with dioxane, and mix thoroughly. (final conc 0.1 mg warfarin/ml)

Sulfaquinoxaline - weigh 0.05 gram sulfaquinoxaline standard into a 50 ml volumetric flask, dissolve in, and make to volume with dioxane. Mix thoroughly, pipette 5 ml into a second 50 ml volumetric flask, make to volume with dioxane, and mix thoroughly. (final conc 0.1 mg sulfaquinoxaline/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.005 gram warfarin (and 0.005 gram sulfaquinoxaline)* into a glass-stoppered or screw-cap 125 ml Erlenmeyer flask, add 50 ml dioxane by pipette, close tightly, and shake for one hour. Allow to settle, and filter through a 0.45 micron millipore filter. (final conc 0.1 gram warfarin and 0.1 gram* sulfaquinoxaline/ml)

* Sample and standard weights should be adjusted as necessary for formulation containing other than 0.025% of each ingredient.

Determination:

For a variable wavelength detector, use 308 nm rather than 254 nm. Warfarin is more easily detected at this wavelength and many interferences are eliminated or reduced to a negligible amount.

Alternately inject three 10 ul portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent each of warfarin and sulfaquinoxaline as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Elmer H. Hayes, EPA Beltsville Chemistry Laboratory, Beltsville, MD.

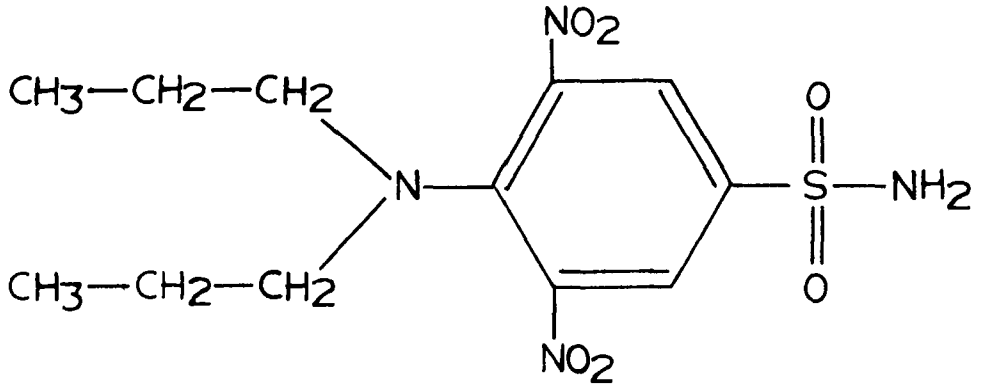
Any criticism, data, or suggestion concerning this method will be appreciated.

March 1978

Oryzalin EPA-1
(tentative)

Determination of Oryzalin by Visible (Colorimetric) Spectroscopy

Oryzalin is the accepted common name for 3,5-dinitro N^4,N^4-dipropylsulfanilamide, a registered herbicide having the chemical structure:



Molecular formula: $C_{12}H_{18}N_4O_6S$

Molecular weight: 346.4

Melting point: 141 to 142°C

Physical state, color, and odor: yellow-orange crystalline solid, no appreciable odor

Solubility: about 2.5 ppm in water at 25°C; readily soluble in polar organic solvents such as acetone, ethanol, methanol, and acetonitrile; slightly soluble in benzene and xylene

Stability: susceptible to UV decomposition; non-corrosive; formulations have a shelf life of more than 2 years; technical material is non-flammable; compatible with most other W.P. formulations and fertilizers if not highly alkaline

Other names: Surflan and Ryzelan (Eli Lilly & Co.), EL-119, Dirimal

Reagents:

1. Oryzalin standard of known % purity
2. 95% Ethanol, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram oryzalin standard into a 100 ml volumetric flask. Dissolve, make to volume with 95% ethanol, and mix thoroughly. Pipette a 5 ml aliquot into a 50 ml volumetric flask, make to volume with 95% ethanol, and again mix thoroughly. (conc 0.1 mg/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram of oryzalin into a 250 ml Erlenmeyer glass-stoppered flask. Add 100 ml 95% ethanol by pipette and shake on a mechanical shaker for one hour. Filter if necessary and pipette 10 ml of the clear filtrate into a 100 ml volumetric flask. Make to volume with 95% ethanol and mix thoroughly. (final conc 0.1 mg oryzalin/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative (visible range) analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 385 nm with 95% ethanol in each cell. Scan both the standard and sample from 600 nm to 350 nm with 95% ethanol in the reference cell. Measure the absorbance of both standard and sample at 385 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent oryzalin as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in mg/ml})(\%\ \text{purity std})}{(\text{abs. std})(\text{conc. sample in mg/ml})}$$

Method submitted by I. F. Sternman, EPA Product Analysis Laboratory, New York, NY.

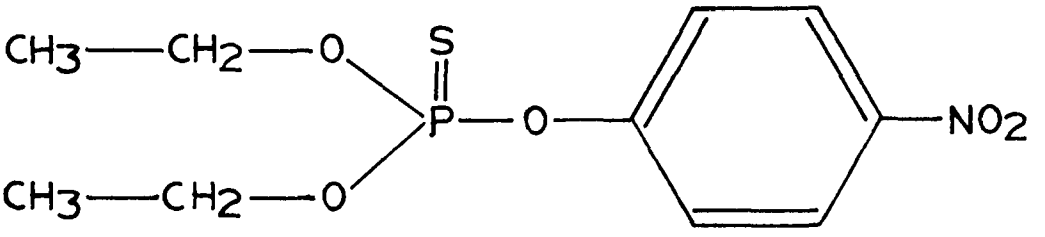
Any criticism, data, or suggestions concerning the use of this method will be appreciated.

June 1978

Parathion EPA-3
(tentative)

Determination of Parathion in the Presence of Carbaryl by Gas Liquid Chromatography (FID-IS)

Parathion is the official name for 0,0-diethyl-0-p-nitrophenol phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_{10}H_{14}NO_5PS$

Molecular weight: 291.3

Melting/Boiling point: m.p. 6.0°C, b.p. 157 to 162°C at 6 mm Hg

Physical state, color, and odor: pale yellow liquid; the technical product is a brown liquid with a garlic-like odor

Solubility: 24 ppm in water at 25°C; slightly soluble in petroleum oils; miscible with most organic solvents

Stability: rapidly hydrolyzed in alkaline media (at pH 5 to 6, 1% in 62 days at 25°C); isomerizes on heating to the OS-diethyl isomer

Other names: ACC 3422, Thiophos (American Cyanamid); E-605, Folidol Bladan (Bayer); Niran (Monsanto); Fosferno (Plant Protection Ltd.); thiophos (USSR); Alkron, Alleron, Aphamite, Corothion, Ethyl Parathion, Etilon, Fosfono, Orthophos, Panthion, Paramar, Paraphos, Parathene, Parawet, Phoskil, Rhodiatox, Soprathion, Strathion

Reagents:

1. Parathion standard of known % purity
2. Dieldrin standard of known HEOD content
3. Acetone, pesticide or spectro grade dieldrin
4. Internal standard solution - weigh 0.75 gram into a 50 ml volumetric flask, dissolve in, and make to volume with acetone. Mix thoroughly. (conc 15 mg/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 2 mm ID glass column packed with 5% SE-30 on 80/100 mesh Chromosorb W HP (or equivalent column)
3. Precision liquid syringe: 5 or 10 ul
4. Mechanical shaker
5. Centrifuge or filtration equipment
6. Usual laboratory glassware

Operating Conditions for FID:

Column temperature:	175°C
Injection temperature:	250°C
Detector temperature:	250°C
Carrier gas:	Helium
Carrier gas pressure:	40 psi (adjusted for particular GC)
Hydrogen pressure:	15 psi (adjusted for particular GC)
Air pressure:	40 psi (adjusted for particular GC)
Chart speed:	0.25"/min or 15"/hr

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram parathion into a 50 ml volumetric flask, add 10 ml internal standard solution by pipette, make to volume with acetone, and mix well. (conc 2 ug parathion and 3 ug dieldrin/ul)

Preparation of Sample:

For liquids and emulsifiable concentrates - weigh a portion of sample equivalent to 0.1 gram parathion into a 50 ml volumetric flask, add 10 ml internal standard solution, make to volume with acetone, and mix well. (conc 2 ug parathion and 3 ug dieldrin/ul)

For dusts and wettable powders - weigh a portion of sample equivalent to 0.4 gram parathion into a 250 ml glass-stoppered flask or screw-cap bottle, add 100 ml acetone by pipette. Close tightly and shake thoroughly to dissolve and extract the parathion. Shake mechanically for 10-15 minutes or shake by hand intermittently for 25-30 minutes. Allow to settle, filter or centrifuge if necessary, taking precaution to avoid loss by evaporation. Pipette a 25 ml aliquot into a 50 ml volumetric flask, add 10 ml internal standard by pipette, make to volume with acetone, and mix thoroughly. (final conc 2 ug parathion and 3 ug dieldrin/ul)

Determination:

Inject 1-2 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is parathion, then dieldrin. (Carbaryl elutes before parathion.) Repeated injections should give the same peak ratios.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of parathion and dieldrin from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

$$RF = \frac{(\text{wt. dieldrin})(\%\text{ purity dieldrin})(\text{pk. ht. or area parathion})}{(\text{wt. parathion})(\%\text{ purity parathion})(\text{pk. ht. or area dieldrin})}$$

Determine the percent parathion for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. dieldrin})(\%\text{ purity dieldrin})(\text{pk. ht. or area parathion})}{(\text{wt. sample})(\text{pk. ht. or area dieldrin})(RF)}$$

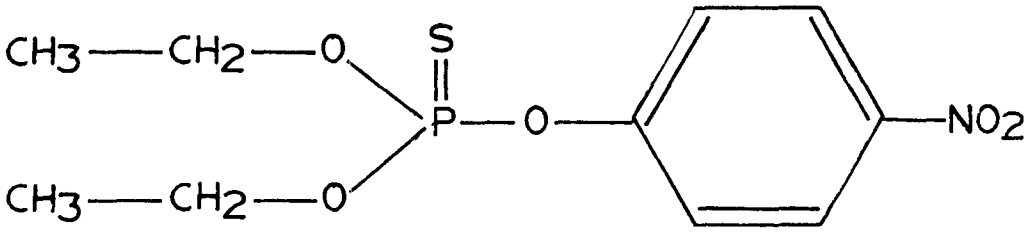
Method submitted by the Commonwealth of Virginia, Division of Consolidated Laboratory Services, 1 North 14th Street, Richmond, VA 23219.

Checked by Elmer Hayes, EPA Beltsville Chemistry Lab, ARC-East, Beltsville, MD 20705.

Any criticism, data, or suggestions concerning this method will be appreciated.

Determination of Parathion in the Presence of Carbaryl by High Pressure Liquid Chromatography (Reversed Phase)

Parathion is the official name for O,O-diethyl-O-p-nitrophenol phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_{10}H_{14}NO_5PS$

Molecular weight: 291.3

Melting/Boiling point: m.p. 6.0°C, b.p. 157 to 162°C at 6 mm Hg

Physical state, color, and odor: pale yellow liquid; the technical product is a brown liquid with a garlic-like odor

Solubility: 24 ppm in water at 25°C; slightly soluble in petroleum oils; miscible with most organic solvents

Stability: rapidly hydrolyzed in alkaline media (at pH 5 to 6, 1% in 62 days at 25°C); isomerizes on heating to the OS-diethyl isomer

Other names: ACC 3422, Thiophos (American Cyanamid); E-605, Folidol Bladan (Bayer); Niran (Monsanto); Fosferno (Plant Protection Ltd.); thiophos (USSR); Alkron, Alleron, Aphamite, Corothion, Ethyl Parathion, Etilon, Fosfono, Orthophos, Panthion, Paramar, Paraphos, Parathene, Parawet, Phoskil, Rhodiatox, Soprathion, Strathion

Reagents:

1. Parathion standard of known % purity
2. Carbaryl standard of known % purity
3. Dioxane, pesticide or spectro grade
4. Internal standard solution - weigh 3 grams dipropyl phthalate into a 100 ml volumetric flask, dissolve in and make to volume with dioxane. Mix thoroughly. (conc 30 mg/ml)

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm. If a variable wavelength UV detector is available, other wavelengths may be useful to increase sensitivity or to eliminate interference.
2. Reversed phase column such as DuPont ODS Permaphase, or Perkin Elmer Sil-X 11 RP
3. High pressure liquid syringe or sample injection loop
4. Millipore filter syringe with 0.45 micron filter pad
5. Usual laboratory glassware

Operating Conditions:

Mobile phase:	20% methanol + 80% water
Column temperature:	50-55°C
Chart speed:	5 min/inch or equivalent
Flow rate:	0.5 to 1.5 ml/min
Attenuation:	Adjusted

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Note: This method is written for a formulation containing a ratio of 3.5 parts parathion to 1 part carbaryl. If a different ratio formulation is to be analyzed, use the concentration of parathion specified (3.5 mg/ml) but change the concentration of carbaryl in the standard to match that in the sample.

Preparation of Standard:

Weigh 0.35 gram parathion and 0.1 gram carbaryl into a 100 ml volumetric flask, add 20 ml internal standard solution by pipette, make to volume with dioxane, and mix thoroughly. (final conc 3.5 mg parathion, 1 mg carbaryl, and 6 mg dipropyl phthalate/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.35 gram parathion (and 0.1 gram carbaryl for example) into a 100 ml volumetric flask, add 20 ml internal standard solution by pipette, and make to volume with dioxane. Close tightly and place in an ultrasonic bath for about 5 minutes. Allow to settle or centrifuge a portion and filter the clear liquid through a 0.45 micron millipore filter. (final conc 3.5 mg parathion, 1 mg carbaryl, and 6 mg dipropyl phthalate/ml)

Determination:

Inject 5 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and peak heights of from 1/2 to 3/4 full scale. The elution order is carbaryl, dipropyl phthalate, and parathion.

Proceed with the determination, making at least three injections each of standard and sample solutions in random order.

Calculation:

Measure the peak heights or areas of parathion and dipropyl phthalate from both the standard-internal standard solution and the sample-internal standard solution.

Determine the RF value for each injection of the standard-internal standard solution as follows and calculate the average:

(DPP = dipropyl phthalate)

$$RF = \frac{(\text{wt. DPP})(\%\text{ purity DPP})(\text{pk. ht. or area parathion})}{(\text{wt. parathion})(\%\text{ purity parathion})(\text{pk. ht. or area DPP})}$$

Determine the percent parathion for each injection of the sample-internal standard solution as follows and calculate the average:

$$\% = \frac{(\text{wt. DPP})(\%\text{ purity DPP})(\text{pk. ht. or area parathion})}{(\text{wt. sample})(\text{pk. ht. or area DPP})(RF)}$$

Calculation of % carbaryl is done in the same way as parathion using, of course, the carbaryl peaks.

Method submitted by Elmer H. Hayes, EPA Beltsville Chemistry Laboratory, Beltsville, MD.

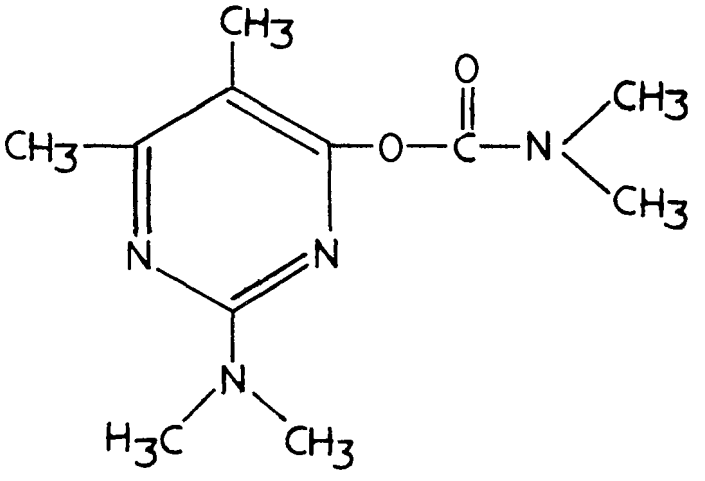
Any criticism, data, or suggestions concerning the use of this method will be appreciated.

March 1978

Pirimicarb EPA-1
(tentative)

Determination of Pirimicarb in Powder Formulations by Ultraviolet Spectroscopy

Pirimicarb is the common name for 2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyl dimethylcarbamate, a registered insecticide (aphicide) having the chemical structure:



Molecular formula: $C_{11}H_{18}N_4O_2$

Molecular weight: 238

Melting point: 90.5°C

Physical state, color, and odor: colorless, odorless, crystalline solid

Solubility: 0.27% in water at 25°C; soluble in most organic solvents

Stability: decomposed by ultraviolet light; decomposed by prolonged boiling with acids or alkalis; forms well-defined water-soluble crystalline salts with organic and inorganic acids (HCl salt is deliquescent); non-corrosive to normal spray equipment

Other names: Pirimor (Plant Protection Ltd); PP062, 5,6-dimethyl-2-dimethylamino-4-pyrimidinyl dimethylcarbamate; 2-dimethylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate

Reagents:

1. Pirimicarb standard of known % purity
2. Chloroform, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram pirimicarb standard into a 100 ml volumetric flask. Dissolve, make to volume with chloroform, and mix thoroughly. Pipette a 10 ml aliquot into a 50 ml volumetric flask and make to volume with chloroform. Mix thoroughly and pipette a 10 ml aliquot into a 50 ml volumetric flask. Make to volume and again mix thoroughly. (final conc 40 ug/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram of pirimicarb into a 250 ml Erlenmeyer glass-stoppered flask. Add 100 ml chloroform by pipette, close tightly, and shake on a mechanical shaker for one hour. Filter if necessary (taking precaution to avoid loss by evaporation), and pipette 10 ml of the clear filtrate into a 50 ml volumetric flask. Make to volume with chloroform, mix thoroughly, and pipette 10 ml into a 50 ml volumetric flask. Make to volume with chloroform and mix thoroughly. (final conc 40 ug pirimicarb/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 307 nm with chloroform in each cell. Scan both the standard and sample from 360 nm to 220 nm with chloroform in the reference cell. Measure the absorbance of both standard and sample at 307 nm.

(absorbance was found to be linear at least to 45 ug/ml)

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent pirimicarb as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in ug/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in ug/ml})}$$

Method submitted by Stelios Gerazounis, EPA Product Analysis Laboratory, New York, NY.

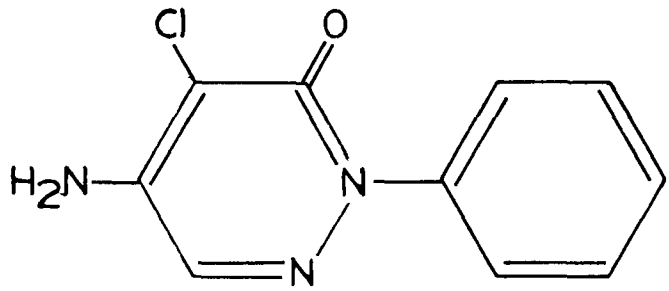
Any criticism, data, or suggestions concerning the use of this method will be appreciated.

March 1978

Pyrazon EPA-1
(tentative)

Determination of Pyrazon in Powder Formulations by Ultraviolet Spectroscopy

Pyrazon is the accepted common name for 5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_8ClN_3O$

Molecular weight: 221.6

Melting point: pure 205-206°C (207° with decomposition); technical 185-195°C

Physical state, color, and odor: tan to brown powder; odorless when pure

Solubility: 400 ppm in water at 20°C; 2.8% in acetone; 2.4% in methanol; 0.07% in benzene and in ether; 0.21% in chloroform; 0.6% in ethyl acetate

Stability: decomposes at melting point; relatively resistant to decomposition by UV; non-corrosive; nonflammable; no limitation on shelf life of concentrate

Other names: Pyramin (BASF Canada), PCA, H119

Reagents:

1. Pyrazon standard of known % purity
2. Methanol, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm silica cells
2. Mechanical shaker
3. Filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of Standard:

Weigh 0.1 gram pyrazon standard into a 100 ml volumetric flask. Dissolve in, make to volume with methanol, and mix thoroughly. Pipette a 5 ml aliquot into a second 50 ml volumetric flask and make to volume with methanol. Mix thoroughly and pipette a 5 ml aliquot into a third 50 ml volumetric flask. Make to volume and again mix thoroughly. (final conc 10 ug/ml)

Preparation of Sample:

Weigh a portion of sample equivalent to 0.1 gram of pyrazon into a 250 ml Erlenmeyer glass-stoppered flask. Add 100 ml methanol by pipette and shake on a mechanical shaker for one hour. Filter if necessary and pipette 5 ml of the clear filtrate into a 50 ml volumetric flask. Make to volume with methanol, mix thoroughly and pipette 5 ml into a second 50 ml volumetric flask. Make to volume with methanol and mix thoroughly. (final conc 10 ug pyrazon/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative analytical settings for the particular instrument being used, balance the pen for 0 and 100% transmission at 286 nm with methanol in each cell. Scan both the standard and sample from 360 nm to 220 nm with methanol in the reference cell. Measure the absorbance of both standard and sample at 286 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent pyrazon as follows:

$$\% = \frac{(\text{abs. sample})(\text{conc. std in ug/ml})(\% \text{ purity std})}{(\text{abs. std})(\text{conc. sample in ug/ml})}$$

Note: It has been established that there is a straight line relationship between absorbance and concentration.

Method submitted by Stelios Gerazounis, EPA Pesticides Chemistry Laboratory, Region II, New York, NY.

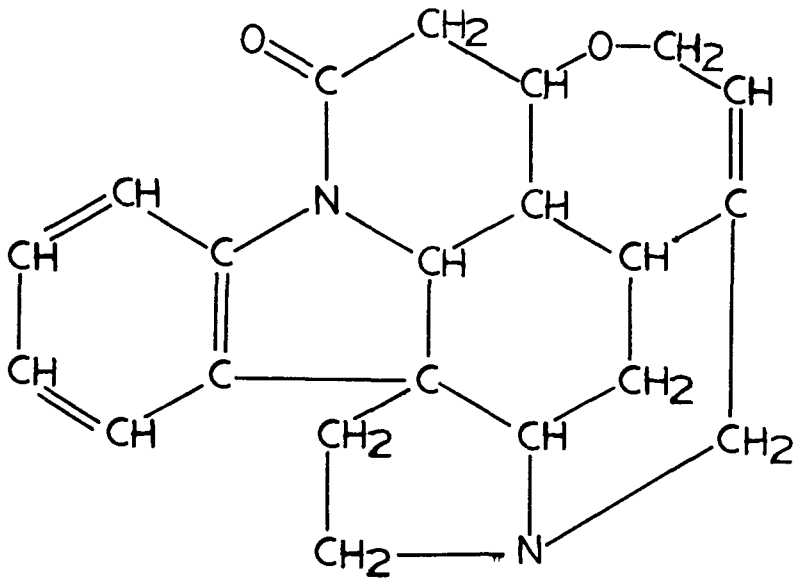
Any comments, criticism, suggestions, data, etc. concerning the use of this method will be appreciated.

March 1978

Strychnine EPA-3
(tentative)

Determination of Strychnine by High Pressure Liquid Chromatography (Reverse Phase)

Strychnine is a registered rodenticide having the chemical structure:



Molecular formula: $C_{21}H_{22}N_2O_2$

Molecular weight: 334.4

Melting point: 268 to 290°C (depending on the speed of heating) with decomposition; b.p. 270°C at 5 mm

Physical state, color, and odor: hard white crystals or powder, very bitter taste; very poisonous!

Solubility: practically insoluble in water, alcohol, ether; slightly soluble in benzene, chloroform

Stability: forms salts with acids; ppt. by alkaloid precipitants

Other names: Kwik-kil, Mouse-tox, Ro-Dec

Reagents:

1. Strychnine standard of known purity
2. Dioxane, pesticide or spectro grade
3. Methanol, pesticide or spectro grade

Equipment:

1. High pressure liquid chromatograph with UV detector at 254 nm. If a variable wavelength UV detector is available, other wavelengths may be useful to increase sensitivity or eliminate interference.
2. Column - DuPont ETH Permaphase, 1/2 m x 2.1 mm I.D.

Equipment (cont'd):

3. High pressure liquid syringe or sample injection loop
4. Sample grinder or pulverizer
5. Mechanical shaker
6. 5 micron millipore filter
7. Usual laboratory glassware

Operating Conditions:

Mobile phase:	97-98% H_2O + 3-2% MeOH (percents may be varied to obtain optimum separation)
Column temperature:	40°C
Chart speed:	12"/hr

Conditions may have to be varied by the analyst for the specific instrument being used to obtain optimum response and reproducibility.

Procedure:

Preparation of Standard:

Weigh 0.1 gram strychnine standard into a 100 ml volumetric flask and make to volume with dioxane. Place into ultrasonic bath for a few minutes to hasten solution. (conc 1 ug/ul)

Preparation of Sample:

Grind 20-25 grams of sample to a fairly fine state in a suitable sample grinder. Weigh an amount of sample equivalent to 0.1 gram strychnine into a 250 ml Erlenmeyer glass-stoppered flask or small screw-cap bottle. Add 100 ml dioxane by pipet, close tightly, and shake on a mechanical shaker for 2 hours. Allow to settle, and filter a portion through a 5 micron millipore filter. (conc 1 ug strychnine/ul)

Determination:

Using a high pressure syringe or sample injection loop, alternately inject 5 ul portions each of standard and sample solutions. Measure the peak height or peak area for each peak and calculate the average for both standard and sample. Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent strychnine as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Elmer H. Hayes, EPA Beltsville Chemistry Laboratory, Beltsville, Md.

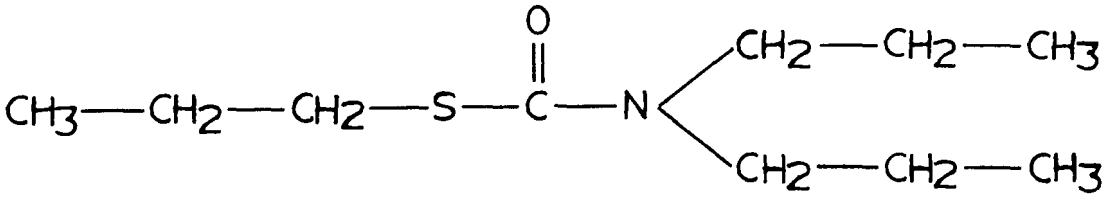
Any criticism, data, or suggestions concerning the use of this method will be appreciated.

March 1978

Vernolate EPA-4
(tentative)

Determination of Vernolate by High Pressure Liquid Chromatography (Reverse Phase)

Vernolate is the common name for S-propyl dipropylthiocarbamate, a registered herbicide having the chemical structure:



Molecular formula: $C_{10}H_{21}NOS$

Molecular weight: 203.4

Boiling point: 140°C at 20 mm Hg, 150°C at 30 mm Hg

Physical state, color, and odor: clear liquid with an aromatic odor

Solubility: about 100 ppm in water at 20-21°C; miscible with common organic solvents

Stability: stable; non-corrosive

Other names: Vernam (Stauffer); R-1607; S-propyl N,N-dipropyl thiocarbamate

Reagents:

1. Vernolate standard of known % purity
2. Dioxane, pesticide or spectro grade
3. Acetonitrile, pesticide or spectro grade

Equipment:

1. High pressure liquid chromatograph with variable ultraviolet detector. Greatest sensitivity is obtained at 230 nm; however, 254 nm can be used with a more concentrated sample.
2. Liquid chromatographic column, one meter x 2.0 mm I.D. Permaphase ODS or equivalent silica column
3. High pressure liquid syringe or sample injection loop
4. Usual laboratory glassware

Operating Conditions for Perkin-Elmer HPLC:

Mobile phase:	75% water + 25% acetonitrile
Column temperature:	Ambient
Column pressure:	1800 psi (observed)
Flow rate:	0.75 ml/min
Detector:	Variable at 230 nm for greater sensitivity; fixed 254 nm can be used if sample is concentrated
Chart speed:	Adjusted
Injection:	5 ul

Procedure:

Preparation of Standard:

Weigh 0.1 gram vernolate standard into a 50 ml volumetric flask, make to volume with dioxane, and mix thoroughly. (conc 2 ug/ul)

Preparation of Sample:

Weigh an amount of sample equivalent to 0.1 gram vernolate into a 50 ml volumetric flask. For emulsifiable concentrates make to volume with dioxane; for dusts or granules add 50 ml of dioxane by pipette. Shake thoroughly to dissolve or extract the vernolate. (conc 2 ug vernolate/ul)

Determination:

Using a high pressure liquid syringe or 10 ul injection loop, alternately inject three 10 ul portions each of the standard and sample solutions. Measure the peak height or area for each peak and calculate the average for both standard and sample.

Adjustments in attenuation or amount injected may have to be made to give convenient size peaks.

Calculation:

From the average peak height or peak area calculate the percent vernolate as follows:

$$\% = \frac{(\text{pk. ht. or area sample})(\text{wt. std injected})(\% \text{ purity of std})}{(\text{pk. ht. or area standard})(\text{wt. sample injected})}$$

Method submitted by Elmer H. Hayes, EPA Beltsville Chemistry Laboratory, Beltsville, Md.

Any criticism, data, or suggestions concerning the use of this method will be appreciated.

Detection of Organothiophosphates by Thin Layer Chromatography

Organothiophosphates in pesticide formulations can be identified by spotting (directly for liquids or an ether-hexane extract for dusts and granules) on precoated plastic sheets and developing in benzene. The separated spots are color-developed by spraying with 2,6-dibromo-N-chloro-p-benzoquinoneimine in cyclohexane and exposing to hydrochloric acid fumes giving a red to orange-brown color which is characteristic of the particular organothiophosphate present.

Reagents:

1. Benzene, pesticide grade
2. 1:1 diethyl ether-hexane mixture, pesticide grade
3. 2,6-dibromo-N-chloro-p-benzoquinoneimine, 0.5% solution in cyclohexane. This reagent and its solutions should be kept refrigerated.
   Note! The above chemical is a suspected carcinogen and should be handled accordingly.
4. Concentrated hydrochloric acid

Equipment:

1. Precoated plastic sheets for TLC, MN Polygram Sil G (0.25 mm silica gel without gypsum), available from Brinkman Instruments Inc.
2. Spotting template
3. Spotting pipettes, 1 to 10 ul, or 10 ul GC syringe
4. Two airtight developing tanks: one for benzene and one for hydrochloric acid
5. Sprayer

Safety note: When toxic or highly corrosive reagents are sprayed on chromatograms, it is necessary to use gloves, face shield, respiratory mask, and appropriate fume hood to protect skin, eyes, and respiratory tract against mists or fumes generated by the spraying device.

Procedure:

Preparation of Sample:

For dusts or granules, shake approximately 2 grams with 10 ml of 1:1 ether-hexane mixture in a 25 ml screw-cap test tube for 10 minutes. Allow to settle, centrifuge if necessary.

For liquids, use sample directly.

Spotting:

With a spotting template for a guide, mark the TLC sheet for sample and standard spots and mark a line at 10 cm using a soft lead pencil.

Spot 10 ul of sample extract or 2 ul of undiluted liquid samples. Appropriate standards should be spotted (1 to 5 ug) among the samples.

Chromatogram and Color Development:

Develop the TLC sheet in benzene in a closed airtight developing tank until the benzene reaches the 10 cm line. Evaporate all the benzene from the plate in a hood. Spray with 0.5% 2,6-dibromo-N-chloro-p-benzoquinoneimine in cyclohexane and allow to evaporate.

Place sheet in a developing tank containing concentrated hydrochloric acid fumes, close tightly and leave for about one minute.

Organothiophosphates will start appearing in 10 to 15 seconds as red to orange-brown spots, the colors being characteristic of the particular organothiophosphates present. Any spots that appear before exposing the sheet to the acid fumes should be disregarded.

Detection Limit and Rf Values:

The lower limit of detection of most organothiophosphates is about 0.25 ug. This allows the detection of a contamination of approximately 0.01%.

The Rf values of some organothiophosphates using benzene are as follows:

dimethoate (Cygon)	.00
demeton methyl (Metasystox)	.00
demeton (Systox)	.00 and .55
azinphos-methyl (Guthion) methyl	.07
azinphos-ethyl (Guthion) ethyl	.07
diazinon	.15
phosmet (Imidan)	streak to .15
malathion	.20
coumaphos (Co-Ral)	.30
fenthion	.48
methyl parathion	.50
ethion	.53
sulfotepp	.55
oxydisulfoton (Disyston-S)	.57
parathion	.57
dicapthon	.57
EPN	.58
disulfoton (Disyston)	.60
sulfallate (Vegadex)	.60
phorate (Thimet)	.66
(Aspon)	.66
ronnel	.70
carbophenothion (Trithion)	.74
chlorpyrifos (Dursban)	.75
(DEF)	.80

Names in ( ) are trade names.

Method prepared and submitted by Danny D. McDaniel and Robert Robertson, EPA Pesticide Products Analysis Lab, National Space Technology Laboratories, Bay St. Louis, MS 39529.

This is the method used in the above laboratories for TLC identification of organothiophosphates.

It is based on the following references:

Menn, J. J., Erwin, W. R. and Gordon, H. T., J. Agric. Food Chem., 5, 601 (1957)

Braithwaite, D. P., Nature, 200, 1011 (1963)

Getz, Melvin E., J.A.O.A.C., Vol. 45, No. 2, 393-396 (1962)

Bontoyan, Warren, J.A.O.A.C., Vol. 49, No. 6, 1169-1174 (1966)

Preface

Enclosed is the third update to the EPA Manual of Chemical Methods for Pesticides and Devices. This update includes 55 new methods. Also included is a list of these 55 methods and a Pesticide Name Cross Reference Index to the 55 Methods.

Continuing with the aim of providing suitable methods that can be used to support enforcement actions, we will appreciate receiving new methods for inclusion in future updates or revisions of this manual. However, in order to limit the ever-expanding size of this manual, we also would appreciate your telling us which specific methods you think should be studied collaboratively for inclusion in the AOAC Official Methods of Analysis.

For the next update, any suggestions for additional methods, graphs, charts, data, or information (general or specific) will be appreciated now or at any future time. Any and all ideas to make this manual more useful are welcome.

Such comments may be made to the Editors.

Editors: Warren R. Bontoyan
Jack B. Looker

Chemical and Biological
Investigations Branch
Environmental Protection Agency
Building 402, ARC-East
Beltsville, MD 20705

Third Update

Pesticide Name Cross Reference Index to the Methods
(55 methods - August)

3336----------Thiophanate EPA-1

AAtrex----------Atrazine EPA-3 & EPA-4
AC 92553----------Pendimethalin EPA-1
Acaron----------Chlordimeform EPA-1
Accotab----------Pendimethalin EPA-1
3-(alpha-acetonylbenzyl)-4-
hydroxycoumarin----------Warfarin EPA-4
ACP 322----------Naptalam EPA-1
Alanap----------Naptalam EPA-1
Altosid----------Methoprene EPA-1
Altosid Briquets----------Methoprene EPA-1
Antene----------Ziram EPA-1
Antimicrobial----------Pentachlorophenol EPA-1 & EPA-2
Antu EPA-1----------UV
Apprex----------Tetrachlorovinphos EPA-1
Aquacide----------Diquat EPA-1
Atranex----------Atrazine EPA-3 & EPA-4
Atratol----------Atrazine EPA-3 & EPA-4
Atrazine EPA-3----------HPLC
Atrazine EPA-4----------HPLC (IS)
atrazine (with metolachlor)----------Mixed pesticides EPA-2

barbasco----------Rotenone EPA-2
Bay 276----------Disulfoton EPA-2
Bay 19639----------Disulfoton EPA-2
Bay 25141----------fensulfothion
Bayer 15922----------Trichlorfon EPA-3 & EPA-4
Bendiocarb EPA-3----------HPLC (IS)
1,2-benzenedicarboxylic acid
dimethyl ester----------Dimethyl phthalate EPA-1
Bermat----------Chlordimeform EPA-1
Bicep----------metolachlor

Bidrin----------Dicrotophos EPA-1

1,2-bis(3-ethoxycarbonyl-2-thioureido) benzene----------Thiophanate EPA-1

Black Leaf 40----------Nicotine EPA-1

Bovinox----------Trichlorfon EPA-3 & EPA-4

Briten----------Trichlorfon EPA-3 & EPA-4

3-tert-butyl-5-chloro-methyluracil----------Terbacil EPA-1

1-n-butyl-3-(3,4-dichlorophenyl)-1-methylurea----------Neburon EPA-2

1-(5-tert-butyl-1,3,4-thiadiazol-2-yl)-1,3-dimethylurea----------Tebuthiuron EPA-1

C 709----------Dicrotophos EPA-1

C 8514----------Chlordimeform EPA-1

Caid----------Chlorophacinone EPA-2 & EPA-3

Calmathion----------Malathion EPA-3

Captan EPA-3----------GC-FID-IS

Captan EPA-4----------HPLC (IS)

captane (France)----------Captan EPA-3 & EPA-4

Carbamine----------Carbaryl EPA-3

Carbaryl EPA-3----------HPLC (IS)

Carbazinc----------Ziram EPA-1

Carbicron----------Dicrotophos EPA-1

carbofos (USSR)----------Malathion EPA-3

Cekubaryl----------Carbaryl EPA-3

Cekufon----------Trichlorfon EPA-3 & EPA-4

Cekumethion----------Methyl parathion EPA-6

Celmone----------Naphthaleneacetic acid EPA-1

Celthion----------Malathion EPA-3

Cercobin----------Thiophanate EPA-1

Cerobin-M----------Thiophanate-methyl EPA-1

CF 125----------Chloroflurecol-methyl ester EPA-1

CGA 24705----------metolachlor

Chem Fish----------Rotenone EPA-2

ChemStorr----------Propionic acid EPA-1

Chlorfenamidine (former name)----------Chlordimeform EPA-1

chlorinated dibenzo-p-dioxins----------Dioxins EPA-1

Chlordimeform EPA-1----------GC-FID-IS

2-chloro-4-ethylamono-6-
isopropylamino-1,3,5-triazine----------Atrazine EPA-3 & EPA-4

6-chloro-N-ethyl-N'-(1-methylethyl)-
1,3,5-triazine-2,4-diamine----------Atrazine EPA-3 & EPA-4

chloroflurenol-methyl ester----------Chloroflurecol-methyl ester EPA-1

Chloroflurecol-methyl ester EPA-1----------UV

chlorofos----------Trichlorfon EPA-3 & EPA-4

chloromethlyoxirane----------Epichlorohydrin EPA-1

Chloroneb EPA-1----------UV

Chlorophacinone EPA-2----------HPLC

Chlorophacinone EPA-3----------UV

2 [(p-chlorophenyl)phenylacetyl]-
1,3-indandione----------Chlorophacinone EPA-2 & EPA-3

chloropropylene oxide----------Epichlorohydrin EPA-1

N'-(4-chloro-o-tolyl)-N,N-
dimethyl formamidine----------Chlordimeform EPA-1

2-chloro-1-(2,4,5-trichlorophenyl)
vinyl dimethyl phosphate, cis isomer-----Tetrachlorovinphos EPA-1

2-chloro-1-(2,4,5-trichlorophenyl
vinyl dimethyl phosphate, Z isomer-------Tetrachlorovinphos EPA-1

Ciclosom----------Trichlorfon EPA-3 & EPA-4

Cobex----------Dinitramine EPA-1

Cobexo----------Dinitramine EPA-1

Codal----------metolachlor

Co-Rax----------Warfarin EPA-4

Corozate----------Ziram EPA-1

Cotoran Multi----------metolachlor

coumafene (France)----------Warfarin EPA-4

Cov-R-Tox----------Warfarin EPA-4

Crinex----------Trichlorfon EPA-3 & EPA-4

Crisatrina----------Atrazine EPA-3 & EPA-4

Crisazine----------Atrazine EPA-3 & EPA-4

Crisquat----------Paraquat EPA-1

cube'----------Rotenone EPA-2

Cuman----------Ziram EPA-1

Curbiset----------Chloroflurecol-methyl ester EPA-1

CVMP----------Tetrachlorvinphos EPA-1

Cynoff----------Pendimethalin EPA-1

Cythion----------Malathion EPA-3

Danex----------Trichlorfon EPA-3 & EPA-4

Dasanit----------fensulfothion

deiquat (Germany)----------Diquat EPA-1

Demosan----------Chloroneb EPA-1

Denapon----------Carbaryl EPA-3

derris----------Rotenone EPA-2

Detmol MA 96% (Albert & Co. Germany)--------Malathion EPA-3

Devicarb----------Carbaryl EPA-3

Devithion----------Methyl parathion EPA-6

Dextrone----------Diquat EPA-1

Dextrone X----------Paraquat EPA-1

Dexuron----------Paraquat EPA-1

dibenzo-p-dioxin----------Dioxins EPA-1

Dicarbam----------Carbaryl EPA-3

1,4-dichloro-3,5-dimethoxybenzene----------Chloroneb EPA-1

2-(3,4-dichlorophenyl)-4-methyl-1,2,4-
oxadiazolidine-3,5-dione----------Methazole EPA-1

Dicrotophos EPA-1----------IR

S-[1,2-di(ethoxycarbonyl)-ethyl]
dimethyl phosphorothiolothionate---------Malathion EPA-3

O,O-diethyl S- 2-(ethylthio)ethyl
phosphorodithioate----------Disulfoton EPA-3

O,O-diethyl) [4-(methylsulfinyl)phenyl]
phosphorodithioate----------fensulfothion

diethyl-p-methylsulfinylphenyl
thiophosphate----------fensulfothion

diethyl [1,2-phenylene bis (imino-
carbonothioyl)] bis [carbamate]----------Thiophanate EPA-1

diethyl 4,4-o-phenylenebis[3-
thioallophanate]----------Thiophanate EPA-1

N^4,N^4-diethyl-alpha,alpha, alpha-
trifluoro-3,5-dinitrotoluene-
2,4-diamine----------Dinitramine EPA-1

S-(2,3-dihydro-5-methoxy-2-oxo-1,3,4-
thiadiazol-3-ylmethyl) dimethyl
phosphorothiolothionate----------Methidathion EPA-2

6,7-dihydropyrido [1,2-a:2',1'-c]
pyrazinedinium ion----------Diquat EPA-1

3-(dimethoxyphosphinyloxy)-N,N-
dimethyl- cis-crotonamide----------Dicrotophos EPA-1

dimethyl 1,2-benzenedicarboxylate----------Dimethyl phthalate EPA-1

2,2-dimethyl-1,3-benzodioxol-4-yl
N-methylcarbamate----------Bendiocarb EPA-3

1,1'-dimethyl-4,4'-bipyridylium ion---------Paraquat EPA-1

0,0,-dimethyl S-(1,3-dicarbethoxyethyl)
phosphorodithioate----------Malathion EPA-3

N,N-dimethyl-2,2-diphenylacetamide----------Diphenamid EPA-1 & EPA-2

0,0-dimethyl dithiophosphate of
diethyl mercaptosuccinate----------Malathion EPA-3

N-[5-(1,1-dimethylethyl)-1,3,4-
thiadiazol-2-yl]-N,N-dimethylurea--------Tebuthirun EPA-1

N,N-dimethyl-N'_(2-methyl-4-chlorophenyl)-
formamidine----------Chlordimeform EPA-1

0,0-dimethyl-0-p-nitrophenyl
phosphorothioate----------Methyl parathion EPA-6

Dimethyl parathion----------Methyl parathion EPA-6

dimethyl [(1,2-phenylene) bis-
iminocarbonylthioyl)] bis
[carbamate]----------Thiophanate-methyl EPA-1

0,0-dimethyl phosphorodithioate
S-ester with 4-(mercaptomethyl)-2-
methoxy-delta 2-1,3,4-
thiadiazolin-5-one----------Methidathion EPA-2

Dimethyl phthalate EPA-1----------GC-FID-IS

dimethyl (2,2,2-trichloro-1-
hydroxyethyl) phosphonate----------Trichlorfon EPA-3 & EPA-4

Dinitramine EPA-1----------GC-FID-IS
Dioxins EPA-1----------GC/MS
Diphacin----------Diphacinone EPA-3
diphacin (Turkey)----------Diphacinone EPA-3
Diphacine Meal Bait----------Diphacinone EPA-3
Diphacinone EPA-3----------HPLC
Diphenamid EPA-1----------IR
Diphenamid EPA-2----------GC-FID-IS
2-(diphenylacetyl)-1,3-indanedione----------Diphacinone EPA-3
Dipterex----------Trichlorfon EPA-3 & EPA-4
Diquat EPA-1----------HPLC (IS)
disulfoton----------Mixed Pesticides EPA-3
Disulfoton----------GC-FID-IS
Disyston (with fensulfothion)----------Disulfoton EPA-3
Di-Syston (in U.S.)----------Disulfoton EPA-3
dithiodemeton----------Disulfoton EPA-3
dithiosustox----------Disulfoton EPA-3
DMP----------Dimethyl phthalate EPA-1
Dowicide----------Pentachlorophenol EPA-1 & EPA-2
Dowicide EC-7----------Pentachlorophenol EPA-1 & EPA-2
Dowicide G----------Pentachlorophenol EPA-1 & EPA-2
Dowlap----------Lamprecid (Trade Name) EPA-1
Dow Pentachlorophenol DP-2----------Pentachlorophenol EPA-1 & EPA-2
Drat----------Chlorophacinone EPA-2 & EPA-3
Drexel Methyl Parathion 4E----------Methyl parathion EPA-6
Drupina 90----------Ziram EPA-1
DuPont Herbicide 732----------Terbacil EPA-1
Dust M----------Tetrachlorvinphos EPA-1
Dyanap----------Naptalam EPA-1
Dyfonate----------Fonofos EPA-1
Dylox----------Trichlorfon EPA-3 & EPA-4
Dymid----------Diphenamid EPA-1 & EPA-2

E 601----------Methyl parathion EPA-6

Ektafos----------Dicrotophos EPA-1

EL 103----------Tebuthiuron EPA-1

Emmatos----------Malathion EPA-3

Emmatos Extra----------Malathion EPA-3

Enide----------Diphenamid EPA-1 & EPA-2

Epichlorohydrin EPA-1----------GC-FID

Equino-Aid----------Trichlorfon EPA-3 & EPA-4

Esgram----------Paraquat EPA-1

1,1'-ethylene-2,2'-bipyridylium ion---------Diquat EPA-1

O-ethyl S-phenyl ethlyphosphonodithioate----Fonofos EPA-1

N-(1-ethylpropyl)-3,4-dimethyl-2,6-
dinitrobenzeneamine----------Pendimethalin EPA-1

N-(1-ethylpropyl)-2,6-dinitro-3,4-
xylidine----------Pendimethalin EPA-1

fensulfothion (with disulfoton)----------Mixed pesticides EPA-3

Ficam----------Bendiocarb EPA-3

Folidol M----------Methyl parathion EPA-6

Folosan----------Tecnazene EPA-1

Fonofos EPA-1----------IR

ForMal----------Malathion EPA-3

Fosferno M 50 ----------Methyl parathion EPA-6

Fruitone N----------Naphthaleneacetic acid EPA-1

Frumin AL----------Disulfoton EPA-3

Fuclasin Ultra----------Ziram EPA-1

Fuklasin----------Ziram EPA-1

Fundal----------Chlordimeform EPA-1

Fundex----------Chlordimeform EPA-1

Fungitox----------Thiophanate-methyl EPA-1

Fungostop----------Ziram EPA-1

Fusarex----------Tecnazene EPA-1

Fyfanon----------Malathion EPA-3

G 30027----------Atrazine EPA-3 & EPA-4
Galecron----------Chlordimeform EPA-1
Gardcide----------Tetrachlorvinphos EPA-1
Gardona----------Tetrachlorvinphos EPA-1
Garvox----------Bendiocarb EPA-3
Gearphos----------Methyl parathion EPA-6
Gesaprim----------Atrazine EPA-3 & EPA-4
Go-Go-San----------Pendimethalin EPA-1
Grain Treat----------Propionic acid EPA-1
Gramonol----------Paraquat EPA-1
Gramoxone----------Paraquat EPA-1
Gramuron----------Paraquat EPA-1
Granurex----------Neburon EPA-2
Graslan----------Tebuthiuron EPA-1
Griffex----------Atrazine EPA-3 & EPA-4
GS 13005----------Methidathion EPA-2

haiari----------Rotenone EPA-2
Herbadox----------Pendimethalin EPA-1
Herboxone----------Paraquat EPA-1
Hexachlorophene EPA-1----------HPLC
Hexavin----------Carbaryl EPA-3
Hexazir----------Ziram EPA-1
Hexide----------Hexachlorophene EPA-1
Hilthion----------Malathion EPA-3

Isobac (sodium salt)----------Hexachlorophene EPA-1
2,3-isopropylidenedioxyphenyl
methylcarbamate----------Bendiocarb EPA-3
isopropyl (2E, 4E)-11-methoxy-3,7,11-
trimethyl-2,4-dodecodienoate----------Methoprene EPA-1
IT 3456----------Chloroflurecol-methyl ester EPA-1

Karbaspray----------Carbaryl EPA-3
Karbofos----------Malathion EPA-3
Kloben----------Neburon EPA-2
Kop-Thion----------Malathion EPA-3
krysid (Russia)----------Antu EPA-1
Kwik-kil----------Strychnine EPA-4
Kypfarin----------Warfarin EPA-4
Kypfos----------Malathion EPA-3

L 34314----------Diphenamid EPA-1 & EPA-2
Labilite----------Thiophanate-methyl EPA-1
Lamprecid (Trade Name) EPA-1----------UV
Leivasom----------Trichlorfon EPA-3 & EPA-4
Liphadione----------Chlorophacinone EPA-2 & EPA-3
LM 91----------Chlorophacinone EPA-2 & EPA-3

M 74 (USSR)----------Disulfoton EPA-3
Maintain A----------Chloroflurecol-methyl ester EPA-1
Maintain CF 125----------Chloroflurecol-methyl ester EPA-1
Maintain S----------Chloroflurecol-methyl ester EPA-1
Malamar----------Malathion EPA-3
Malaphele----------Malathion EPA-3
Malaspray----------Malathion EPA-3
Malathion EPA-3----------HPLC (IS)
Malathion ULV Concentrate----------Malathion EPA-3
Malatol----------Malathion EPA-3
maldison (Australia)----------Malathion EPA-3
Malmed----------Malathion EPA-3
Maltox----------Malathion EPA-3
mercaptothion (So. Africa)----------Malathion EPA-3
mercaptothion (Argentina)----------Malathion EPA-3
Merpan----------Captan EPA-3 & EPA-4
Metacide----------Methyl parathion EPA-6

Methazole EPA-1----------IR

Methidathion EPA-2----------GC-FID-IS

Methoprene EPA-1----------GC-FID-IS

S-[(5-methoxy-2-oxo-1,3,4-thiadiazol-3(2H)-yl)methyl]O,O-dimethyl phosphorodithioate----------Methidathion EPA-2

Methyl-2-chloro-9-hydroxyfluorene-9-carboxylate----------Chloroflurecol-methyl ester EPA-1

N-(2-methyl-4-chlorophenyl)-N',N'-dimethyl formamidine----------Chlordimeform EPA-1

2,2-methylenebis (3,4,6-trichlorophenol)----------Hexachlorophene EPA-1

Methyl nonyl ketone EPA-1----------GC-FID-IS

Methyl parathion EPA-6----------HPLC

3-(1-methyl-2-pyrrolidyl)pyridine----------Nicotine EPA-1

metolachlor (with atrazine)----------Mixed pesticides EPA-2

metrifonate----------Trichlorfon EPA-3 & EPA-4

Metron----------Methyl parathion EPA-6

Mezene----------Ziram EPA-1

MGK Dog and Cat Repellent----------Methyl nonyl ketone EPA-1

Microzul----------Chlorophacinone EPA-2 & EPA-3

Mildothane----------Thiophanate-methyl EPA-1

Milocep----------metolachlor

Mixed pesticides EPA-2 (Atrazine & Metolachlor)----------GC-FID-IS

Mixed pesticides EPA-3 (Disulfoton & Fensulfothion)----------GC-FID-IS

MLT----------Malathion EPA-3

Mouse-tox----------Strychnine EPA-4

Multimet----------Bendiocarb EPA-3

Multiprop----------Chloroflurecol-methyl ester EPA-1

N 2790----------Fonofos EPA-1

NAA----------Naphthaleneacetic acid EPA-1

NAA 800----------Naphthaleneacetic acid EPA-1

Nabac----------Hexachlorophene EPA-1

Nac----------Carbaryl EPA-1

Nafusaku----------Naphthaleneacetic acid EPA-1

1-naphthaleneacetic acid----------Naphthaleneacetic acid EPA-1

N-1-naphthylphthalamic acid----------Naptalam EPA-1

Naphthaleneacetic acid EPA-1----------HPLC

1-naphthly-N-methylcarbamate----------Carbaryl EPA-3

alpha-naphthylthiourea----------Antu EPA-1

Naptalam EPA-1----------UV

NC 6897----------Bendiocarb EPA-3

Neburex----------Neburon EPA-2

Neburon EPA-2----------UV

Neguvon----------Trichlorfon EPA-3 & EPA-4

neko----------Rotenone EPA-2

NF 35----------Thiophanate EPA-1

Nicocyan----------Pendimethalin EPA-1

Nicotine EPA-1----------HPLC (IS)

nicouline----------Rotenone EPA-2

4-nitro-3-(trifluoromethyl)phenyl----------Lamprecid (Trade Name) EPA-1

Nitrox 80----------Methyl parathion EPA-6

NPA----------Naptalam EPA-1

Ontrack 8E----------metolachlor

Orthocide----------Captan EPA-3 & EPA-4

oxydiazol----------Methazole EPA-1

Para-Col----------Paraquat EPA-1

Paraquat EPA-1----------HPLC (IS)

Parataf----------Methyl parathion EPA-6

Paratox----------Methyl parathion EPA-6

Partron M----------Methyl parathion EPA-6

Pathclear----------Paraquat EPA-1

Pay-Off----------Pendimethalin EPA-1

P.C.Q.----------Diphacinone EPA-3

penchoral----------Pentachlorophenol EPA-1 & EPA-2

Pendimethalin EPA-1----------GC-FID-IS

Penncap-M----------Methyl parathion EPA-6

penoxalin----------Pendimethalin EPA-1

penoxyn----------Pendimethalin EPA-1

Pentachlorophenol EPA-1----------GC-FID-IS

Pentachlorophenol EPA-2----------HPLC (IS)

Pentacon----------Pentachlorophenol EPA-1 & EPA-2

Penwar----------Pentachlorophenol EPA-1 & EPA-2

Phyomone----------Naphthaleneacetic acid EPA-1

Pillarquat----------Paraquat EPA-1

Pilarxone----------Paraquat EPA-1

Planofix----------Naphthaleneacetic acid EPA-1

Plucker----------Naphthaleneacetic acid EPA-1

polychlorinated dibenzo-p-dioxin----------Dioxins EPA-1

polychlorinated dioxins----------Dioxins EPA-1

Pomarsol Z Forte----------Ziram EPA-1

Prentox----------Rotenone EPA-2

Priltox----------Pentachlorophenol EPA-1 & EPA-2

Primacol----------Naphthaleneacetic acid EPA-1

Primagram----------metolachlor

Primatex----------metolachlor

Primatol A----------Atrazine EPA-3 & EPA-4

Probe----------Methazole EPA-1

Prodaram----------Ziram EPA-1

Promar----------Diphacinone EPA-1

propanoic acid----------Propionic acid EPA-1

Propionic acid EPA-1----------GC-FID

Propionic Acid Grain Preserver----------Propionic acid EPA-1

Prowl----------Pendimethalin EPA-1

Proxol----------Trichlorfon EPA-3 & EPA-4

6Q8----------Naptalam EPA-1

Rabon----------Tetrachlorvinphos EPA-1

Rabone----------Tetrachlorvinphos EPA-1

Ramik----------Diphacinone EPA-3

Ramucide----------Chlorophacinone EPA-2 & EPA-3

Ratomet----------Chlorophacinone EPA-2 & EPA-3
Ratox----------Warfarin EPA-4
Raviac----------Chlorophacinone EPA-2 & EPA-3
Ravyon----------Carbaryl EPA-3
RAX----------Warfarin EPA-4
RDL----------Tetrachlorovinphos EPA-1
Reglox----------Diquat EPA-1
reglon (USSR)----------Diquat EPA-1
Reglone----------Diquat EPA-1
Ro-Dec----------Strychnine EPA-4
Rodent Cake----------Diphacinone EPA-3
Rodex----------Warfarin EPA-4
Rodex Blox----------Warfarin EPA-4
Rootone----------Naphthaleneacetic acid EPA-1
Rotenone EPA-2----------HPLC
Rozol----------Chlorophacinone EPA-2 & EPA-3

S 767----------fensulfothion
Santobrite----------Pentachlorophenol EPA-1 & EPA-2
Santophen----------Pentachlorophenol EPA-1 & EPA-2
SD 3562----------Dicrotophos EPA-1
SD 8447----------Tetrachlorvinphos EPA-1
Sentry Grain Preserver----------Propionic acid EPA-1
Septene----------Carbaryl EPA-3
Sevin----------Carbaryl EPA-3
sevin (USA, USSR)----------Carbaryl EPA-3
Shell Atrazine Herbicide----------Atrazine EPA-3 & EPA-4
Sigma----------Thiophanate-methyl EPA-1
Sinbar----------Terbacil EPA-1
Sinituho----------Pentachlorophenol EPA-1 & EPA-2
SN 36268----------Chlordimeform EPA-1
Solvirex----------Disulfoton EPA-2
Spanone----------Chlordimeform EPA-1

Spike----------Tebuthiuron EPA-1

Stik----------Naphthaleneacetic acid EPA-1

Stirofos----------Tetrachlorvinphos EPA-1

Strychnine EPA-4----------HPLC (IS)

Strychnos nux-vomica----------Strychnine EPA-4

Sumitox----------Malathion EPA-3

Supracide----------Methidathion EPA-2

Sweep----------Paraquat EPA-1

TCNB----------Tecnazene EPA-1

Tebuthiuron EPA-1----------UV

Tecnazene EPA-1----------GC-FID-IS

Tekkam----------Naphthaleneacetic acid EPA-1

Tekwaisa----------Methyl parathion EPA-6

Terbacil EPA-1----------UV

Tercyl----------Carbaryl EPA-3

Terracur P----------Fensulfothion

Terraklene----------Paraquat EPA-1

Tersan SP----------Chloroneb EPA-1

1,2,4,5-tetrachloro-3-nitrobenzene----------Tecnazene EPA-1

2,3,5,6-tetrachloronitrobenzene----------Tecnazene EPA-1

Tetrachlorvinphos EPA-1----------GC-FID-IS

TFM----------Lamprecid (Trade Name) EPA-1

Thiophanate EPA-1----------UV

thiophanate-ethyl----------Thiophanate EPA-1

Thiophanate-methyl EPA-1----------UV

TipOff----------Naphthaleneacetic acid EPA-1

Topitox----------Chlorophacinone EPA-2 & EPA-3

Topsin----------Thiophanate EPA-1

Topsin E----------Thiophanate EPA-1

Topsin M----------Thiophanate-methyl EPA-1

TotaCol----------Paraquat EPA-1

Toxer Total----------Paraquat EPA-1

Tox-Hid----------Warfarin EPA-4

Transplantone----------Naphthaleneacetic acid EPA-1

Tre-Hold----------Naphthaleneacetic acid EPA-1
Tricarnam----------Carbaryl EPA-3
Tricarbamix Z----------Ziram EPA-1
Trichlorfon EPA-3----------GC-FID-IS
Trichlorfon EPA-4----------HPLC (IS)
trichlorphon----------Trichlorfon EPA-3 & EPA-4
cis-N-trichloromethylthio-4-
cyclohexane-1,2-dicarboximide----------Captan EPA-3 & EPA-4
alpha, alpha, alpha-trifluoro-4-
nitro-meta-cresol----------Lamprecid (Trade Name) EPA-1
3-trifluoro-4-nitrophenol----------Lamprecid (Trade Name) EPA-1
Trinex----------Trichlorfon EPA-3 & EPA-4
Triscabol----------Ziram EPA-1
tubatoxin----------Rotenone EPA-2
Tugon----------Trichlorfon EPA-3 & EPA-4

UC 7744----------Carbaryl EPA-3
Ultracide----------Methidathion EPA-2
2-undecanone----------Methyl nonyl ketone EPA-1
USB 3584----------Dinitramine EPA-1

Vancide MZ-96----------Ziram EPA-1
VCS 438----------Methazole EPA-1
Vectal SC----------Atrazine EPA-3 & EPA-4
Vegfru----------Malathion EPA-3
Vertac Methyl Parathion Technisch 80%----------Methyl parathion EPA-6
Voncaptan----------Captan EPA-3 & EPA-4

Warfarin EPA-4----------HPLC
Warfarin Plus----------Warfarin EPA-4
Warfarin Q----------Warfarin EPA-4
Weedol----------Paraquat EPA-1
Weedone----------Pentachlorophenol EPA-1 & EPA-2
Weedtrine D----------Diquat EPA-1
Wofatox----------Methyl parathion EPA-6

Z-C Spray----------Ziram EPA-1

Zerlate----------Ziram EPA-1

zinc dimethyldithiocarbamate----------Ziram EPA-1

Zincmate----------Ziram EPA-1

Ziram EPA-1----------UV

Ziramvis----------Ziram EPA-1

Zirasan 90----------Ziram EPA-1

Zirberk----------Ziram EPA-1

Zirex 90----------Ziram EPA-1

Ziride----------Ziram EPA-1

Zithol----------Ziram EPA-1

Zitox----------Ziram EPA-1

zoocoumarin (Netherlands & USSR)----------Warfarin EPA-4

ZR 515----------Methoprene EPA-1

Analytical Methods - Introduction

Many of the methods in this manual have been developed and are used by chemists in state and federal regulatory laboratories. Some are "old-time methods" that have been used over the years, and some are "new methods" recently developed to utilize new instrumentation or to analyze for new compounds in new formulations.

These methods have been written in a relatively standard format for several reasons:

(1) to allow the neophyte pesticide chemist to more easily understand and perform the various analyses

(2) to provide a standardized form so that the validity and application of the method can be more easily evaluated by the experienced pesticide chemist

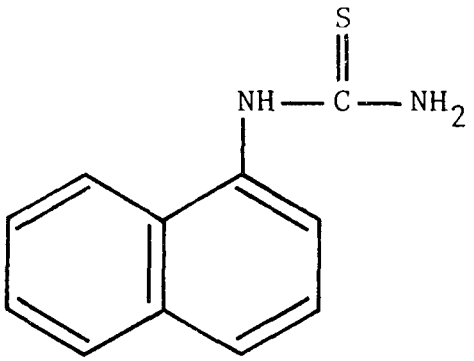
(3) to allow changes in one or more sections without entirely rewriting the entire method

The editorial committee welcomes the submission of new methods and especially the correction of errors, criticism, suggestions with supporting data, new ideas, and general comments on the published methods.

Note: Throughout these methods, the term "teflon" has been used to denote Teflon, the registered trademark of E. I. du Pont de Nemours & Co. for chemically resistant fluorocarbon resin.

Determination of Antu by Ultraviolet Spectroscopy

Antu is the accepted (BSI, ISO) common name for alpha-naphthylthiourea, a registered rodenticide having the chemical structure:



Molecular formula: $C_{11}H_{10}N_2S$

Molecular weight: 202.3

Physical state-color-odor: pure - white crystals
technical - blue-gray powder

Melting point: 198°C

Solubility: 0.06 gram per 100 ml in water at room temperature; 8.6 grams per 100 ml in triethylene glycol; 2.43 grams per 100 ml in acetone

Stability: stable on exposure to air or sun

Other names: krysid (Russia)

Reagents:

1. Antu standard of known purity
2. Methanol, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of standard:

Weigh 80 mg antu standard into a 100 ml volumetric flask, dissolve in and make to volume with methanol; mix thoroughly. Pipette 5 ml into a second 100 ml volumetric flask and make to volume with methanol. Mix thoroughly and pipette 5 ml into a third 100 ml volumetric flask and make to volume with methanol; mix thoroughly. (final conc 2 ug/ml)

Preparation of sample:

Weigh a portion of sample equivalent to 80 mg antu into a 250 ml glass-stoppered flask or screw-cap bottle. Add 100 ml methanol by pipette, stopper tightly and shake on a mechanical shaker for thirty minutes. Allow to settle, centrifuge or filter if necessary, taking precautions to avoid evaporation of the solvent. Pipette 5 ml into a 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette 5 ml into another 100 ml volumetric flask, make to volume with methanol, and mix thoroughly.
(final conc 5 ug antu/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen at 0 and 100% transmission with methanol in each cell. Scan both standard and sample solutions from 360 to 200 nm with methanol in the reference cell. Measure the absorbance of standard and sample solutions using the maxima at 220 nm and a baseline at 360 nm. If interference by the inert ingredients is suspected at 220 nm, make measurements at 281 nm. The concentration should be increased to 10 ug/ml for measurement at 281 nm.

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent antu as follows:

$$\% = \frac{\text{(abs. sample) (conc. std. in ug/ml) (\% purity)}}{\text{(abs. std.) (conc. sample in ug/ml)}}$$

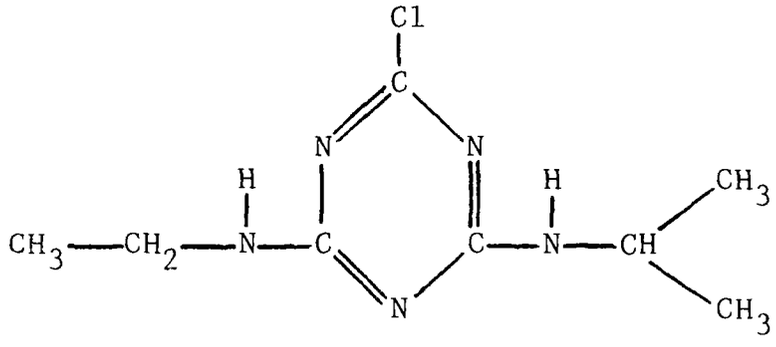
Absorbance is linear at both wavelengths when plotted against concentration.

Method submitted by EPA (former) Product Analysis Laboratory, Region II, New York, NY
January 1977

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Atrazine by High Performance Liquid Chromatography

Atrazine is the accepted (ANSI, BSI, ISO, WSSA) common name for 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine, a registered herbicide having the chemical structure:



Molecular formula: $C_8H_{14}ClN_5$

Molecular weight: 215.7

Physical state-color-odor: colorless crystalline solid

Melting point: 173 to 175°C

Solubility: 33 ppm in water at 25°C; 1.2% in ethyl ether, 1.8% in methanol, 2.8% in ethyl acetate, 5.2% in chloroform, 18.3% in dimethyl sulfoxide

Stability: stable in neutral and slightly acidic or basic media; hydrolyzes in acid and alkaline conditions of higher temperatures to the herbicidally inactive hydroxy derivative; non-flammable; non-corrosive under normal use conditions; very stable shelf life with only slight sensitivity to natural light and extreme temperature; compatible with most other pesticides

Other names: AAtrex; Atranex; Atratol; Crisatrina; Crisazine; G 30027; Gesaprim; Griffex; Primatol A; Shell Atrazine Herbicide; Vectal SC; 6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine

Reagents:

1. Atrazine standard of known purity
2. Methanol, HPLC or pesticide grade
3. Acetic acid, ACS

Equipment:

1. High Performance Liquid Chromatograph with UV detector at 254 nm. If a variable wavelength detector is available, other wavelengths may be used to increase sensitivity or to eliminate interference.
2. Column: Radial Pak C18 (or equivalent column and parameter adjustments)
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 85% methanol + 14% water + 1% acetic acid
Column temperature: ambient
Flow rate: 7 ml/min
Wavelength: 254 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg atrazine standard into a 25 ml volumetric flask, dissolve in and make to volume with methanol, stopper tightly, and place in an ultrasonic bath until completely dissolved. Filter a portion through a 0.45 micron filter. (conc 4 mg/ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 mg atrazine into a 25 ml volumetric flask, make to volume with methanol and place in an ultrasonic bath as above. Filter a portion through a 0.45 micron filter. (conc 4 mg/ml)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solutions.

Calculation:

Measure the peak height or peak area for each peak and calculate the average for both standard and sample. Using these averages, calculate the percent atrazine as follows:

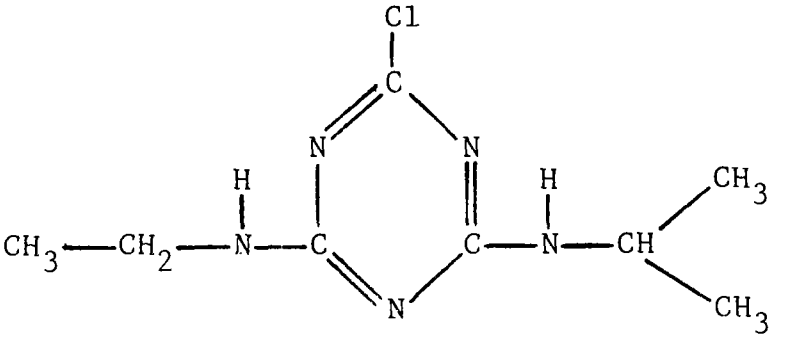
$$\% = \frac{(\text{peak height or area sample})(\text{weight standard injected})(\% \text{ purity standard})}{(\text{peak height or area standard})\ (\text{weight sample injected})}$$

This method had its origin at the Beltsville Chemistry Lab but is a result of several modifications from the HPLC courses sponsored by EPA - Beltsville and NEIC, Denver, Colorado

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Atrazine by High Performance Liquid Chromatography

Atrazine is the accepted (ANSI, BSI, ISO, WSSA) common name for 2-chloro-4-ethylamino-6-isopropylamimo-1,3,5-triazine, a registered herbicide having the chemical structure:



Molecular formula: $C_8H_{14}ClN_5$

Molecular weight: 215.7

Physical state-color-odor: colorless crystalline solid

Melting point: 173 to 175°C

Solubility: 33 ppm in water at 25°C; 1.2% in ethyl ether; 1.8% in methanol; 2.8% in ethyl acetate; 5.2% in chloroform; 18.3% in dimethyl sulfoxide

Stability: stable in neutral and slightly acidic or basic media; hydrolyzes in acid and alkaline conditions of higher temperatures to the herbicidally inactive hydroxy derivative; non-flammable; non-corrosive under normal use conditions; very stable shelf life with only slight sensitivity to natural light and extreme temperature; compatible with most other pesticides

Other names: AAtrex; Atranex; Atratol; Crisatrina; Crisazine; G 30027; Gesaprim; Griffex; Primatol A; Shell Atrazine Herbicide; Vectal SC; 6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine

Reagents:

1. Atrazine standard of known purity
2. Diethyl phthalate (internal standard) of known purity
3. Acetonitrile, HPLC grade
4. Methanol, HPLC grade
5. Internal standard solution - weigh 200 mg diethyl phthalate into a 100 ml volumetric flask, dissolve in and make to volume with methanol; mix well. (conc 2 mg/ml)

Equipment:

1. High Performance Liquid Chromatograph with UV detector at 254 nm. If a variable wavelength detector is available, other wavelengths may be used to increase sensitivity or to eliminate interference.
2. Column: uBondapak C18 (30 cm x 3.9 mm ID) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 42% acetonitrile + 58% water
Column temperature: 33°C
Flow rate: 2.5 ml/min
Wavelength: 254nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg atrazine standard into a 125 ml screw-cap flask, add 100 ml internal standard solution by pipette, close tightly, and shake to dissolve. Filter a portion through a 0.45 micron filter. (conc 1 mg atrazine and 2 mg diethyl phthalate per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 mg atrazine into a 125 ml screw-cap flask and add 100 ml internal standard solution by pipette. Close tightly, shake a few minutes by hand, place in an ultrasonic bath for about 2 minutes, and shake on a mechanical shaker for one hour. Filter a portion through a 0.45 micron filter. (conc as above)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solutions.

Calculation:

Measure the peak heights or areas of the atrazine and the diethyl phthalate for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area atrazine}}{\text{peak height or area diethyl phthalate}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area atrazine}}{\text{peak height or area diethyl phthalate}}$$

Average the standard and sample ratios, and calculate the percent atrazine as follows:

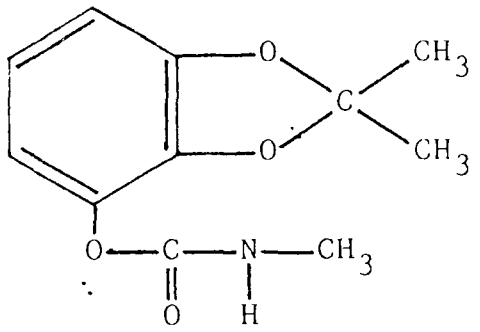
$$\% = \frac{(\text{ratio of sample})\ (\text{weight standard})\ (\%\ \text{purity of standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

Method submitted by EPA - NEIC, Denver, Colorado (Chuck Rzeszutko) December 1979

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Bendiocard by High Performance Liquid Chromatography

Bendiocarb is the accepted (ANSI, BSI, ISO) common name for 2,2-dimethyl-1,3-benzodioxol-4-yl N-methylcarbamate, a registered insecticide having the chemical structure:



Molecular formula: $C_{11}H_{13}NO_4$

Molecular weight: 223.23

Physical state-color-odor: white crystalline solid

Melting point: 129 to 130°C

Solubility: at 25°C: 0.004% in water, 0.03% in kerosene, 1.0% in o-xylene, 4% in ethanol and benzene, and 20% in acetone, dichloromethane, dioxin, and chloroform

Stability: the hydrolysis (to the phenol) half-life in solution in 0.01M aqueous sodium phosphate buffer at pH 7 and 25°C is 20 days

Other names: Ficam; Garvox; Multimet; NC 6897; 2,3-isopropylidenedioxyphenyl methylcarbamate

Reagents:

1. Bendiocarb standard of known purity
2. Methyl benzoate (internal standard) of known purity
3. Methanol, HPLC grade
4. Water, HPLC grade

5. Internal standard solution - weigh 180 mg methyl benzoate into a 250 ml volumetric flask, dissolve in and make to volume with methanol; mix thoroughly. (conc. 0.72 mg/ml)

Equipment:

1. High Performance Liquid Chromatograph with a variable wavelength UV detector at 280 nm. If a variable wavelength detector is not available operating parameters and concentrations may have to be changed to obtain the necessary separation and sensitivity.
2. Column: uBondapak C18 (30 cm x 3.9 mm ID) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 50% methanol + 50 % water
Column temperature: ambient
Flow rate: 2 ml/min
Wavelength: 280 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 110 mg bendiocarb standard into a 100 ml volumetric flask, dissolve in and make to volume with methanol; mix thoroughly. Pipette a 10 ml aliquot into a 50 ml volumetric flask, add 20 ml internal standard solution by pipette, and make to volume with methanol. Mix thoroughly and filter a portion through a 0.45 micron filter. (conc .0.22 mg bendiocarb and 0.288 mg methyl benzoate per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 110 mg bendiocarb into a 100 ml volumetric flask, dissolve in and make to volume with methanol; mix thoroughly. Pipette a 10 ml aliquot into a 50 ml volumetric flask, add 20 ml internal standard solution by pipette, and make to volume with methanol. Mix thoroughly and filter a portion through a 0.45 micron filter. (conc as above)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Proceed with the determination making alternately three injections each of standard and sample solutions. Elution order is bendiocarb then methyl benzoate.

Calculation:

Measure the peak heights or areas of the bendiocarb and the methyl benzoate for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area bendiocarb}}{\text{peak height or area methyl benzoate}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area bendiocarb}}{\text{peak height or area methyl benzoate}}$$

Average the standard and sample ratios, and calculate the percent bendiocarb as follows:

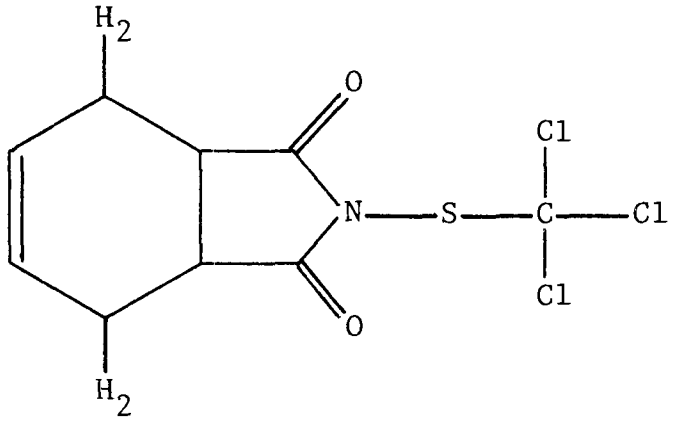
$$\% = \frac{(\text{ratio of sample})\ (\text{weight standard})\ (\%\ \text{purity of standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

Method submitted by EPA - NEIC, Denver, Colorado (M. Sher Ali)
November 1980

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Captan by Gas Chromatography (FID-IS)

Captan is the common name for cis-N-trichloromethylthio-4-cyclo-hexene-1,2-dicarboximide, a registered fungicide having the chemical structure:



Molecular formula: $C_9H_8Cl_3NO_2S$

Molecular weight: 300.6

Physical state-color-odor: (pure) - white crystalline solid
(technical) - yellow amorphous solid with a pungent odor

Melting point: (pure) - 178°C (decomposes)
(technical) - 160 to 170°C (93 to 95% purity)

Solubility: less than 0.05 ppm in water at room temperature; insoluble in petroleum oils; at 25°C the solubility w/w is 7% in xylene, 5% in chloroform, 3% in acetone, and 1% in isopropanol

Stability: stable under alkaline conditions; decomposes at its melting point; non-corrosive but decomposition products are corrosive

Other names: captane (France); Merpan; Orthocide; Voncaptan

Reagents:

1. Captan standard of known purity
2. Dibutyl phthalate (internal standard), analytical grade
3. Acetone, pesticide grade

4. Internal standard solution - weigh 100 mg dibutyl phthalate into a 100 ml volumetric flask, dissolve in and make to volume with acetone; mix well. (conc 1 mg/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 1/4" glass packed with 3% OV-1 on 100 to 120 mesh Supelcoport
3. Precision liquid syringe
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Ultrasonic bath
7. Usual laboratory glassware

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Operating conditions for FID:

Column temperature: 180°C
Injection port temperature: 250°C
Detector temperature: 250°C
Carrier gas: nitrogen - 30 ml/min (adjusted as necessary)
Hydrogen flow: 30 ml/min (adjusted as necessary)
Air flow: 600-800 ml/min (adjusted as necessary)

Procedure:

Preparation of standard:

Weigh 75 mg captan standard into a small (30 to 40 ml) glass vial with a polyseal-lined cap, add 25 ml internal standard solution by pipette, and close tightly. Shake for several minutes and place in a sonic bath for about 2 minutes and shake a few minutes more. Allow to settle, centrifuge to settle-out the particulates. (conc 3 mg captan and 1 mg dibutyl phthalate per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 75 mg captan into a small vial as above and follow the same procedure. (conc - as above)

GC Determination:

Inject 2 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the determination, making at least three injections each of standard and sample

solutions. The elution order is dibutyl phthalate then captan.

Calculation:

Measure the peak areas of the captan and dibutyl phthalate for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak area captan}}{\text{peak area dibutyl phthalate}}$$

$$\text{Ratio of sample} = \frac{\text{peak area captan}}{\text{peak area dibutyl phthalate}}$$

Average the standard and sample ratios, and calculate the percent captan as follows:

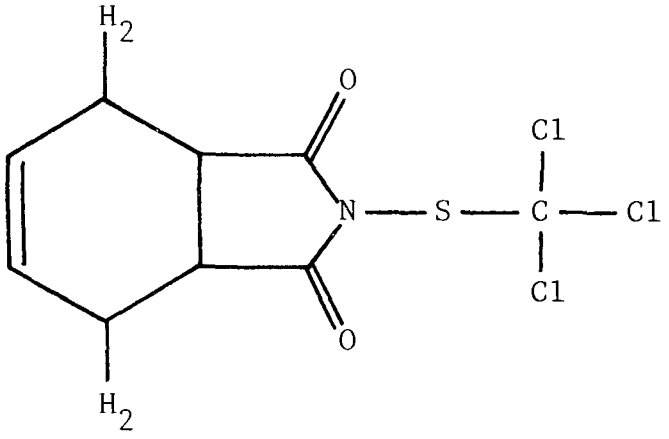
$$\% = \frac{(\text{ratio of sample})\ (\text{weight of standard})\ (\%\ \text{purity of standard})}{(\text{ratio of standard})\ (\text{weight of sample})}$$

Method submitted by NEIC, Denver, Colorado (Chuck Rzeszutko), June 1979

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Captan by High Performance Liquid Chromatography

Captan is the common name for cis-N-trichloromethylthio-4-cyclo-hexene-1,2-dicarboximide, a registered fungicide having the chemical structure:



Molecular formula: $C_9H_8Cl_3NO_2S$

Molecular weight: 300.6

Physical state-color-odor: pure - white crystalline solid
technical - yellow amorphos solid with a pungent odor

Melting point: pure - 178°C (decomposes)
technical - 160 to 170°C (93 to 95% purity)

Solubility: less than 0.05 ppm in water at room temperature; insoluble in petroleum oils; at 25°C the solubility w/w is 7% in xylene, 5% in chloroform, 3% in acetone, and 1% in isopropanol

Stability: stable under alkaline conditions; decomposes at its melting point; non-corrosive but decomposition products are corrosive

Other names: captane (France); Merpan; Orthocide; Voncaptan

Reagents:

1. Captan standard of known purity
2. Dibutyl phthalate (internal standard) of known purity

3. Methylene chloride, HPLC grade, dried with anhydrous sodium sulfate
4. Water, HPLC grade
5. Internal standard solution - weigh 150 mg dibutyl phthalate into a 500 ml volumetric flask, dissolve in and make to volume with dried methylene chloride; mix well. (0.3 mg/ml)

Equipment:

1. High Performance Liquid Chromatograph with UV detector at 254 nm. If a variable wavelength detector is available, other wavelengths may be used to increase sensitivity or to eliminate interference.
2. Si-100 10 um (Spectra-Physics) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filter
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 100% methylene chloride (dried with anhydrous sodium sulfate)
Column temperature: ambient
Flow rate: 1.5 ml/min
Wavelength: 254 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 50 mg captan standard into a 50 ml volumetric flask, dissolve in and make to volume with internal standard solution; mix thoroughly and filter a portion through a 0.45 micron filter. (conc 1 mg captan and 0.3 mg dibutyl phthalate per ml)

Preparation of sample:

Weigh a portion of liquid sample into a 50 ml volumetric flask, make to volume with internal standard solution, and mix well. For solid or dry samples, weigh a portion equivalent to 50 mg captan into a 125 ml screw-cap flask and add 50 ml internal standard solution by pipette, and mix well. Filter a portion through a 0.45 micron filter. (conc as above)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Proceed with the determination making alternately three injections each of standard and sample solutions.

Calculation:

Measure the peak heights or areas of the captan and the dibutyl phthalate for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area captan}}{\text{peak height or dibutyl phthalate}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area captan}}{\text{peak height or area dibutyl phthalate}}$$

Average the standard and sample ratios, and calculate the percent captan as follows:

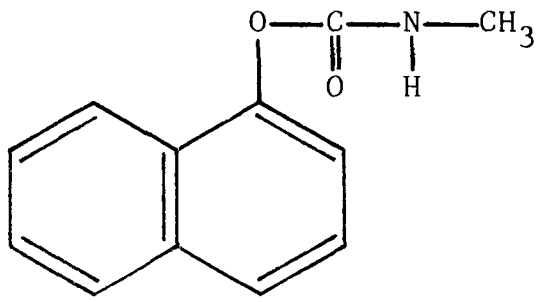
$$\% = \frac{(\text{ratio of sample})\ (\text{weight standard})\ (\%\ \text{purity standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

Method submitted by Mark W. Law, EPA Beltsville Chemistry Lab, Beltsville, MD April 1980

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Carbaryl by High Performance Liquid Chromatography

Carbaryl is the accepted (BSI, ISO) common name for 1-naphthyl-N-methylcarbamate, a registered insecticide having the chemical structure:



Molecular formula: $C_{12}H_{11}NO_2$

Molecular weight: 201.2

Physical state-color-odor: white crystalline solid

Melting point: 142°C

Solubility: 40 ppm in water at 30°C; soluble in most polar organic solvents such as acetone and mixed cresols

Stability: stable to light, heat, and hydrolysis under normal storage conditions; non-corrosive to metals, packing materials, or application equipment; compatible with most pesticides except those strongly alkaline which hydrolyze it to 1-naphthol

Other names: Carbamine; Cekubaryl; Denapon; Devicarb; Dicarbam; Hexavin; Karbaspray; Nac; Ravyon; Septene; Sevin; sevin (USA, USSR); Tercyl; Tricarnam; UC 7744

Reagents:

1. Carbaryl standard of known purity
2. Diethyl phthalate (internal standard) of known purity
3. Acetonitrile, HPLC grade
4. Methanol, HPLC grade

5. Internal standard solution - weigh 2 grams diethyl phthalate into a 250 ml volumetric flask, dissolve in and make to volume with methanol; mix thoroughly. (conc 8 mg/ml)

Equipment:

1. High Performance Liquid Chromatograph with a variable wavelength UV detector at 280 nm. If a variable wavelength detector is not available, operating parameters and concentrations may have to be changed to obtain the necessary separation and sensitivity.
2. Column: uBondapak C18 (30 cm x 3.9 mm ID) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 50% acetonitrile + 50% water
Column temperature: 30°C
Flow rate: 2 ml/min
Wavelength: 280 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg carbaryl standard into a 125 ml screw-cap flask, add 100 ml internal standard by pipette, close tightly, and shake to dissolve. Filter a portion through a 0.45 micron filter. (conc 1 mg carbaryl and 8 mg diethyl phthalate per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 mg carbaryl into a 125 ml screw-cap flask, add 100 ml internal standard by pipette, close tightly, and shake to dissolve the carbaryl. A few minutes in an ultrasonic bath may help to disperse and dissolve the sample. Filter through a 0.45 micron filter. (conc as above)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solutions. Elution order is carbaryl then diethyl phthalate.

Calculation:

Measure the peak heights or areas of the carbaryl and the diethyl phthalate for both standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area carbaryl}}{\text{peak height or area diethyl phthalate}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area carbaryl}}{\text{peak height or area diethyl phthalate}}$$

Average the standard and sample ratios, and calculate the percent carbaryl as follows:

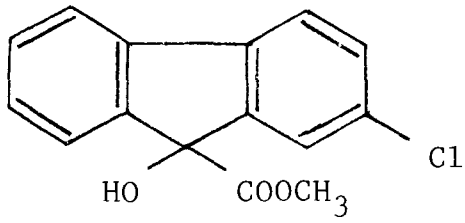
$$\% = \frac{(\text{ratio of sample})\ (\text{weight standard})\ (\%\ \text{purity of standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

Method submitted by EPA - NEIC, Denver, Colorado (Chuck Rzeszutko)
August 1979

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Chloroflurecol-methyl ester in Liquid Formulations by Ultraviolet Spectroscopy

Chloroflurecol-methyl ester is the common name (approved by BSI and used in the United States and Great Britain) for methyl-2-chloro-9-hydroxyfluorene-9-carboxylate, a registered plant growth regulator having the chemical structure:



[Technical Maintain CF 125 has 65 - 70% of the above compound plus:

18 - 25% methyl-9-hydroxyfluorene-9-carboxylate
10 - 12% methyl-2,7-dichloro-9-hydroxyfluorene-9-carboxylate

Since most formulations contain all three isomers, a technical Maintain CF 125 standard must be used for analysis.]

Molecular formula: $C_{15}H_{11}ClO_3$

Molecular weight: 274.7

Physical state-color-odor: odorless, white crystals when pure

Melting point: 152°C

Solubility: grams per 100 ml solvent at 20°C: acetone - 26, benzene - 8, carbon tetrachloride - 2.4, cyclohexane - 0.24, ethanol - 8, isopropanol - 2.4, methanol - 15, petroleum ether (bp 50-70°C) - 0.16, water - 0.00218

Stability: stable at room temperature; compatible with other growth regulators and with NH 30

Other names: chloroflurenol-methyl ester (ISO and France); CF 125; curbiset; IT 3456; Maintain CF 125; Maintain A; Maintain S; Multiprop

Reagents:

1. Maintain CF 125 standard of known assay
2. Methanol, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedures:

Preparation of standard:

Weigh 75 mg Maintain CF 125 standard into a 100 ml volumetric flask, dissolve in and make to volume with methanol, and mix thoroughly. Pipette 10 ml into a second 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Pipette 10 ml into a third 100 ml volumetric flask, again make to volume with methanol and mix thoroughly. (final conc 7.5 ug/ml)

Preparation of sample:

Weigh a portion of sample equivalent to 75 mg Maintain CF 125 into a 100 ml volumetric flask, make to volume with methanol, and mix thoroughly. Make a second and third dilution as above to give a final concentration of 7.5 ug/ml.

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen at 0 and 100% transmission at 275 nm with methanol in each cell. Scan both standard and sample solutions from 350 to 230 nm with methanol in the reference cell. Measure the absorbance of standard and sample solutions at 275 nm using a reference point at 350 nm.

Calculations:

From the above absorbances and using the standard and sample concentrations, calculate the percent Maintain CF 125 as follows:

$$\% = \frac{\text{(abs. sample) (conc. std. in ug/ml) (\% purity standard)}}{\text{(abs. std.) (conc. sample in ug/ml)}}$$

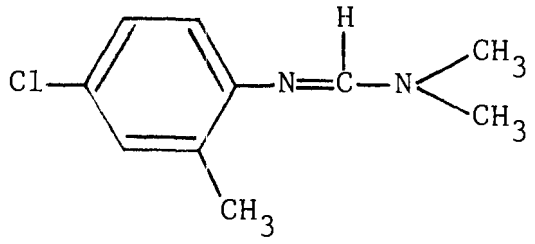
There is a straight line relationship between absorbance and concentration for up to 12.5 ug/ml.

Method submitted by EPA (former) Product Analysis Laboratory, Region II, New York, NY
November 1977

Any criticisms, suggestions, or data concerning this method will be appreciated.

Determination of Chlordimeform by Gas Chromatography (FID-IS)

Chlordimeform is the accepted (ANSI, BSI, ISO) common name for N'-(4-chloro-o-tolyl)-N,N-dimethyl formamidine, a registered acaricide, insecticide, and ovicide having the chemical structure:



Molecular formula: base - $C_{10}H_{13}ClN_2$ HCl salt - $C_{10}H_{14}Cl_2N_2$

Molecular weight: base - 196.7 HCl salt - 233.1

Physical state-color-odor: colorless crystals with a faint amine-like odor (both base and HCl salt); technical (97+%) - yellow liquid partly crystalline

Melting point: base - 32°C HCl salt - 225 to 227°C with decomposition

Boiling point: base - 163 to 165°C at 14 mm Hg

Solubility: base - 250 ppm in water at 20°C; more than 20% in acetone, benzene, chloroform, ethyl acetate, hexane, methanol
HCl salt - more than 50% in water, more than 30% in methanol, 1 to 2 % in chloroform, 0.1% in benzene or hexane

Stability: chlordimeform is hydrolyzed in neutral and acidic media first to N-formylchlorotoluidine then to 4-chlorotoluidine; very slowly hydrolyzed in acid media but forms salts; a 0.5% solution of the HCl (pH 3 to 4) is stable for some days at 20°C.

Other names: Acaron; Bermat; C 8514; chlorfenamidine (former name); Fundal; Fundex; Galecron; SN 36268; Spanone; N-(2-methyl-4-chlorophenyl)-N',N'-dimethyl formamidine; N,N-dimethyl-N'-(2-methyl-4-chlorophenyl)-formamidine

Reagents:

1. Chlordimeform standard of known purity
2. gamma BHC internal standard of known purity
3. Carbon disulfide, ACS grade or better
4. Internal standard solution - weigh 2.5 gram gamma BHC into a 250 ml volumetric flask, dissolve in and make to volume with carbon disulfide. (conc 10 mg/ml)

Equipment:

1. Gas chromatograph with flame ionization detector
2. Column: 6" x 4 mm ID glass packed with a 1:1 mixture of 10% DC-200 and 15% QF-1 on Gas Chrom Q
3. Precision liquid syringe
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating conditions for FID:

Column temperature: 185°C
Injection port temperature: 220°C
Detector temperature: 300°C
Carrier gas: nitrogen - flow adjusted as necessary
Hydrogen flow: adjusted as necessary
Air flow: adjusted as necessary

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 90 mg chlordimeform into a small flask or bottle, add 25 ml of internal standard solution by pipette, stopper tightly, and mix well. (conc 3.6 mg chlordimeform and 10 mg gamma BHC per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 90 mg chlordimeform into a small flask or bottle, add 25 ml of internal standard solution by pipette, stopper tightly, and mix well for liquids. For solid samples, shake on a mechanical shaker for 30 minutes; allow to settle, centrifuge or filter a portion if necessary taking precautions to avoid evaporation. (conc 3.6 mg chlordimeform and 10 mg gamma BHC per ml)

GC Determination:

Inject several ul (method submitted did not give injection volume) of standard and, if necessary, adjust the instrument parameters and the volume injected to give complete separation within a reasonable time and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the determination, making at least three injections each of standard and sample solutions. Elution order was not specified.

Calculation:

Measure the peak heights or areas of the chlordimeform and gamma BHC for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio standard} = \frac{\text{peak height or area chlordimeform}}{\text{peak height or area gamma BHC}}$$

$$\text{Ratio sample} = \frac{\text{peak height or area chlordimeform}}{\text{peak height or area gamma BHC}}$$

Average the standard and sample ratios, and calculate the percent chlordimeform as follows:

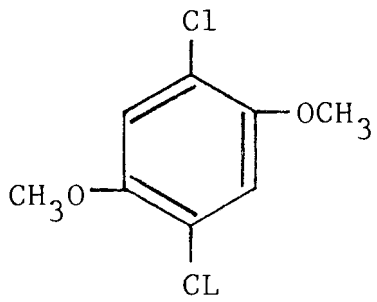
$$\% = \frac{(\text{ratio sample})\ (\text{weight standard})\ (\%\ \text{purity standard})}{(\text{ratio standard})\ (\text{weight sample})}$$

Method submitted by Mississippi State Chemical Laboratory, Mississippi State, Mississippi 39762
date: unknown but around 1975

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Chloroneb by Ultraviolet Spectroscopy

Chloroneb is the accepted (ANSI, BSI, ISO) common name for 1,4-dichloro-2,5-dimethoxybenzene, a registered fungicide having the chemical structure:



Molecular formula: $C_8H_8Cl_2O_2$

Molecular weight: 207.1

Physical state-color-odor: white crystalline solid with a musty odor

Melting point: 133 to 135°C

Boiling point: 268°C

Solubility: 8 ppm in water at 25°C; soluble in most common solvents: methylene chloride - 13.3%, dimethyl formamide - 11.8%, acetone - 11.5%, xylene - 8.9%

Stability: stable at temperatures up to boiling point; stable in common solvents and in the presence of dilute acid or alkali; subject to microbial decomposition in moist soil.

Other names: Demosan; Tersan SP

Reagents:

1. Chloroneb standard of known purity
2. Methanol, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of standard:

Weigh 100 mg chloroneb standard into a 100 ml volumetric flask, dissolve in and make to volume with methanol; mix thoroughly. Pipette a 10 ml aliquot into a second 100 ml volumetric flask, make to volume with methanol and mix thoroughly. Pipette a 25 ml aliquot into a third 100 ml volumetric flask and make to volume with methanol; mix thoroughly. (final conc 25 ug/ml)

Preparation of sample:

For granular formulations, grind a portion of sample to a fine powder with a mortar and pestle. Weigh a portion of ground sample equivalent to 100 mg chloroneb into a 300 ml glass-stoppered flask or screw-cap bottle, add 100 ml methanol by pipette, close tightly, and shake on a mechanical shaker for one hour. Allow to settle, centrifuge or filter if necessary, taking precautions to avoid evaporation of solvent. Dilute 10 ml to 100 ml and then 25 ml to 100 ml as above (second and third flasks) to give final concentration of 25 ug/ml.

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen at 0 and 100% transmission at 296 nm with methanol in each cell. Scan both standard and sample solutions from 330 to 230 nm with methanol in the reference cell. Measure the absorbance of standard and sample solutions at 296 nm using a reference point at 330 nm.

Calculations:

From the above absorbances and using the standard and sample concentrations, calculate the percent chloroneb as follows:

$$\% = \frac{\text{(abs. sample) (conc. std. in ug/ml) (\% purity of std.)}}{\text{(abs. std.) (conc. sample in ug/ml)}}$$

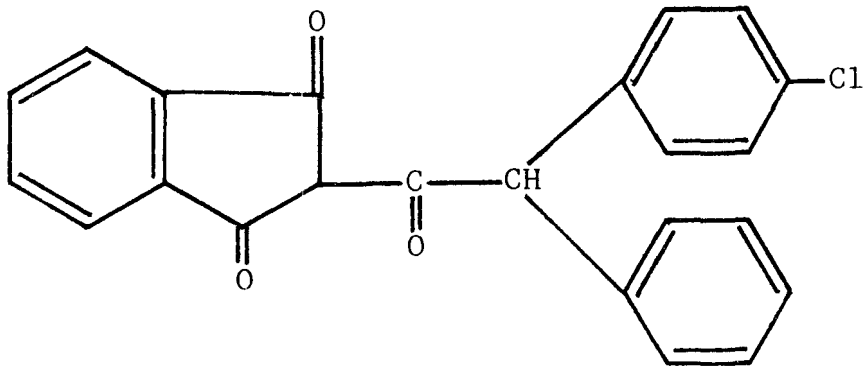
There is a straight line relationship between absorbance and concentration for up to 60 ug/ml.

Method submitted by EPA (former) Product Analysis Laboratory, Region II,
New York, NY
January 1977

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Chlorophacinone by High Performance Liquid Chromatography

Chlorophacinone is the accepted (BSI, ISO) common name for 2-[(p-chlorophenyl)phenylacetyl]-1,3-indandione, a registered rodenticide having the chemical structure:



Molecular formula: $C_{23}H_{15}ClO_3$

Molecular weight: 374.8

Physical state-color-odor: odorless, white crystalline solid

Melting point: 140°C

Solubility: sparingly soluble in water; soluble in organic solvents such as acetone, ethanol, ethyl acetate

Stability: stable and resistant to weathering; non-corrosive; compatible with cereals, fruits, roots, and other rodenticide baits; oxidized in bait formulations

Other names: Caid; Drat; Liphadione; LM 91; Microzul; Ramucide; Ratomet; Raviac; Rozol; Topitox

Reagents:

1. Chlorophacinone standard of known purity
2. Methanol/PIC A - (1 bottle PIC A in one liter of 90% methanol + 10% Water filtered through a 0.45 micron filter)
3. Water/PIC A - (1 bottle PIC A in one liter of water filtered through a 0.45 micron filter)

Equipment:

1. High Performance Liquid Chromatograph with a variable wavelength UV detector at 280 nm. If a variable wavelength detector is not available, operating parameters and concentrations may have to be changed to obtain the necessary separation and sensitivity.
2. Column: "column A" - uBondapak C18 (30 cm x 3.9 mm ID)
   "column B" - Radial Pak C18
3. High pressure liquid syringe or sample injection loop: 5 or 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: "column A" - 72%(90% methanol/10% water/PIC A) + 28%(water/PIC A)
"column B" - 80%(90% methanol/10% water/PIC A) + 20%(water/PIC A)
Column temperature: "column A" - ambient
"column B" - 32°C
Flow rate: "column A" - 1.0 to 1.5 ml/min
"column B" - 6 ml/min
Wavelength: 280 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg chlorophacinone standard into a 100 ml volumetric flask, dissolve in and make to volume with the methanol/PIC A regeant; mix well.
(conc 1 mg/ml)
For "column A" - make a first dilution of 1:10 (5 ml to 50 ml) and a second dilution of 1:10 (5 ml to 50 ml) using the methanol/PIC A reagent. (final conc 0.01 mg/ml)
For "column B" - make a dilution of 6 ml to 100 ml with the methanol/PIC A reagent. (final conc 0.06 mg.ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 mg chlorophacinone into a 125 ml screw-cap flask, add 100 ml methanol/PIC A reagent by pipette, close tightly, and shake on a mechanical shaker for one hour.
For "column A" - make the same dilution as above. (conc 0.01 mg/ml)
For "column B" - make the same dilution as above. (conc 0.06 mg/ml)

HPLC Determination:

Filter all solution through a 0.45 micron filter before injecting into the HPLC. Inject 5 ul (Column A) or 10 ul (Column B) of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solutions.

Calculation:

Measure the peak height or peak area for each peak and calculate the average for both standard and sample. Using these averages, calculate the percent chlorophacinone as follows:

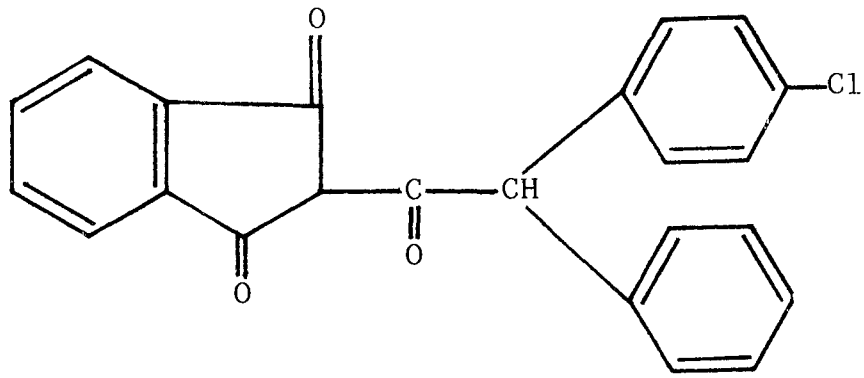
$$\% = \frac{(\text{peak height or area sample})(\text{weight standard injected})(\% \text{ purity standard})}{(\text{peak height or area standard})\ (\text{weight sample injected})}$$

This method is a combination of a method by Mark W. Law, EPA, Beltsville, MD dating back to August 1979 and a modification (Radial Pak column) submitted by Phil Gee and G. Thomas Gale, EPA - NEIC, Denver, CO dated April, 1980.

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Chlorophacinone in Wax Block Baits by Ultraviolet Spectroscopy

Chlorophacinone is the accepted (BSI, ISO) common name for 2-[(p-chlorophenyl) phenylacetyl]-1,3-indandione, a registered rodenticide having the chemical structure:



Molecular formula: $C_{23}H_{15}ClO_3$

Molecular weight: 374.6

Physical state-color-odor: odorless, white crystalline solid

Melting point: 140°C

Solubility: sparingly soluble in water; soluble in organic solvents such as acetone, ethanol, ethyl acetate

Stability: stable and resistant to weathering; non-corrosive; compatible with cereals, fruits, roots, and other rodenticide baits; oxidized in bait formulations

Other names: Caid; Drat; Liphadione; LN 91; Microzul; Ramucide; Ratomet; Raviac; Rozol; Topitox

Reagents:

1. Chlorophacinone standard of known purity
2. Benzene, reagent grade
3. Carbon disulfide, reagent grade
4. Ethanol, USP grade 95%
5. Ethanol adjusted to pH 0.5 (on pH meter) with concentrated hydrochloric acid
6. Hexane, reagent grade
7. Florisil 60/100 mesh (regular - not high performance)

Equipment:

1. Ultraviolet spectrophometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. pH meter
4. Glass chromatographic columns, 1" diameter by 8" (minimum) tall
5. Steambath
6. Usual laboratory glassware

Procedure:

In this method, a standard, sample, and fortified sample are run parallel to each other. A percent recovery is determined and used to calculate the corrected percent chlorophacinone from the percent found in the determination.

Preparation of standard:

For a stock standard solution - weigh 50 mg chlorophacinone into a 100 ml volumetric flask, dissolve in and make to volume with benzene; mix well. (conc 0.5 mg/ml) Use one ml of this solution for the determination - see column clean-up below.

Preparation of sample:

Weigh a portion of sample equivalent to 0.5 mg chlorophacinone (10 grams for a 0.005% formulation) into a 250 ml screw-cap flask, add 100 ml benzene by graduated cylinder, close tightly, and shake on a mechanical shaker for one hour. Decant the extract through Whatman #4 (or equivalent) filter paper, collecting the filtrate in a 400 ml beaker. Add 50 ml benzene to the flask and shake for 30 minutes; decant through the same filter collecting the filtrate in the same 400 ml beaker. Add another 50 ml benzene, shake again for 30 minutes, and decant through the same filter as above. Use the combined extracts for the determination - see column clean-up below.

Preparation of fortified sample:

Weigh another portion of sample as above but add 0.5 ml of stock standard solution (0.25 mg chlorophacinone) and extract exactly as above. Use the combined extracts for the determination - see column clean-up below.

Column clean-up:

Pack three 1" diameter x 8" length glass columns with 20 grams (each) of regular florisil; wet with benzene.
Quantitatively place the standard, sample, and fortified sample onto the pre-wetted columns with benzene. Wash each column with 300 ml benzene followed by 100 ml carbon disulfide and 100 ml nexane. Discard the washings. Elute the chlorophacinone from the columns with 130 ml of the 0.5 pH EtOH/HC1 solution. Collect the eluates in 250 ml beakers. Concentrate on a steambath to approximately 75 ml and quantitatively transfer to 100 ml volumetric flasks and make to volume with 95% ethanol. Filter 10 to 20 ml through Whatman #3 (or equivalent) filter paper. Use the filtered solutions for UV determination.

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen at 0 and 100% transmission at 360 nm with 0.5 pH EtOH/HC1 solution in each cell. Scan the standard, sample, and fortified sample solutions from 240 to 360 nm with 0.5pH EtOH/HC1 solution in the reference cell. Measure the absorbance at 321 nm and 350 nm for each solution.

Calculations:

From the above absorbances and the weights of standard, sample, and fortified sample, make the following calculations:

$$\text{mg sample found} = \frac{(\text{abs}_{321} - \text{abs}_{350}\ \text{sample})\ (\text{mg standard})}{(\text{abs}_{321} - \text{abs}_{350}\ \text{standard})}$$

$$\text{mg fortified sample found} = \frac{(\text{abs}_{321} - \text{abs}_{350}\ \text{fortified sample})\ (\text{mg standard})}{(\text{abs}_{321} - \text{abs}_{350}\ \text{standard})}$$

$$\% \text{ recovery} = \frac{(\text{mg fortified sample found}) - (\text{mg sample found})\ (100)}{(\text{mg chlorophacinone added for fortification})}$$

$$\% \text{ chlorophacinone} = \frac{(\text{abs}_{321} - \text{abs}_{350}\ \text{sample})\ (\text{mg standard})\ (100)}{(\text{abs}_{321} - \text{abs}_{350}\ \text{standard})\ (\text{mg sample})}$$

$$\% \text{ corrected chlorophacinone} = \frac{(\% \text{ chlorophacinone found})\ (100)}{(\% \text{ recovery})}$$

Notes:

1. All glassware must be cleaned with Pierce PBS-35 concentrate (dilute: 40 ml per 1000 ml water) or equivalent. Otherwise interferring substances remain on the glassware and interfere at the following UV analysis.

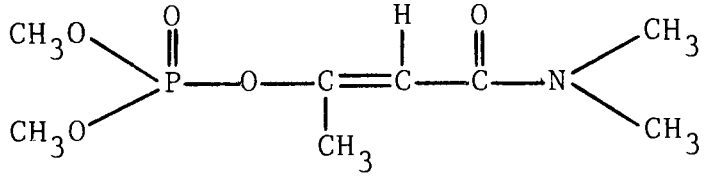
2. Since there is concern over the use of benzene in the laboratory, the amount used can be decreased by:
   (1) decreasing the sample size to 5 gram (0.005% formulation) and extracting with 50 ml, 25 ml, 25 ml portions
   (2) using only enough benzene to wash the paraffin from the column (less than 300 ml) until no more paraffin can be detected
   (3) once the recovery of a particular sample has been determined to be very good, analysis of a fortified sample can be omitted during repeat analyses.

Method submitted by University of Hawaii at Manoa, Department of Agricultural Biochemistry, Honolulu, Hawaii (Wanda L. Chang and Y. Kawano)
October 1979

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Dicrotophos by Infrared Spectroscopy

Dicrotophos is the accepted (BSI, ISO) common name for 3-(dimethoxyphosphinyloxy)-N,N-dimethyl-cis-crotonamide, a registered insecticide having the chemical structure:



Molecular formula: $C_8H_{16}O_5PN$

Molecular weight: 237.2

Physical state-color-odor: yellow to brown liquid with a mild ester odor

Boiling point: 400°C

Solubility: miscible with water, acetone, methanol, ethanol, isopropanol, xylene; very slightly soluble in kerosene and diesel fuel

Stability: stable up to 40°C when stored in glass or polyethylene containers; decomposes after 31 days at 75°C or 7 days at 90°C. The half-life of an aqueous solution at 38°C and pH 9.1 is 1200 hours, at pH 1.1 it is 2400 hours. Formulations on most carriers are unstable; acidic solutions are more stable than basic solutions. Compatible with most other pesticides. Relatively non-corrosive to Monel, copper, nickel, and aluminum; somewhat corrosive to cast iron, mild steel, brass, and stainless steel 304; does not attack glass, polyethylene, or stainless steel 316.

Other names: Bidrin; C709; Carbicron, Ektafos; SD 3562

Reagents:

1. Dicrotophos standard of known purity
2. Carbon tetrachloride, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam, with matched 0.5 mm NaCl or KBr cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of standard:

Weigh 90 mg dicrotophos standard into a 10 ml volumetric flask, dissolve in and make to volume with carbon tetrachloride. Add a little anhydrous sodium sulfate to insure dryness. (conc 9 mg/ml)

Preparation of sample:

For liquids - weigh a portion of sample equivalent to 900 mg dicrotophos into a 100 ml volumetric flask, make to volume with carbon tetrachloride, and mix thoroughly. Add a little anhydrous sodium sulfate to insure dryness.

For dusts, granules, and wettable powders - weigh a portion of sample equivalent to 900 mg dicrotophos into a 250 - 300 ml glass-stoppered flask or screw-cap bottle, add 100 ml carbon tetrachloride by pipette and some anhydrous sodium sulfate, close tightly, and shake on a mechanical shaker for one to two hours. Allow to settle, centrifuge or filter if necessary, taking precautions to prevent evaporation of solvent. (conc 9 mg/ml)

IR Determination:

With carbon tetrachloride in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample solutions from 960 to 880 cm^{-1} (10.4 to 11.4 um). Determine the absorbance of standard and sample using the peak at 926 cm^{-1} 10.8 um) and a reference point at 901 cm^{-1} (11.1 um).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent dicrotophos as follows:

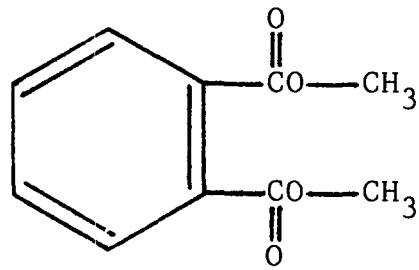
$$\% = \frac{\text{(abs. sample) (conc. std. in mg/ml) (\% purity of std.)}}{\text{(abs. std.) (conc. sample in mg/ml)}}$$

This method was submitted by the Mississippi State Chemistry Laboratory sometime around 1975. It was submitted as a basic outline and not a fully written procedure. I have taken the liberty of writing it in our standard IR format.

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Dimethyl phthalate by Gas Chromatography (FID-IS)

Dimethyl phthalate (common name and chemical name) is a registered insect repellent having the chemical structure:



Molecular formula: $C_{10}H_{10}O_4$

Molecular weight: 194.2

Physical state-color-odor: colorless to faintly yellow viscous liquid, slight aromatic odor

Boiling point: 282 to 285°C

Solubility: practically insoluble in water (0.43 g/100 ml), petroleum ether, and other paraffin hydrocarbons; miscible with alcohol, ether, chloroform, and most organic liquids

Stability: stable, though hydrolyzed by alkalis

Other names: DMP; 1,2-benzenedicarboxylic acid dimethyl ester; dimethyl 1,2-benzenedicarboxylate

Note: This method was developed for "mosquito cloth wipes" but can easily be adapted for other types of formulations.

Reagents:

1. Dimethyl phthalate standard of known purity
2. Pentachloronitrobenzene, purified or analytical grade

3. Acetone, pesticide or analytical grade
4. Internal standard solution - weigh 4.0 grams pentachloronitrobenzene into a 500 ml volumetric flask, dissolve in and make to volume with acetone; mix thoroughly. (conc 8 mg/ml)

Equipment:

1. Gas chromatograph with flame ionization detector
2. Column: 6' x 1/8" stainless steel packed with 3% XE-60 on 80 to 100 mesh Chromosorb W (or equivalent column)
3. Precision liquid syringe: 10 ul
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating conditions for FID:

Column temperature: 160°C
Injection port temperature: 220°C
Detector temperature: 250°C
Carrier gas: nitrogen - flow (adjusted as necessary)
Hydrogen flow: (adjusted as necessary)
Air flow: (Adjusted as necessary)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 400 mg dimethyl phthalate standard into a screw-cap flask or bottle and add 100 ml internal standard solution by pipette; mix thoroughly. (conc 4 mg dimethyl phthalate and 8 mg pentachloronitrobenzene per ml)

Preparation of sample:

Cut small squares from different areas of cloth to obtain a representative sample. Weigh a portion of the cut up sample equivalent to 400 mg dimethyl phthalate into a 250 ml screw-cap flask and add 100 ml internal standard solution by pipette. Shake on a mechanical shaker for 30 minutes. Filter or centrifuge, as necessary, taking precaution to avoid evaporation of the acetone. (conc 4 mg dimethyl phthalate and 8 mg pentachloronitrobenzene per ml)

GC Determination:

Inject 2 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the determination, making at least three injections each of standard and sample solutions. The elution order is dimethyl phthalate then pentachloronitrobenzene.

Calculation:

Measure the peak heights or areas of the dimethyl phthalate and pentachloronitrobenzene for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area dimethyl phthalate}}{\text{peak height or area pentachloronitrobenzene}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area dimethyl phthalate}}{\text{peak height or area pentachloronitrobenzene}}$$

Average the standard and sample ratios, and calculate the percent dimethyl phthalate as follows:

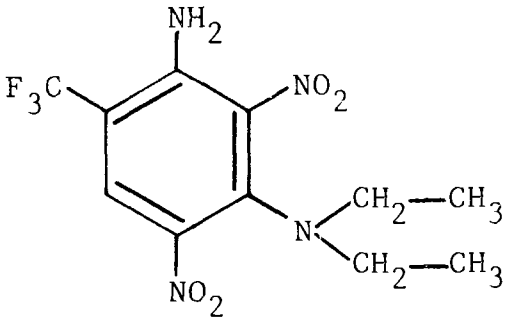
$$\% = \frac{(\text{ratio of sample})\ (\text{weight of standard})\ (\%\ \text{purity of standard})}{(\text{ratio of standard})\ (\text{weight of sample})}$$

Method submitted by E. S. Greer, EPA (formerly) Product Analysis Laboratory. Region IX, San Francisco, CA (Mr. Greer is now at Beltsville, MD) February 1976

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Dinitramine by Gas Chromatography (FID-IS)

Dinitramine is the accepted (BSI, ISO, WSSA) common name for N^4,N^4-diethyl-a,a,a-trifluoro-3,5-dinitrotoluene-2,4-diamine, a registered herbicide having the chemical structure:



Molecular formula: $C_{11}H_{13}F_3N_4O_4$

Molecular weight: 322.2

Physical state-color-odor: yellow crystalline solid

Melting point: 98 to 99°C

Solubility: grams per 100 ml solvent at 20°C; acetone - 104, benzene - 47.3, ethanol - 10.7, chloroform - 67, hexane - 1.4, xylene - 22.7, water - 0.0001 (1 ppm)

Stability: relatively stable at room temperature; decomposes above 200°C; subject to photodegradation; non-corrosive

Other names: Cobex, Cobexo; USB 3584

Reagents:

1. Dinitramine standard of known purity
2. Dibutyl phthalate (internal standard), (Dibutyl phthalate of known purity)

3. Acetone, pesticide grade
4. Internal standard solution - weigh 1.0 gram dibutyl phthalate into a 100 ml volumetric flask, dissolve in and make to volume with acetone; mix well. (conc 10 mg/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 1/4" glass packed with 4% SE-30 on 80 to 100 mesh Chromosorb W HP (or equivalent column)
3. Precision liquid syringe: 10 ul
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating conditions for FID:

Column temperature: 185°C
Injection port temperature: 200°C
Detector temperature: 235°C
Carrier gas: Helium (or nitrogen) - 30 ml/min (adjusted as necessary)
Hydrogen flow: (adjusted as necessary)
Air flow: (adjusted as necessary)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 110 mg dinitramine standard into a 100 ml volumetric flask, add 10 ml internal standard solution by pipette, make to volume with acetone, and mix thoroughly. (conc 1.1 mg dinitramine and 1 mg dibutyl phthalate per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 110 mg dinitramine into a 100 ml volumetric flask, add 10 ml internal standard solution by pipette, make to volume with acetone, and mix thoroughly. (conc 1.1 mg dinitramine and 1 mg dibutyl phthalate per ml)
If formulations other than liquid are encountered, proceed as follows: weigh a portion of sample equivalent to 110 mg dinitramine into a 250 ml glass-stoppered flask or screw-cap bottle, add 10 ml internal standard

solution and 90 ml of acetone by pipette, stopper tightly and shake on a mechanical shaker for one hour. Allow to settle, centrifuge or filter if necessary, taking precautions to avoid evaporation of the acetone. (Conc as above)

GC Determination:

Inject 3 to 4 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the determination, making at least three injections each of standard and sample solutions. The elution order is dinitramine then dibutyl phthalate.

Calculation:

Measure the peak heights or areas of the dinitramine and dibutyl phthalate for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio standard} = \frac{\text{peak height or area dinitramine}}{\text{peak height or area dibutyl phthalate}}$$

$$\text{Ratio sample} = \frac{\text{peak height or area dinitramine}}{\text{peak height or area dibutyl phthalate}}$$

Average the standard and sample ratios, and calculate the percent dinitramine as follows:

$$\% = \frac{(\text{ratio sample})\ (\text{weight standard})\ (\%\ \text{purity standard})}{(\text{ration standard})\ (\text{weight sample})}$$

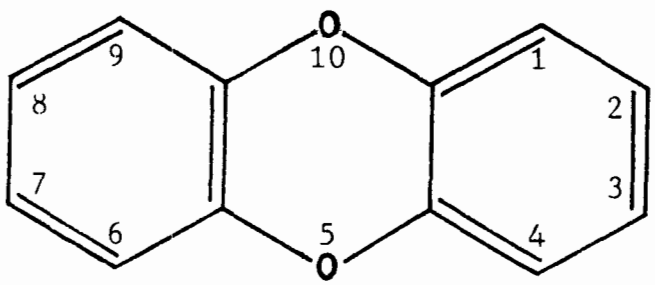
Method submitted by EPA (former) Product Analysis Laboratory, Region II, New York, NY
March 1977

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Dioxins at the Parts Per Billion Level in Technical and Formulated 2,4-D and 2,4,5-T Using GC/MS

Chlorinated dibenzo-p-dioxins occur as contaminants in 2,4-D and 2,4,5-T herbicides. These dioxins are formed when chlorinated benzenes are treated with high temperature and pressure under alkaline conditions such as are used in the manufacture of chlorophenoxy acid herbicides. Although they are by-products of the manufacturing process, they are considered contaminants. Some of these materials are known to be extremely toxic to test animals, therefore, they are highly undesireable in the environment.

Polychlorinated dioxins are formed by chlorination of dibenzo-p-dioxin which has the structural formula:



The substitution of from one to eight chlorines takes place at the carbon atoms numbered 1,2,3,4,6,7,8,9 on the above structure. These polychlorinated dioxins are sparingly soluble in most organic solvents and have limited solubility in water. The molecular weights range from 185 for no chlorine ($C_{12}H_8O_2$) to 460 for eight chlorines ($C_{12}Cl_8O_2$).

This method will identify all 8 dioxin species at the parts per billion level. The low resolution GC/MS procedure has a sensitivity of about 1 ppb for most isomers but will not separate all known dioxins.

Reagents:

1. Dioxin standards - available from Altech Inc.
2. Silica gel, MCB grade 923
3. Alumina, Woelm B, Super 1 used as is
4. Acetonitrile, pesticide grade
5. Carbon tetrachloride, pesticide grade
6. Hexane, pesticide grade
7. Methyl Alcohol, pesticide grade
8. Methylene chloride, pesticide grade
9. Sodium sulfate, anhydrous, granular

10. Sodium hydroxide - 1 N solution
11. Sulfuric acid - 1 N solution and concentrated
12. 1 + 1 acetonitrile water (with 10% methyl alcohol)
13. 1 + 1 methyl alcohol/water

Equipment:

1. Low resolution GC/MS caple of single ion monitoring. The sensitivity of the instrument should be at least 1 ng for any given dioxin standard when monitoring a single ion.
2. GC column for above: 6' x 2 MM ID glass packed with 1.5% OV-101 on 80/100 Chromosorb W HP (or equivalent column)
3. Precision microliter syringes (Hamilton or equivalent)
4. Usual laboratory glassware

Operation conditions:

Column temperature: 200 to 250°C depending on the dioxin species for which the analyst is being done.
All other parameters should be those giving the best conditions for the particular instrument being used.

Procedure:

Technical 2,4-D and 2,4,5-T acids:

Dissolve 10 gram of acid in 400 ml of 1 + 1 acetonitrile/water (with 10% methyl alcohol) solution. When totally dissolved, transfer to a 1000 ml separatory funnel and extract with 3 x 100 ml portions of hexane. Combine the hexane extracts in another separatory funnel.

Wash the combined hexane extracts as follows, discarding each wash solution:
4 x 100 ml portions of 1 + 1 methyl alcohol/water
3 x 100 ml portions of 1 N NaOH solution
3 x 100 ml portions of 1 N H_2SO_4 solution
3 x 100 ml portions of water

Filter the hexane through sodium sulfate and evaporate with dry nitrogen to about 25 ml. Shake the hexane with 4 x 25 ml portions of concentrated H_2SO_4 and discard the acid. Wash with 2 x 25 ml portions of water and discard the water. Filter through sodium sulfate and evaporate to about 5 to 10 ml using dry nitrogen.

Prepare alumina column as follows: 3" Wohlem alumina topped with 1" sodium sulfate: wash with 200 ml hexane and discard the hexane.

Transfer the evaporated hexane sample solution to the column with a minimum of hexane. Elute with 100 nl hexane and discard the eluate. Eluate with 2% methylene chloride in hexane and discard. Elute with 200 ml 30% methylene chloride in hexane and save the eluate. Evaporate with dry nitrogen to 0.5 to 1.0 ml for GC/MS.

Esters and Formulations:

Set up silica gel column using 30 grams in a 2 cm x 60 cm column topped with sodium sulfate. Transfer 2 to 5 grams sample to column and eluate with 200 ml 30% methylene chloride in hexane. Follow the above procedure beginning with the paragraph "Wash the combined hexane extracts....."

Interferences from PCBs:

If PCBs are suspected of interfering with the analysis, they can be eliminated as follows. Prepare a 30 cm x 12 mm ID chromatographic column by adding 1 1/2" of alumina and topping with 1" of anhydrous sodium sulfate. Wash column with methylene chloride and purge with a stream of dry nitrogen. Activate column at 225°C for approximately 6 hours and store at 125°C until ready to use.

Prewet column with hexane and transfer 1 ml sample solution to column using two 1 ml portions of hexane. Elute sample with 20 ml of carbon tetrachloride and discard eluate. Elute with 15 ml of methylene chloride. Collect eluate and evaporate to just dryness with a stream of nitrogen. Dilute to 0.5 to 1.0 ml for analysis.

Determination:

For GC/MS, inject aliquots of the sample extract and appropriate standards into the instrument which has been tuned to maximum efficiency and sensitivity for dioxins.

The ions to be monitored for the 8 dioxin species are:

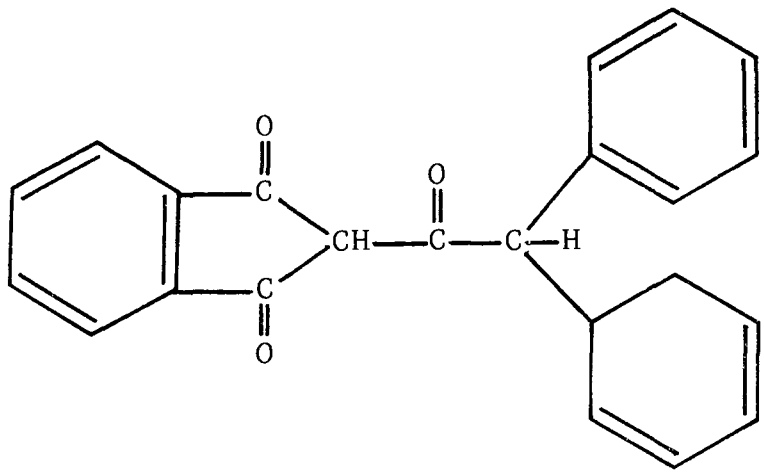
monochloro-----218 amu
dichloro-------252 amu
trichloro------288 amu
tetrachloro----322 amu
pentachloro----356 amu
hexachloro-----391 amu
heptachloro----426 amu
octachloro-----460 amu

Method submitted by EPA Beltsville Chemistry Laboratory (Ronald F. Thomas and Everett S. Greer) Beltsville, MD April 1982

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Diphacinone by High Performance Liquid Chromatography

Diphacinone is the accepted common name for 2-(diphenylacetyl)-1,3-indandione, a registered rodenticide having the chemical structure:



Molecular formula: $C_{23}H_{16}O_3$

Molecular weight: 340.4

Physical state-color-odor: odorless, yellow crystals

Melting point: 145°C

Solubility: slightly soluble in water and benzene; soluble in acetone and acetic acid; forms a sodium salt which is sparingly soluble in water

Stability: resists hydrolysis; stable toward mild oxidants; non-corrosive

Other names: diphacin (Turkey); Diphacin; Diphacin Meal Bait; P.C.Q.; Promar; Ramik; Rodent cake

Reagents:

1. Diphacinone standard of known purity
2. Methanol/PIC A - (1 bottle PIC A in one liter of 90% methanol/10% water filtered through a 0.45 micron filter)

3. Water/PIC A - (1 bottle PIC A in one liter of water filtered through a 0.45 micron filter

Equipment:

1. High Performance Liquid Chromatograph with a variable wavelength UV detector at 312 nm. If a variable wavelength detector is not available, operating parameters and concentrations may have to be changed to obtain the necessary separation and sensitivity.
2. Column: MCH-10 (30 cm x 4 mm ID)
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 65% (90% methanol/10% water/PIC A) = 35% (water/PIC A)
Column temperature: 32°C
Flow rate: 1.5 ml/min
Wavelength: 312 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 60 mg diphacinone standard into a 100 ml volumetric flask, dissolve in and make to volume with the methanol/PIC A solution. Dilute 5 ml to 50 ml with this same solution. Filter a portion through a 0.45 micron filter. (conc 0.06 mg/ml)

Preparation of sample:

Weigh a portion of sample equivalent to 60 mg diphacinone into a 100 ml volumetric flask, make to volume with the methanol/PIC A solution, and mix thoroughly. Dilute 5 ml to 50 ml with this same solution. Filter a portion through a 0.45 micron filter. (conc as above)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give a good separation in a reasonable

time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solutions.

Calculation:

Measure the peak height or peak area for each peak and calculate the average for both standard and sample. Using these averages, calculate the percent diphacinone as follows:

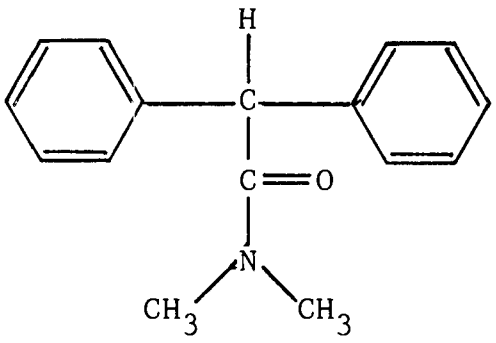
$$\% = \frac{(\text{peak height or area sample})(\text{weight standard injected})(\% \text{ purity standard})}{(\text{peak height or area standard})\ (\text{weight sample injected})}$$

Method submitted by EPA - NEIC, Denver, Colorado (Phil Gee & G. Thomas Gale)

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Diphenamid by Infrared Spectroscopy

Diphenamid is the accepted (ANSI, BSI, ISO, MAPJ, WSSA) common name for N,N-dimethyl-2,2-diphenylacetamide, a registered herbicide having the chemical structure:



Molecular formula: $C_{16}H_{17}NO$

Molecular weight: 239.3

Physical state-color-odor: white or off-white crystalline solid, has no appreciable odor

Melting point: 134.5 to 135.5°C (pure); 128 to 135°C (95% technical)

Solubility: grams per 100 ml solvent at 27°C: acetone - 19, dimethyl formamide - 16.5, phenyl cellosolve - 32, xylene - 5, water - 0.026 (260 ppm)

Stability: moderately stable to heat and UV light; compatible with most other pesticides; non-corrosive, non-flammable

Other names: Dymid; Enide; L-34314

Reagents:

1. Diphenamid standard of known purity
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam, with matched 0.5 mm KBr cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of standard:

Weigh 150 mg diphenamid standard into a 25 ml volumetric flask, dissolve in and make to volume with carbon disulfide. Add a little anhydrous sodium sulfate to insure dryness, and shake well. (conc 6 mg/ml)

Preparation of sample:

For liquids - weigh a portion of sample equivalent to 600 mg diphenamid into a 100 ml volumetric flask, make to volume with carbon disulide and mix thoroughly. Add a little anhydrous sodium sulfate to insure dryness and shake well. (conc 6 mg/ml)

For dusts, granules, and wettable powders - weigh a portion of sample equivalent to 600 mg diphenamid into a 250 - 300 glass-stoppered flask or screw-cap bottle, add 100 ml carbon disulfide by pipette and some anhydrous sodium sulfate, close tightly, and shake on a mechanical shaker for one hour. Allow to settle, centrifuge or filter if necessary, taking precautions to avoid evaporation of solvent. (conc. 6 mg/ml)

IR Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both the standard and sample solutions from 740 to 665 cm^{-1} (13.5 to 15.0 um). Determine the absorbance of standard and sample using the peak at 700 cm^{-1} (14.3 um) and a baseline from 725 to 678 cm^{-1} (13.8 to 14.75 um).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent diphenamid as follows:

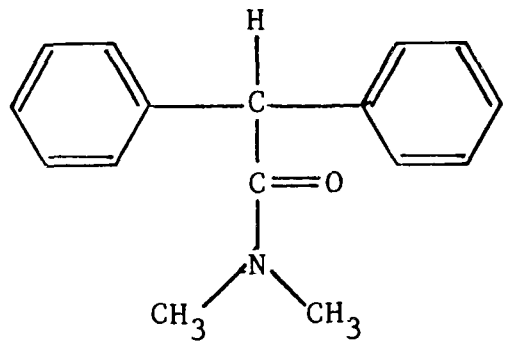
$$\% = \frac{(\text{abs. sample})\ (\text{conc. std. in mg/ml})\ (\%\ \text{purity of std.})}{(\text{abs. std.})\ (\text{conc. sample in mg/ml})}$$

This method has been used several times in the past (back to the middle and late 1960's) in the Beltsville Laboratory; it seems satisfactory, but has never been formally checked-out.

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Diphenamid by Gas Liquid Chromatography (FID-IS)

Diphenamid is the accepted (ANSI, BSI, ISO, MAPJ, WSSA) common name for N,N-dimethyl-2,2-diphenylacetamide, a registered herbicide having the chemical structure:



Molecular formula: $C_{16}H_{17}NO$

Molecular weight: 239.3

Physical state-color-odor: white or off-white crystalline solid, has no appreciable odor

Melting point: 134.5 to 135.5°C (pure); 128 to 135°C (95% technical)

Solubility: grams per 100 ml solvent at 27°C = acetone - 19; dimethyl formamide - 16.5; phenyl cellosolve - 32; xylene - 5, water - 0.026 (260 ppm)

Stability: moderately stable to heat and UV light; compatible with most other pesticides; non-corrosive; non-flammable

Other names: Dymid; Enide; L-34314

Reagents:

1. Diphenamid standard of known purity
2. HEOD (100%, or dieldrin of known HEOD content) internal standard (See note #1)
3. Chloroform, pesticide grade
4. Internal standard solution - weigh 3.5 grams HEOD (or dieldrin equivalent to 3.5 grams HEOD) into a 250 ml volumetric flask, dissolve in and make to volume with chloroform, and mix well. (conc 14 mg/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 4 mm ID glass packed with 3% Poly I (polyethylene imine) 110 on 80 to 100 mesh Gas Chrom Q (or equivalent column - suggest trying SP-1000 on Chromosorb 750, if available)
3. Precision liquid syringe: 10 ul
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating conditions for FID:

Column temperature: 260°C
Injection port temperature: 300°C
Detector temperature: 300°C
Carrier gas: Nitrogen - (flow adjusted as necessary)
Hydrogen flow: (adjusted as necessary)
Air flow: (adjusted as necessary)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 200 mg diphenamid standard into a 100 ml volumetric flask, add 50 ml internal solution by pipette, and make to volume with chloroform; mix well. (conc 2 mg diphenamid and 7 mg HEOD per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 200 mg diphenamid into a 250 ml glass-stoppered flask or screw-cap bottle, add 50 ml internal standard by pipette and 50 ml chloroform by pipette, close tightly, and shake on a mechanical shaker for about one hour. Allow to settle, centrifuge or filter if necessary, taking precautions to avoid evaporation of the acetone. (conc approx. 2 mg diphenamid and 7 mg HEOD per ml)

GC Determination:

Inject 2 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the determination, making at least three injections each of standard and sample solutions. The elution order is diphenamid then HEOD.

Calculation:

Measure the peak heights or areas of the diphenamid and HEOD for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio standard} = \frac{\text{peak height or area diphenamid}}{\text{peak height or area HEOD}}$$

$$\text{Ratio sample} = \frac{\text{peak height or area diphenamid}}{\text{peak height or area HEOD}}$$

Average the standard and sample ratios, and calculate the percent diphenamid as follows:

$$\% = \frac{(\text{ratio sample})\ (\text{weight standard})\ (\%\ \text{purity standard})}{(\text{ratio standard})\ (\text{weight sample})}$$

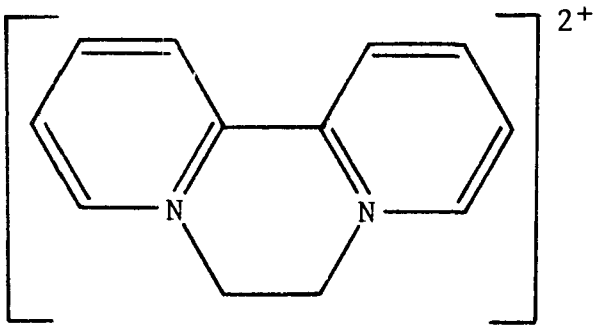
Method submitted by Division of Regulatory Services, Lexington, Kentucky

Note #1
Any information as to other internal standards will be appreciated - prefer not to use pesticides as internal standards

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Diquat by High Performance Liquid Chromatography

Diquat is the accepted (BSI, ISO) common name for 1,1'-ethylene-2,2'-bipyridylium ion; usually present as the dibromide monohydrate salt. Diquat is a registered herbicide and desiccant and has the chemical (cation) structure:



Molecular formula: $C_{12}H_{12}N_2$ (cation); $C_{12}H_{12}N_2Br_2$ (dibromide salt)

Molecular weight: 184.2 (cation); 344.1 (dibromide salt)

Physical state-color-odor: (dibromide salt) - white to yellow crystals
(aqueous solution) - dark reddish brown

Melting point: decomposes above 300°C, charring rather than melting or boiling

Solubility: (dibromide) - very soluble in water (70 grams/100 ml at 20°C); slightly soluble in alcohol and hydroxylic solvents; practically insoluble in non-polar organic solvents

Stability: (dibromide) - stable in acid or neutral solutions but unstable under alkaline conditions; may be inactivated by inert clays and anionic surfactants; decomposes in UV light; unformulated products are corrosive to metals

Other names: deiquat (Germany); reglon (USSR); Aquacide; Dextrone; Reglone; Reglox; Weedtrine-D; 6,7-dihydrodipyrido[1,2-a:2',1'-c] pyrazinedinium ion

Reagents:

1. Diquat (dibromide) standard of known purity
2. Phenol (internal standard) of known purity (make sure that the phenol gives a clean chromatogram with no co-eluting peaks)
3. Aqueous mobile phase - (0.0025M 1-heptane sulfonic acid sodium salt and 0.04M tetramethylammonium chloride adjusted to pH 3.0 with sulfuric acid) Filter through a 0.45 micron filter.
4. Organic mobile phase - (0.06M tetramethylammonium chloride in 200 ml water adjusted to pH 3.0 with sulfuric acid plus 800 ml acetonitrile) Filter through a 0.45 micron filter.
5. Internal standard solution - weigh 1 gram phenol into a 500 ml volumetric flask, dissolve in and make to volume with aqueous mobile phase. (conc 2 mg/ml)

Equipment:

1. High Performance Liquid Chromatograph with UV detector at 254 nm. If a variable wavelength detector is available, other wavelengths may be used to increase sensitivity or to eliminate interference.
2. Column: MicroPak MCK-10 (30 cm x 4 mm ID) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 85% aqueous mobile phase + 15% organic mobile phase
Column temperature: ambient
Flow rate: 2 ml/min
Wavelength: 254 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 50 mg diquat (dibromide) standard into a 100 ml volumetric flask, dissolve in and make to volume with internal standard solution; mix well. Filter a portion through a 0.45 micron filter. (conc 0.5 mg diquat (dibromide) and 2 mg phenol per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 50 mg diquat (dibromide) into a 125 ml screw-cap flask, add 100 ml internal standard solution by pipette, close tightly, and shake on a mechanical shaker for 30 minutes. Filter a portion through a 0.45 micron filter. (conc 0.5 mg diquat (dibromide) and 2 mg phenol per ml)

HPLC Determination:

Inject 10 ul standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solution.

Calculation:

Measure the peak heights or areas of the diquat (dibromide) and the phenol for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio standard} = \frac{\text{peak height or area diquat (dibromide)}}{\text{peak height or area phenol}}$$

$$\text{Ratio sample} = \frac{\text{peak height or area diquat (dibromide)}}{\text{peak height or area phenol}}$$

Average the standard and sample ratios, and calculate the percent diquat (dibromide) as follows:

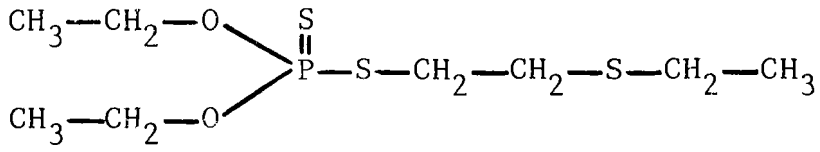
$$\% = \frac{\text{(ratio of sample) (weight of standard) (\% purity of standard)}}{\text{(ratio of sample) (weight of sample)}}$$

Method submitted by EPA - NEIC, Denver, Colorado (G. Thomas Gale)
January 1980

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Disultoton by Gas Chromatography (FID-IS)

Disulfoton is the accepted (BSI, ISO) common name for O,O-diethyl S-[2-(ethylthio)ethyl] phosphorodithioate, a registered insecticide and acaricide having the chemical structure:



Molecular formula: $C_8H_{19}O_2PS_3$

Molecular weight: 274.4

Physical state-color-odor: pure - colorless to pale yellow liquid with a characteristic odor of sulfur compounds; technical - dark yellowish oil with an aromatic odor

Boiling point: 62°C at 0.01 mm Hg

Solubility: 25 ppm in water at room temperature; readily soluble in most organic solvents

Stability: subject to hydrolysis under alkaline conditions; stable in normal storage

Other names: Bay 276; Bay 19639; Disyston; Di-Syston (in U.S.); dithiodemeton; dithiosustox; Frumin AL; M-74 (USSR); Solvirex

Reagents:

1. Disulfoton standard of known purity
2. Dibutyl phthalate of known purity
3. Acetone, pesticide grade
4. Internal standard solution - weigh 600 mg dibutyl phthalate into a 250 ml volumetric flask, dissolve in and make to volume with acetone; mix well. (conc 2.4 mg/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 1/4" glass packed with 10% OV-1 on 80 to 100 mesh Chromosorb W (or equivalent column)
3. Precision liquid syringe: 10 ul
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating parameters for FID:

Column temperature: 220°C
Injection port temperature: 250°C
Detector temperature: 250°C
Carrier gas: Nitrogen (flow adjusted as necessary)
Hydrogen flow: (adjusted as necessary)
Air flow: (adjusted as necessary)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg disulfoton standard into 125 ml screw-cap flask, add 50 ml of internal standard solution by pipette, and shake to dissolve. (conc 2 mg disulfoton and 2.4 mg dibutyl phthalate per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 mg disulfoton into a 125 ml screw-cap flask, add 50 ml internal standard solution by pipette, and shake on a mechanical shaker for about one hour. Allow to settle, centrifuge or filter if necessary, taking precaution to avoid evaporation of the acetone. (conc approx. 2 mg disulfoton and 2.4 mg dibutyl phthalate per ml)

GC Determination:

Inject 2 to 4 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the determination, making at least three injections each of standard and sample solutions. The elution order is disulfoton then dibutyl phthalate.

Calculation:

Measure the peak heights or areas of the disulfoton and dibutyl phthalate for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio standard} = \frac{\text{peak height or area disulfoton}}{\text{peak height or area dibutyl phthalate}}$$

$$\text{Ratio sample} = \frac{\text{peak height or area disulfoton}}{\text{peak height or area dibutyl phthalate}}$$

Average the standard and sample ratios, and calculate the percent disulfoton as follows:

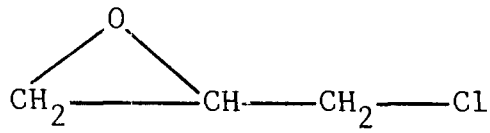
$$\% = \frac{(\text{ratio sample})\ (\text{weight standard})\ (\%\ \text{purity standard})}{(\text{ratio standard})\ (\text{weight sample})}$$

Method submitted by E. S. Greer, August 1977, EPA (formerly) Product Analysis Laboratory, San Francisco, CA and presently Beltsville Chemical Laboratory, Beltsville, MD

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Epichlorohydrin by Gas Chromatography (FID)

Epichlorohydrin is the classical common name for 1-chloro-2,3-epoxypropane, a registered insect fumigant having the chemical structure:



Molecular formula: C_3H_5ClO

Molecular weight: 92.53

Physical state-color-odor: very volatile, narcotic liquid, with a chloroform-like odor

Melting point: -25.6°C

Boiling point: 115 to 117°C

Solubility: miscible with most organic solvents; immiscible with water and petroleum hydrocarbons

Stability: unstable

Other names: chloropropylene oxide; chloromethyloxirane

Reagents:

1. Epichlorohydrin standard of known purity
2. Acetone, ACS grade (other solvents may be used if they do not interfere)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 2 mm ID glass packed with Chromosorb 102 80/100 mesh

Note: This packing material is not particularly suitable for epichlorohydrin as a component in other formulations, because of the strong absorptivity of this packing, and the resultant necessity for baking-off the absorbed materials at high temperatures. It is suggested that formulations be extracted by column chromatography.

3. Precision liquid syringe
4. Usual laboratory glassware

Operating conditions for FID:

Column temperature: 150°C
Injection port temperature: 200°C
Detector temperature: 200°C
Carrier gas (helium or nitrogen), flow adjusted as necessary
Hydrogen flow: adjusted as necessary
Air flow: adjusted as necessary

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 150 mg epichlorohydrin standard into a 100 ml volumetric flask, make to volume with acetone, and mix well. (conc 1.5 mg/ml)

Preparation of sample:

Weigh a portion of sample equivalent to 150 mg epichlorohydrin into a 100 ml volumetric flask, make to volume with acetone, and mix well. (conc 1.5 mg/ml)

GC Determination:

Inject 2 to 3 ul standard and, if necessary, adjust instrument parameters and the volume injects to give peak heights of 1/2 to 3/4 full scale. Proceed with the determination, making at least three injections each of standard and sample solutions.

Calculation:

Measure the peak heights or areas of both standard and sample and calculate the percent epichlorohydrin as follows:

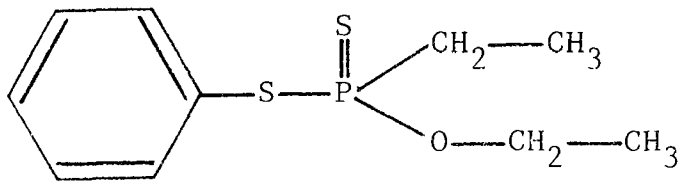
$$\% = \frac{(\text{peak height or area sample})(\text{weight standard injected})(\% \text{ purity})}{(\text{peak height or area standard})(\text{weight sample injected})}$$

Method submitted by EPA, CBIB, Beltsville Chemistry Lab, Beltsville, MD (Elmer H. Hayes and Mark W. Law)

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Fonofos by Infrared Spectroscopy

Fonofos is the accepted (BSI, ISO) common name for O-ethyl S-phenyl ethylphosphonodithioate, a registered insecticide having the chemical structure:



Molecular formula: $C_{10}H_{15}OPS_2$

Molecular weight: 246.3

Physical state-color-odor: light yellow liquid with a pungent, mercaptan-like odor

Boiling point: 130°C at 0.1 mm Hg

Solubility: practically insoluble in water; miscible with organic solvents such as: acetone, kerosene, methyl isobutyl ketone, xylene

Stability: stable under normal conditions

Other names: Dyfonate; N-2790

Reagents:

1. Fonofos standard of known purity
2. Carbon disulfide, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam, with matched 0.2 mm KBr cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of standard:

Weigh 100 mg fonofos standard into a 10 ml volumetric flask, dissolve in and make to volume with carbon disulfide. Add a little anhydrous sodium sulfate to insure dryness. (conc 10 mg/ml)

Preparation of sample:

For liquids and emulsifiable concentrates - weigh a portion of sample equivalent to 500 mg fonofos into a 50 ml volumetric flask, mix with and make to volume with carbon disulfide. Add a little anhydrous sodium sulfate to insure dryness.

For dusts, granules, and wettable powders - weigh a portion of sample equivalent to 1 gram (1000 mg) fonofos into a 250 ml glass-stoppered flask or screw-cap bottle, add 100 ml carbon disulfide by pipette, close tightly, and shake on a mechanical shaker for one hour. Allow to settle, centrifuge or filter if necessary, taking precautions to avoid evaporation of solvent. If sample is of low percentage, it may be necessary to use a soxhlet extration apparatus.

(conc 10 mg/ml)

IR Determination:

With carbon disulfide in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan the standard and sample solutions from 690 to 540 cm^{-1} (14.5 to 18.5 um). Determine the absorbance of standard and sample using the peak at 610 cm^{-1} (16.4 um) and a basepoint at 580 cm^{-1} 917.25 um).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent fonofos as follows:

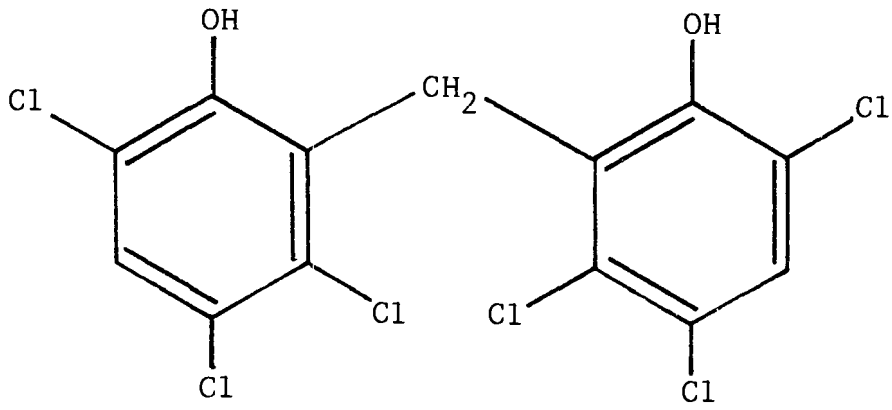
$$\% = \frac{(\text{abs. sample})\ (\text{conc. std. in mg/ml})\ (\%\ \text{purity})}{(\text{abs. std.})\ (\text{conc. sample in mg/ml})}$$

This method was written in the general IR format used in this manual - it was submitted by the State of Virginia - date unknown - in outline form. This method has been used in the Beltsville Lab a few times, but has never been checked thoroughly.

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Hexachlorophene by High Performance Liquid Chromatography

Hexachlorophene is the common name for 2,2-methylenebis (3,4,6-trichlorophenol), a registered foliage fungicide and bactericide, plant bactericide, and soil fungicide with some acaricidal activity. It has the chemical structure:



Molecular formula: $C_{13}H_6Cl_6O_2$

Molecular weight: 406.9

Physical state-color-odor: white powder

Melting point: 164 to 165°C

Solubility: practically insoluble in water; soluble in acetone, alcohol, chloroform, ether, propylene glycol, polyethylene glycol, olive oil, cottonseed oil, and dilute aqueous solutions of the alkalis.

Stability: stable

Other names: Hexide; Nabac; Isobac (sodium salt)

Note: see end of method for a modified procedure using a RadialPak column and methanol instead of acetonitrile.

Reagents:

1. Hexachlorophene standard of known purity
2. Acetonitrile/PIC A - (1 bottle PIC A in one liter of 90% acetonitrile + 10% water filtered through a 0.45 micron filter)
3. Water/PIC A - (1 bottle PIC A in one liter water filtered through a 0.45 micron filter)
4. Isopropanol, HPLC grade

Equipment:

1. High Performance Liquid Chromatograph with a variable wavelength UV detector at 296 nm. If a variable wavelength detector is not available, operating parameters and concentrations may have to be changed to obtain the necessary separation and sensitivity.
2. Column: uBondapak C18 (30 cm x 3.9 mm ID) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 87% (90% acetonitrile/10% water/PIC A) + 23% (water/PIC A)
Column temperature: ambient
Flow rate: 1.5 ml/min
Wavelength: 296 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg hexachlorophene standard into a 100 ml volumetric flask, dissolve in and make to volume with isopropanol; mix well. Filter a portion through a 0.45 micron filter. (conc 1 mg/ml)

Preparation of sample:

Weigh a portion of sample (liquid or E. C.) equivalent to 100 mg hexachlorophene into a 100 ml volumetric flask, mix with and make to volume with isopropanol; mix thoroughly. Filter a portion through a 0.45 micron filter. (conc 1 mg/ml) For dry formulations, use a 125 ml screw-cap flask and add 100 ml isopropanol by pipette. Shake for 30 minutes, and filter a portion.

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solutions.

Calculation:

Measure the peak height or peak area for each peak and calculate the average for both standard and sample. Using these averages, calculate the percent hexachlorophene as follows:

$$\% = \frac{(\text{peak height or area sample})(\text{weight standard injected})(\% \text{ purity standard})}{(\text{peak height or area standard})\ (\text{weight sample injected})}$$

Method submitted by Mark W. Law, EPA, Beltsville, MD March 1978

The following modification of the above method was developed at the several HPLC schools sponsored by EPA over the last few years.

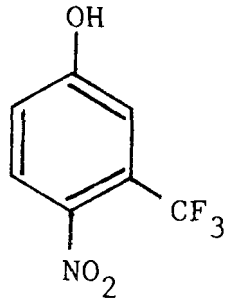
Column: Radial Pak C18
Mobile phase: 90% (90% methanol/10% water/PIC A) + 10% (water/PIC A)
Flow rate: 8 ml/min
Amount injected: 20 ul

All other parameters, concentrations, and calculations are the same as given above.

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Lamprecid by Ultraviolet Spectroscopy

Lamprecid is the trade name (Hoechst AG - West Germany) for alpha, alpha, alpha-trifluoro-4-nitro-meta-cresol. Lamprecid is a selective fish killer used to control sea lampreys. Its chemical structure is:



Molecular formula: $C_7H_4F_3NO_3$ (free phenol) $C_7H_3F_3NO_3Na$ (sodium salt)

Molecular weight: 207.11 229.09

Physical state-color-odor: solid

Melting point: 76°C

Solubility: soluble in ethanol; sodium salt is very water soluble

Stability:

Other names: Dowlap: TFM; 3-trifluoro-4-nitrophenol; 4-nitro-3-(trifluoromethyl) phenol

Reagents:

1. Lamprecid standard of known purity
2. Sodium hydroxide, 1N aqueous solution

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Usual laboratory volumetric glassware

Procedure:

Preparation of standard:

Weigh an amount of standard Lamprecid equivalent to 100 mg of 100% purity into a 100 ml volumetric flask, add 10 ml 1 N NaOH solution, and make to volume with water. Mix thoroughly and pipette 5 ml into a 1000 ml volumetric flask and make to volume with water. (final conc 5 ug/ml)

Preparation of Sample:

Weigh an amount of sample equivalent to 100 mg Lamprecid into a 100 ml volumetric flask, add 10 ml 1 N NaOH solution, and make to volume with water. Mix thoroughly; pipette 10 ml into a 1000 ml volumetric flask and make to volume with water. (final conc 5 ug Lamprecid/ml)

UV Determination:

With the spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen at 0 and 100% transmission at 395 nm with a blank reagent solution* in each cell.

*blank reagent solution - 10 ml 1 N NaOH solution diluted to 100 ml, then 5 ml diluted to 1000 ml.

Scan both standard and sample solutions from 500 to 200 nm with blank reagent solution in the reference cell. Measure the absorbance of standard and sample solutions at 395 nm using a baseline from 310 to 280 nm.

Calculations:

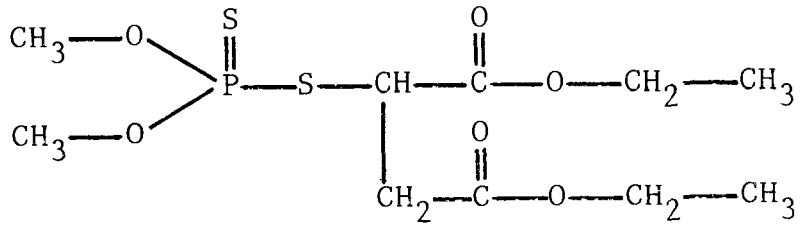
From the above absorbances and using the standard and sample concentrations, calculate the percent Lamprecid as follows:

$$\% = \frac{\text{(abs. sample) (conc. std. in ug/ml) (\% purity)}}{\text{(abs. std.) (conc. sample in ug/ml)}}$$

This method has been used successfully in the Beltsville Chemistry Laboratory several times in the past - the late 1960's and early 1970's; however no new data is available. Any information about analysis of Lamprecid will be appreciated.

Determination of Malathion by High Performance Liquid Chromatography

Malathion is the accepted (ANSI, BSI, ISO) common name for O, O-dimethyl dithiophosphate of diethyl mercaptosuccinate, a registered insecticide having the chemical structure:



Molecular formula: $C_{10}H_{19}O_6PS_2$

Molecular weight: 330.4

Physical state-color-odor: clear, colorless to amber liquid; technical grade 95% has a garlic-like odor

Melting point: 2.85°C

Boiling point: 156 to 157°C at 0.7 mm Hg with slight decomposition

Solubility: 145 ppm in water; limited solubility in petroleum oils but miscible with most organic solvents; light petroleum oil (30-60°C) is soluble in malathion to the extent of 35%

Stability: rapidly hydrolyzed at pH above 7.0 or below 5.0 but is stable in aqueous solutions buffered at pH 5.26; incompatible with alkaline pesticides and is corrosive to iron, hence lined containers must be used

Other names: mercaptothion (So. Africa); carbofos (USSR); mercaptotion (Argentina); maldison (Australia); Calmathion; Celthion; Cythion; Detmol MA 96% (Albert & Co. Germany); Emmatos; Emmatos Extra; ForMal; Fyfanon; Hilthion; Karbofos; Kop-Thion; Kypfos;

Malaspray; Malamar; Malaphele; Malathion; Malathion ULV Concentrate; Malatol; Malmed; Maltox; MLT; Sumitox; Vegfru Malatox; Zithol 0,0-dimethyl S-(1,2-dicarbethoxyethyl) phosphorodithioate; S-[1,2-di(ethoxycarbonyl)-ethyl] dimethyl phosphorothiolothionate

Reagents:

1. Malathion standard of known purity
2. Benzyl benzoate (internal standard) of known purity
3. Acetonitrile, HPLC grade
4. Methanol, HPLC grade
5. Internal standard solution - weigh 100 mg benzyl benzoate into a 100 ml volumetric flask, dissolve in and make to volume with methanol; mix thoroughly. Dilute 50 ml to 500 ml and mix well. (conc 0.1 mg/ml)

Equipment:

1. High Performance Liquid Chromatograph with UV detector at 254 nm. If a variable wavelength detector is available, other wavelengths may be used to increase sensitivity or to eliminate interference.
2. Column: uBondapak C18 (30 cm x 3.9 mm ID) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 60% acetonitrile + 40% water
Column temperature: 33°C
Flow rate: 2 ml/min
Wavelength: 254 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg malathion standard into a 125 ml screw-cap flask, add 100 ml internal standard solution by pipette, close tightly, and shake to dissolve. Filter a portion through a 0.45 micron filter. (conc 1 mg malathion and 0.1 mg benzyl benzoate per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 mg malathion into a 125 ml screw-cap flask, add 100 ml internal standard solution by pipette, close tightly and place in an ultrasonic bath for several minutes, then shake on a mechanical shaker for one hour. Filter through a 0.45 micron filter. (conc as above)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample.

Calculation:

Measure the peak heights or areas of the malathion and the benzyl benzoate for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area malathion}}{\text{peak height or area benzyl benzoate}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area malathion}}{\text{peak height or area benzyl benzoate}}$$

Average the standard and sample ratios, and calculate the percent malathion as follows:

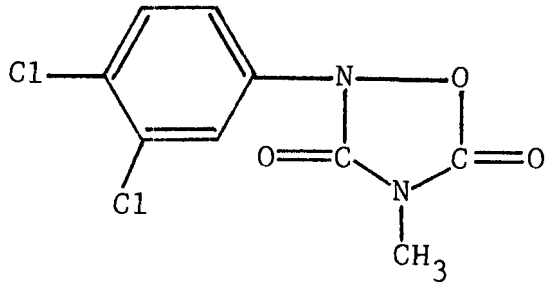
$$\% = \frac{(\text{ratio of sample})\ (\text{weight standard})\ (\%\ \text{purity of standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

Method submitted by EPA - NEIC, Denver, Colorado (G. Thomas Gale)
January 1980

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Methazole by Infrared Spectroscopy

Methazole is the accepted (ANSI, BSI, WSSA) common name for 2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_6Cl_2N_2O_3$

Molecular weight: 261.1

Physical state-color-odor: tan, dry solid; odorless when pure

Melting point: 123 to 124°C

Solubility: 1.5 ppm in water at 25°C; o.65% in methanol; 5.5% in xylene; 9.0% in acetone; soluble in chloroform and benzene

Stability: decomposes before boiling; subject to some decomposition by germicidal UV when dissolved in methanol and to sunlight when dissolved in water.

Other names: oxydiazol; Probe: VCS 438

Reagents:

1. Methazole standard of known purity
2. Chloroform, pesticide or spectro grade
3. Sodium sulfate, anhydrous, granular

Equipment:

1. Infrared spectrophotometer, double beam with matched 0.5mm NaCl cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of standard:

Weigh 100 mg methazole standard into a small glass-stoppered flask or screw-cap bottle, add 50 ml chloroform by pipette and a little anhydrous sodium sulfate to insure dryness, shake thoroughly, and allow to settle. (conc 2 mg/ml)

Preparation of sample:

Weigh a portion of sample equivalent to 200 mg methazole into a 250 ml glass-stoppered flask or screw-cap bottle, add 100 ml chloroform by pipette and some anhydrous sodium sulfate. Shake on a mechanical shaker for about one hour. Allow to settle, centrifuge or filter if necessary taking precautions to avoid evaporation of solvent. (conc 2 mg/ml)

IR Determination:

With chloroform in the reference cell, and using the optimum quantitative analytical settings for the particular IR instrument being used, scan both standard and sample solutions from 1538 to 1818 cm^{-1} (6.5 to 5.5 um). with a horizontal baseline from 1960 to 1666 cm^{-1} (5.1 to 6.0 um).

Calculation:

From the above absorbances and using the standard and sample concentrations, calculate the percent methazole as follows:

$$\% = \frac{\text{(abs. sample) (conc. std. in mg/ml) (\% purity)}}{\text{(abs. std.) (conc. sample in mg/ml)}}$$

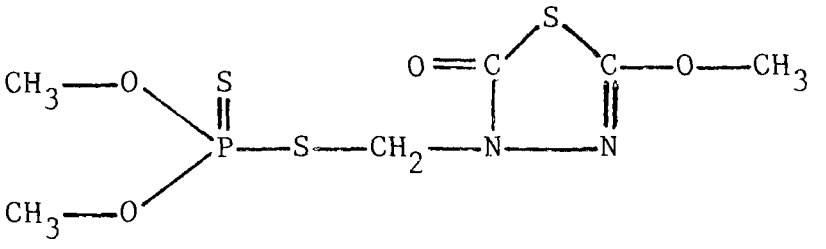
The absorbance is linear from 0.8 to 3.2 mg/ml.

Method submitted by EPA (former) Product Analysis Laboratory, Region II, New York, NY
March 1977

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Methidathion by Gas Chromatography (FID-IS)

Methidathion is the accepted (ANSI, BSI, ISO) common name for O,O-dimethyl phosphorodithioate S-ester with 4-(mercaptomethyl) 2-methoxy-delta 2-1,3,4-thiadiazolin-5-one, a registered insecticide and acaricide having the chemical structure:



Molecular formula: $C_6H_{11}N_2O_4PS_3$

Molecular weight: 302.3

Physical state-color-odor: colorless crystals, characteristic odor of organophosphates

Melting point: 39 to 40°C

Solubility: 240 ppm in water at 25°C; readily soluble in acetone, benzene, methanol

Stability: stable in neutral and weakly acid media but much less stable in alkali; compatible with captan, thiram, zineb, and acaricides; rapidly metabolized in plants

Other names: GS-13005; Supracide; Ultracide; S-(2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl) dimethyl phosphorothiolothionate; S-[(5-methoxy-2-oxo-1,3,4-thiadiazol-3(2H-yl) methyl]O,O-dimethyl phosphorodithioate

Reagents:

1. Methidathion standard of known purity
2. Dibutyl phthalate (internal standard), analytical grade
3. Acetone, pesticide grade

4. Internal standard solution - weigh 100 mg dibutyl phthalate into a 100 ml volumetric flask, dissolve in and make to volume with acetone, and mix well. (conc 1 mg/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 1/4" glass packed with 3% OV-1 on 100/200 mesh Supelcoport (or equivalent column)
3. Precision liquid syringe
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating conditions for FID:

Column temperature: 190°C
Injection port temperature: 250°C
Detector temperature: 250°C
Carrier gas: nitrogen - 30 ml/min (adjusted as necessary)
Hydrogen flow: adjusted as necessary
Air flow: adjusted as necessary

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg methidathion standard into a small glass-stoppered flask or polyseal-cap glass vial, add 25 ml internal standard solution by pipette, and shake to dissolve. (conc 4 mg methidathion and 1 mg dibutyl phthalate per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 mg methidathion into a small flask or vial as above, add 25 ml internal standard solution as above, and shake thoroughly to dissolve and extract the methidathion. For course or granular materials, shake mechanically for 10 to 15 minutes. Allow to settle and if necessary centrifuge (or filter) to clarify. (conc 4 mg methidathion and 1 mg dibutyl phthalate per ml)

GC Determination:

Inject 2 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the determination, making at least three injections each of standard and sample solutions. The elution order is dibutyl phthalate then methidathion.

Calculation:

Measure the peak heights or areas of the methidathion and dibutyl phthalate for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area methidathion}}{\text{peak height or area dibutyl phthalate}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area methidathion}}{\text{peak height or area dibutyl phthalate}}$$

Average the standard and sample ratios, and calculate the percent methidathion as follows:

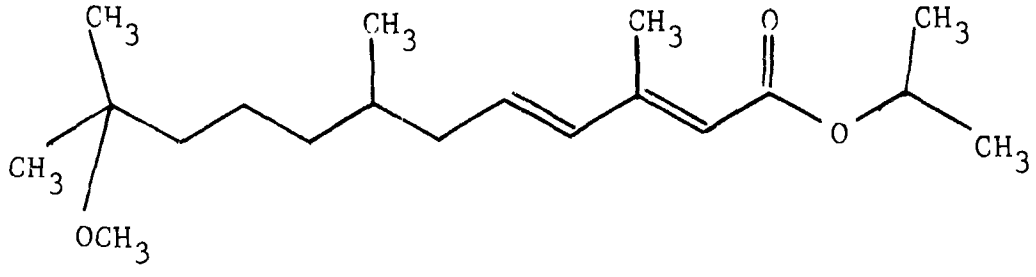
$$\% = \frac{(\text{ratio of sample})(\text{weight of standard})(\% \text{ purity of standard})}{(\text{ratio of standard})\ (\text{weight of sample})}$$

Method submitted by NEIC, Denver, Colorado (Chuck Rzeszutko), August 1979

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Methoprene by Gas Chromatography (FID-IS)

Methoprene is the accepted (ANSI) common name for isopropyl (2E,4E)-11-methoxy-3,7,11-trimethyl-2,4-dodecadienoate, a registered insect growth regulator having the chemical structure:



Molecular formula: $C_{19}H_{34}O_3$

Molecular weight: 310.5

Physical state-color-odor: amber liquid

Boiling point: 100°C at 0.05 mm Hg

Solubility: approximately 1.4 ppm in water; soluble in non-aqueous organic solvents

Stability:

Other names: Altosid; Altosid Briquets; ZR-515

Reagents:

1. Methoprene standard of known purity
2. Dibutyl phthalate internal standard of known purity
3. Chloroform, pesticide grade
4. Internal standard solution - weigh 1.4 gram dibutyl phthalate into a 100 ml volumetric flask, dissolve in and make to volume with chloroform, and mix well. (conc 14 mg/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 1/4" glass packed with 3.8% SE-30 on 80 to 100 mesh Diatoport S (or equivalent column)
3. Precision liquid syringe
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating conditions for FID:

Column temperature: 210°C
Injection port temperature: 225°C
Detector temperature: 230°C
Carrier gas: Helium - 20 ml/min (adjusted as necessary)
Hydrogen flow: 25 ml/min (adjusted as necessary)
Air flow: 40 ml/min (adjusted as necessary)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 110 mg methoprene standard into a 50 ml volumetric flask, add 5 ml internal standard solution by pipette, make to volume with chloroform, and mix thoroughly. Pipette a 5 ml aliquot into a second 50 ml volumetric flask and make to volume with chloroform; mix thoroughly. (conc 0.22 mg methoprene and 0.14 mg dibutyl phthalate per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 110 mg methoprene into a 125 ml glass-stoppered flask, add 5 ml internal standard solution by pipette, add 45 ml chloroform (graduated cylinder or pipette), stopper tightly, and shake for one hour on a mechanical shaker. Allow to settle, centrifuge or filter a portion if necessary, taking precaution to avoid evaporation of chloroform. Dilute a 5 ml portion to 50 ml as above. (conc as above)

GC Determination:

Inject 1 to 2 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the determination making at least three injections each of standard and sample solutions. The elution order is dibutyl phtnalate then methoprene.

Calculation:

Measure the peak heights or areas of the methoprene and dibutyl phthalate for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio standard} = \frac{\text{peak height or area methoprene}}{\text{peak height or area dibutyl phthalate}}$$

$$\text{Ratio sample} = \frac{\text{peak height or area methoprene}}{\text{peak height or area dibutyl phthalate}}$$

Average the standard and sample ratios, and calculate the percent methoprene as follows:

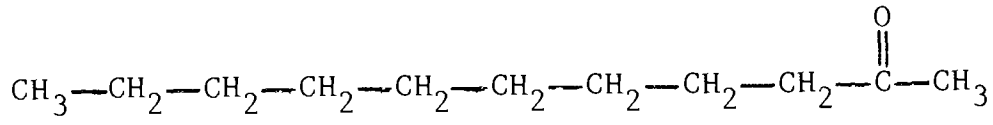
$$\% = \frac{(\text{ratio sample})\ (\text{weight standard})\ (\%\ \text{purity standard})}{(\text{ratio standard})\ (\text{weight sample})}$$

Method submitted by EPA (former) Product Analysis Laboratory, Region II,
New York, NY
January 1977

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Methyl Nonyl Ketone by Gas Chromatography (TCD-IS)

Methyl nonyl ketone is the popular name for 2-undecanone, a registered animal repellent having the chemical structure:



Molecular formula: $C_{11}H_{22}O$

Molecular weight: 170.3

Physical state-color-odor: clear liquid

Melting point: 11 to 13°C

Boiling point: 231.5 to 232.5°C (technical 95% purity - 223°C)

Solubility: insoluble in water; miscible with petroleum distillates and most other common organic solvents

Stability: effectiveness as a repellent last about 24 hours

Other names: MGK Dog and Cat Repellent

Reagents:

1. Methyl nonyl ketone standard of known purity
2. 2-ethyl-1,3-hexanediol (internal standard), analytical grade
3. Acetone, pesticide grade
4. Internal standard solution - weigh 2.5 grams 2-ethyl-1,3-hexanediol into a 100 ml volumetric flask, make to volume with acetone, and mix well. (conc 25 mg/ml)

Equipment:

1. Gas chromatograph with a thermal conductivity detector (TCD)
2. Column: 6' x 1/8" SS packed with 10% SE-30 on 80/100 Diatoport S or
   4' x 1/4" glass packed with 3.8% SE-30 on 80/100 Diatoport S
   (or equivalent column)
3. Precision liquid syringe
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating conditions for TCD:

Column temperature: 145°C for 1/8" column; 120°C for 1/4" column
Injection port temperature: 225°C
Detector temperature: 150°C
Filament current: 200 ma
Carrier gas: helium - flow adjusted as necessary

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 400 mg methyl nonyl ketone standard into a 25 ml volumetric flask, add 10 ml internal standard solution by pipette, and make to volume with acetone; mix well. (conc 16 mg methyl nonyl ketone and 10 mg internal standard per ml)

Preparation of sample:

For liquid samples, weigh an amount equivalent to 400 mg methyl nonyl ketone into a 25 ml volumetric flask, add 10 ml internal standard solution by pipette, and make to volume with acetone; mix well.
For granules and dusts, weigh a portion of sample equivalent to 400 mg methyl nonyl ketone into a small glass-stoppered flask or screw-cap bottle, add 10 ml of internal standard solution by pipette and 15 ml acetone by pipette, close tightly and shake on a mechanical shaker for 30 minutes. Allow to settle, and if necessary centrifuge or filter to clarify.
(conc 16 mg methyl nonyl ketone and 10 mg internal standard per ml)

GC Determination:

Inject 3 to 5 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the determination, making at least three injections each of standard and sample solutions. The elution order is 2-ethyl-1,3-hexanediol then methyl nonyl ketone.

Calculations:

Measure the peak heights or areas of the methyl nonyl ketone and the 2-ethyl-1,3-hexanediol for both standard and sample solutions and calculate the ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area methyl nonyl ketone}}{\text{peak height or area 2-ethyl-1,3-hexanediol}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area methyl nonyl ketone}}{\text{peak height or area 2-ethyl-1,3-hexanediol}}$$

Average the standard and sample ratios, and calculate the percent methyl nonyl ketone as follows:

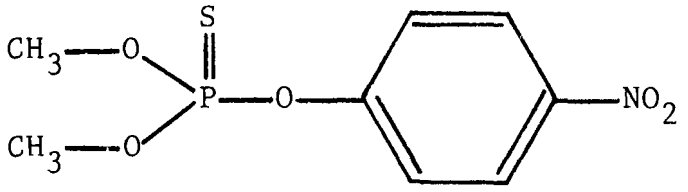
$$\% = \frac{(\text{ratio of sample})(\text{weight of standard})(\% \text{ purity of standard})}{(\text{ratio of standard})\ (\text{weight of sample})}$$

Method submitted by EPA (former) Product Analysis Laboratory, Region II, New York, NY January 1976

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Methyl Parathion by High Performance Liquid Chromatography

Methyl parathion is the accepted (BSI, ISO) common name for O,O-dimethyl-O-p-nitrophenyl phosphorothioate, a registered insecticide having the chemical structure:



Molecular formula: $C_8H_{10}NO_5PS$

Molecular weight: 263.2

Physical state-color-odor: white crystalline solid; the technical product is a light to dark tan liquid of about 80% purity, crystallizing at about 29°C

Melting point: 35 to 36°C

Solubility: 55 to 60 ppm in water at 25°C; slightly soluble in light mineral and petroleum oils; soluble in most other organic solvents

Stability: hydrolyzed by alkalis; compatible with most other pesticides except alkaline materials; isomerizes on heating; it is a good methylating agent

Other names: Cekumethion; Devithion; Dimethyl Parathion; Drexel Methyl Parathion 4E; E601; Folidol M; Fosferno M50; Gearphos; Metacide; Metaphos; Metron; Nitrox 80; Parataf; Paratox; Partron M; Penncap-M; Tekwaisa; Vertac Methyl Parathion Technisch 80%; Wofatox

Reagents:

1. Methyl parathion standard of known purity
2. Methanol, HPLC grade
3. Water, HPLC grade
4. Acetic acid, ACS

Equipment:

1. High Performance Liquid Chromatograph with UV detector at 254 nm. If a variable wavelength detector is available, other wavelengths may be used to increase sensitivity or to eliminate interference.
2. Column: Radial-Pak C18 or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 77% methanol + 22% water + 1% acetic acid (one solution)
Column temperature: ambient
Flow rate: 5 to 7 ml/min
Wavelength: 254 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg methyl parathion into a 125 ml screw-cap flask, add 100 ml methanol by pipette, close tightly, and shake to dissolve. Filter through a 0.45 micron filter. (conc 1 mg/ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 ml methyl parathion into a 125 ml screw-cap flask, add 100 ml methanol by pipette, close tightly, and shake for 30 minutes on a mechanical shaker. (A few minutes in an ultrasonic bath may help to effect solution) Filter through a 0.45 micron filter. (conc 1 mg/ml)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solutions.

Calculation:

Measure the peak height or peak area for each peak and calculate the average for both standard and sample. Using these averages, calculate the percent methyl parathion as follows:

$$\% = \frac{(\text{peak height or area sample})(\text{weight standard injected})(\% \text{ purity standard})}{(\text{peak height or area standard})\ (\text{weight sample injected})}$$

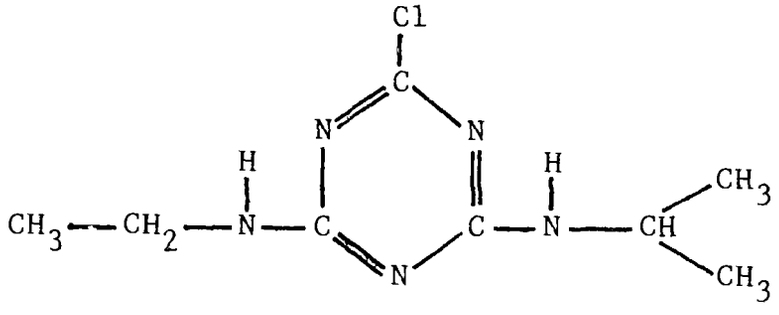
This is a modification of Methyl Parathion EPA-1 for using a Radial-Pak column and acid suppression.

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Atrazine and Metolachlor Mixtures by Gas Chromatography (FID-IS)

Atrazine:

Atrazine is the accepted (ANSI, BSI, ISO, WSSA) common name for 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine, a registered herbicide having the chemical structure:



Molecular formula: $C_8H_{14}ClN_5$

Molecular weight: 215.7

Physical state-color-odor: colorless crystalline solid

Melting point: 173 to 175°C

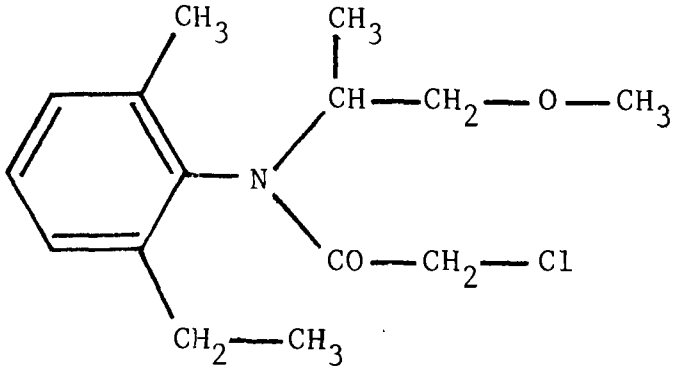
Solubility: 33 ppm in water at 25°C; 1.2% in ethyl ether; 1.8% in methanol; 2.8% in ethyl acetate; 5.2% in chloroform; 18.3% in dimethyl sulfoxide

Stability: stable in neutral and slightly acidic or basic media; hydrolyzes in acid and alkaline conditions of higher temperatures to the herbicidally inactive hydroxy derivative; non-flammable; non-corrosive under normal use conditions; very stable shelf life with only slight sensitivity to natural light and extreme temperature; compatible with most other pesticides

Other names: AAtrex; Atranex; Atratol; Crisatrina; Crisazine; G 30027; Gesaprim; Griffex; Primatol A; Shell Atrazine Herbicide; Vectal SC; 6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine

Metolachlor:

Metolachlor is the accepted (ANSI, ISO, WSSA) common name for 2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide, a registered herbicide having the chemical structure:



Molecular formula: $C_{15}H_{22}NO_2Cl$

Molecular weight: 283.8

Physical state-color-odor: odorless, white to tan liquid

Boiling point: 100°C at 0.001 mm Hg

Solubility: 530 ppm in water at 20°C; miscible with xylene, toluene, dimethyl formamide, methyl cellusolve, butyl cellusolve, ethylene dichloride, and cyclohexanone; insoluble in ethylene glycol and propylene glycol

Stability: compatible with most pesticides and fluid fertilizers when used at normal rates; non-corrosive to steel or tin; not harmful to plastic or fiberglass spray tanks; shelf life estimated to be 5 years minimum based on no significant decomposition at 70°C for 3 weeks or at 50°C for 20 weeks; no crystallization at temperatures below 0°C

Other names: Bicep; CGA-24705; Codal; Cotoran Multi; Milocep; Ontrack 8E; Primagram; Primatex

Reagents:

1. Atrazine standard of known purity
2. Metolachlor standard of known purity
3. Alachlor (internal standard) of known purity
4. Acetone, pesticide grade
5. Internal standard solution - weigh 500 mg alachlor into a 50 ml volumetric flask, dissolve in and make to volume with acetone; mix well. (conc 10 mg/ml)

Equipment:

1. Gas chromatograph with a flame ionization detector (FID)
2. Column: 6' x 2 mm ID glass packed with 3% SE-30 on 100/120 mesh Chromosorb W HP
3. Precision liquid syringe: 10 ul
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating conditions:

Column temperature: 150°C
Injection port temperature: 250°C
Detector temperature: 250°C
Carrier gas: helium - flow: adjusted as necessary
Hydrogen flow: adjusted as necessary
Air flow: adjusted as necessary

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 80 mg each of atrazine standard and metolachlor standard into a 100 ml volumetric flask, add 10 ml internal standard solution by pipette, make to volume with acetone, close tightly and mix thoroughly. (conc 0.8 mg atrazine, 0.8 mg metolachlor, and 1 mg alachlor per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 80 mg atrazine and/or metolachlor (if the percent of atrazine and metolachlor differ too much for one solution, make two solutions) into a 100 ml volumetric flask, add 10 ml internal solution, make to volume with acetone, close tightly and mix thoroughly.

(conc as above)

GC Determination:

Inject 1 or 2 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the determination, making at least three injections each of standard and sample solutions. The elution order is atrazine, alachlor, then metolachlor.

Calculation:

Measure the peak heights or areas of the atrazine, alachlor, and metolachlor for both standard and sample solutions and calculate the following ratios:

$$\text{atrazine: ratio of standard} = \frac{\text{peak height or area atrazine}}{\text{peak height or area alachlor}}$$

$$\text{ratio of sample} = \frac{\text{peak height or area atrazine}}{\text{peak height or area alachlor}}$$

$$\text{metolachlor: ratio of standard} = \frac{\text{peak height or area metolachlor}}{\text{peak height or area alachlor}}$$

$$\text{ratio of sample} = \frac{\text{peak height or area metolachlor}}{\text{peak height or area alachlor}}$$

Average the standard and sample ratios, and calculate the percent atrazine and metolachlor as follows:

$$\%\ \text{atrazine} = \frac{(\text{ratio of sample})(\text{weight standard})(\%\ \text{purity standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

$$\%\ \text{metolachlor} = \frac{(\text{ratio of sample})(\text{weight standard})(\%\ \text{purity standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

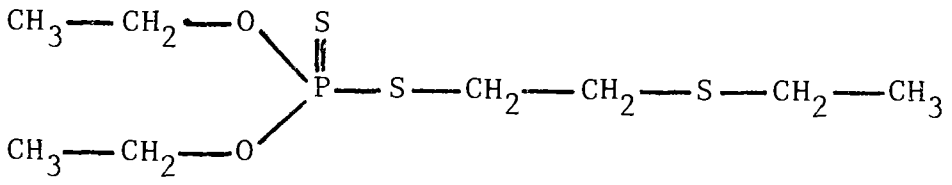
This method is an adaptation of Atrazine EPA-2 (Tentative) October 1975
EPA Beltsville Chemistry Lab, Beltsville, MD (Jack B. Looker)
April 1978

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Disulfoton and Fensulfothion Mixtures by Gas Chromatography (FID-IS)

Disulfoton:

Disulfoton is the accepted (BSI, ISO) common name for O,O-dimethyl S-[2-(ethylthio)ethyl]phosphorodithioate, a registered insecticide and acaricide having the chemical structure:



Molecular formula: $C_8H_{19}O_2PS_3$

Molecular weight: 274.4

Physical state-color-odor: pure - colorless to pale yellow liquid with a characteristic odor of sulfur compounds
technical - dark yellowish oil with an aromatic odor

Boiling point: 62°C at 0.1 mm Hg

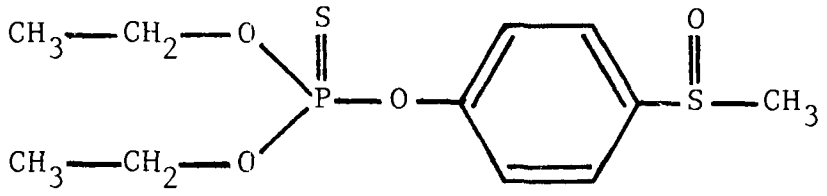
Solubility: 25 ppm in water at room temperature; readily soluble in most organic solvents

Stability: subject to hydrolysis under alkaline conditions; stable in normal storage

Other names: Bay 276; Bay 19639; Disyston; Di-Syston (in U.S.); dithiodemeton; dithiosustox; Frumin AL; M-74 (USSR); Solvirex

Fensulfothion:

Fensulfothion is the accepted (BSI, ISO) common name for O,O-diethyl O-[4-(methylsulfinyl)phenyl]phosphorothioate, a registered insecticide and nematicide having the chemical structure:



Molecular formula: $C_{11}H_{17}O_4PS_2$

Molecular weight: 308.35

Physical state-color-odor: oily yellowish-brown liquid

Boiling point: 138 to 141°C at 0.0 mm Hg

Solubility: slightly soluble in water (1600 ppm); soluble in most organic solvents except aliphatic

Stability: believed to be compatible with most insecticides and fungicides except alkaline materials; subject to hydrolysis; readily oxidized to the sulphone; isomerizes readily to the S ethyl isomer

Other names: Bay 25141; Dasanit; S767; Terracur P; diethyl-p-methylsulfinylphenyl thiophosphate

Reagents:

1. Disulfoton standard of known purity
2. Fensulfothion standard of known purity
3. Dipentyl phthalate (internal standard) of known purity
4. Acetone, pesticide grade
5. Internal standard solution - weigh 750 mg dipentyl phthalate into a 50 ml volumetric flask, dissolve in and make to volume with acetone; mix well. (conc 15 mg/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 2 mm ID glass packed with 5% SE-30 on 80/100 mesh Chromosorb W HP (or equivalent column)
3. Precision liquid syringe: 10 ul
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating conditions for FID:

Column temperature: 210°C
Injection port temperature: 250°C
Detector temperature: 250°C
Carrier gas: helium or nitrogen - flow: adjusted as necessary
Hydrogen flow: adjusted as necessary
Air flow: adjusted as necessary

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg disulfoton and 100 mg fensulfothion standards into a 50 ml volumetric flask, add 5 ml internal standard solution by pipette, make to volume with acetone, close tightly and mix thoroughly. (conc 2 mg disulfoton, 2 mg fensulfothion, and 1.5 mg dipentyl phthalate per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 mg disulfoton and/or fensulfothion (if the percent of disulfoton and fensulfothion differ too much for one solution, make two solutions) into a 50 ml volumetric flask, add 5 ml internal standard solution by pipette, make to volume with acetone, close tightly and mix thoroughly. (conc as above)
For solid samples, use a 125 ml screw-cap flask instead of a 100 ml volumetric flask and add 5 ml internal standard solution and 45 ml acetone by pipette)

GC Determination:

Inject 5 ul of standard and, if necessary adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the

determination, making at least three injections each of standard and sample solutions. The elution order is disulfoton, dipentyl phthalate, then fensulfothion.

Calculation:

Measure the peak heights or areas of the disulfoton, dipentyl phthalate, and fensulfothion for both standard and sample solutions and calculate the following ratios:

$$\text{disulfoton: ratio of standard} = \frac{\text{peak height or area disulfoton}}{\text{peak height or area dipentyl phthalate}}$$

$$\text{ratio of sample} = \frac{\text{peak height or area disulfoton}}{\text{peak height or area dipentyl phthalate}}$$

$$\text{fensulfothion: ratio of standard} = \frac{\text{peak height or area fensulfothion}}{\text{peak height or area dipentyl phthalate}}$$

$$\text{ratio of sample} = \frac{\text{peak height or area fensulfothion}}{\text{peak height or area dipentyl phthalate}}$$

Average the standard and sample ratios, and calculate the percent disulfoton and fensulfothion as follows:

$$\%\ \text{disulfoton} = \frac{(\text{ratio of sample})(\text{weight standard})(\%\ \text{purity standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

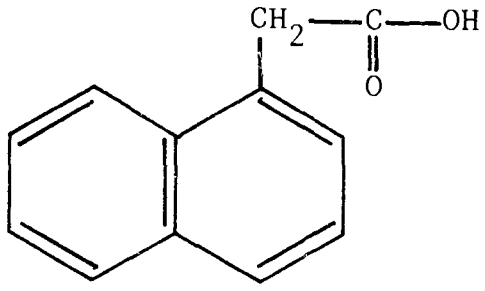
$$\%\ \text{fensulfothion} = \frac{(\text{ratio of sample})(\text{weight standard})(\%\ \text{purity standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

Method submitted by Mark W. Law, EPA Chemistry Lab, Beltsville, MD
March 1976

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Naphthaleneacetic acid and Its Ammonium Salt by High Performance Liquid Chromatography

Naphthaleneacetic acid is the accepted (BSI, ISO) common name for 1-naphthaleneacetic acid, a registered plant growth regulator having the chemical structure:



Molecular formula: $C_{12}H_{10}O_2$

Molecular weight: 186.21

Physical state-color-odor: odorless, white crystals or amorphorous powder

Melting point: 134 to 125°C

Solubility: 420 ppm in water at 20°C; slightly soluble in carbon tetrachloride and xylene; very soluble in acetone, chloroform, ethanol, and isopropanol

Stability: non-flammable; non-corrosive; stable on storage; compatible with other pesticides

Other names: Celmone; Fruitone N; NAA; NAA 800; Nafusaku; Phyomone; Planofix; Plucker; Primacol; Rootone; Stik; Tekkam; TipOff; Transplantone; Tre-Hold

Reagents:

1. Naphthaleneacetic acid standard of known purity
2. Methanol, ACS

3. 1% Acetic acid in methanol solution
4. 0.0025M Phosphoric acid aqueous solution

Equipment:

1. High Performance Liquid Chromatograph with a variable wavelength UV detector at 272 nm. If a variable wavelength detector is not available, operating parameters and concentrations may have to be changed to obtain the necessary separation and sensitivity.
2. Column: uBondapak C18 (30 cm x 3.9 mm ID) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 65% Methanol + 35% 0.0025M Phosphoric acid aqueous solution
Column temperature: 55°C (ambient temperature could be used with a change in parameters)
Flow rate: 1.2 ml/min
Wavelength: 272 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg naphthaleneacetic acid standard into a 100 ml volumetric flask, dissolve in and make to volume with 1% acetic acid - methanol solution. Mix well and dilute a 25 ml aliquot to 100 ml with the acetic acid - methanol solution. Filter a portion through a 0.45 micron filter. (conc 0.25 mg/ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 mg naphthaleneacetic acid into a 100 ml volumetric flask, dissolve in and make to volume with 1% acetic acid - methanol solution. Mix well and dilute 25 ml to 100 ml as above. Filter a portion through a 0.45 micron filter. (conc as above)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solutions.

Calculation:

Measure the peak height or area for each peak and calculate the average for both standard and sample. Using these averages, calculate the percent naphthaleneacetic acid as follows:

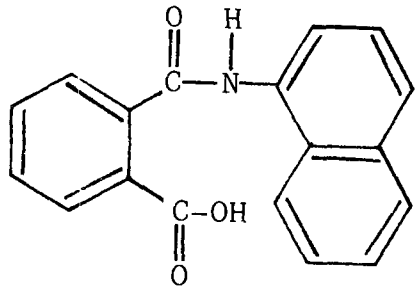
$$\% = \frac{(\text{peak height or area sample})(\text{weight standard injected})(\% \text{ purity standard})}{(\text{peak height or area standard})\ (\text{weight sample injected})}$$

Method submitted by E. S. Greer, EPA (formerly) Product Analysis Laboratory, Region IX, San Francisco, California (Mr. Greer is now at Beltsville, MD) August 1977

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Naptalam by Ultraviolet Spectroscopy

Naptalam is the accepted (BSI, ISO, WSSA) common name for N-1-naphthylphthalamic acid, a registered herbicide having the chemical structure:



Molecular formula: $C_{18}H_{13}NO_3$

Molecular weight: 291.3

Physical state-color-odor: purple crystalline powder with an unpleasant odor

Melting point: 185°C

Solubility: 200 ppm in water, 5900 ppm in acetone, 2100 ppm in isopropanol; slightly soluble in benzene and ethanol; insoluble in hexane and xylene; alkali metal salts are readily soluble in water

Stability: Hydrolyzed in solutions of pH more than 9.5; unstable at elevated temperatures, tending to form the imide; non-corrosive; non- explosive

Other names: Alanap; ACP 322; NPA; 6Q8: Dyanap

Reagents:

1. Naptalam standard of known purity
2. Hexane, pesticide or spectro grade
3. Glacial acetic acid
4. Sodium hydroxide, 0.25N

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells.
2. Filtration apparatus, medium porosity fritted glass crucibles, buchner funnels
3. Usual laboratory glassware

Procedure:

Preparation of standard:

Weigh 100 mg naptalam standard into a 100 ml volumetric flask, dissolve in and make to volume with 0.25N NaOH. Mix thoroughly and pipette 5 ml into a 250 ml volumetric flask; make to volume with distilled water and mix thoroughly. (final conc 20 ug/ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 mg naptalam into a 50 ml beaker, add 1 ml glacial acetic acid and mix thoroughly. Add 10 ml hexane, swirl, and let stand until the naptalam precipitates (ten minutes or so). Filter through a medium porosity fritted glass crucible and wash the beaker and filtered precipitate three times with small amounts of hexane. Change buchner flask and wash the filtered precipitate through the frittered glass crucible by dissolving the precipitate in 0.25N NaOH. Rinse the 50 ml beaker with portions of the 0.25N NaOH also. Transfer the filtrate to a 200 ml volumetric flask and make to volume with a 0.25N NaOH. Mix thoroughly and pipette 10 ml into a 250 ml volumetric flask; make to volume with distilled water and mix thoroughly.

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen at 0 and 100% transmission at 282 nm with distilled water in each cell. Scan both standard and sample solutions from 350 to 220 nm with distilled water in the reference cell.

Calculations:

From the above absorbances and using the standard and sample concentrations, calculate the percent naptalam as follows:

$$\% = \frac{\text{(abs. sample) (conc. std. in ug/ml) (\% purity)}}{\text{(abs. std.) (conc. sample in ug/ml)}}$$

Gravimetric factor: naptalam acid x 1.0755 = naptalam sodium salt

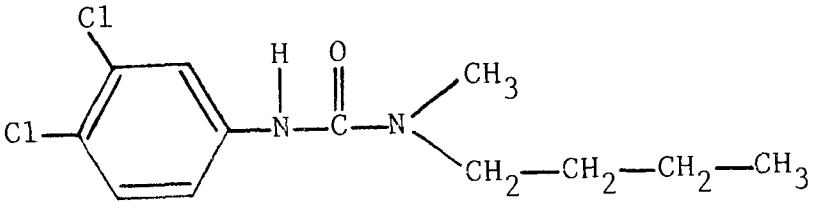
Method originally from Mississippi State Chemical Laboratory, Mississippi State, Mississippi 39762.

Method checked by Jack Looker, Beltsville Chemistry Laboratory, CBIB, BFSD, OPTS, EPA. There is a straight line relationship between absorbance and concentration for up to 50 ug/ml.

Any criticism, suggestions, or data concerning the use of this method will be appreciated.

Determination of Neburon by Ultraviolet Spectroscopy

Neburon is the accepted (BSI, ISO, WSSA) common name for 1-n-butyl-3-(3,4-dichlorophenyl)-1-methylurea, a registered herbicide having the chemical structure:



Molecular formula: $C_{12}H_{16}Cl_2N_2O$

Molecular weight: 275.18

Physical state-color-odor: odorless, white crystalline solid

Melting Point: 102 to 103°C

Solubility: 4.8 ppm in water at 24°C; very low in common hydrocarbon solvents

Stability: stable toward oxidation and moisture under normal storage conditions

Other names: Granurex; Kloben; Neburex

Reagents:

1. Neburon standard of known purity
2. Methylene chloride, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells.
2. Mechanical shaker
3. Filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of standard:

Weigh 100 mg neburon standard into a 100 ml volumetric flask, dissolve in and make to volume with methylene chloride. Mix thoroughly and pipette 10 ml into a second 100 ml volumetric flask. Make to volume with methylene chloride, mix thoroughly, and pipette 5 ml into a third 100 ml volumetric flask. Make to volume with methylene chloride and mix thoroughly. (final conc 5 ug/ml).

Preparation of sample:

Weigh a portion of sample equivalent to 100 ml neburon into a 250 ml glass-stoppered flask or screw-cap bottle, add 100 ml methylene chloride by pipette, stopper tightly, and shake on a mechanical shaker for at least fifteen minutes. Allow to settle, centrifuge or filter if necessry taking precautions to avoid evaporation of solvent. Dilute 10 ml to 100 ml and then 5 ml to 100 ml as under standard preparation. (final conc 5 ug neburon/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen at 0 and 100% transmission at 252 nm with methylene chloride in each cell. Scan both the standard and sample solutions from 350 to 200 nm with methylene chloride in the reference cell. Measure the absorbance of standard and sample at 252 nm.

Calculations:

From the above absorbances and using the standard and sample concentrations, calculate the percent neburon as follows:

$$\% = \frac{(\text{abs. sample})\ (\text{conc. std. in ug/ml})\ (\% \text{ purity})}{(\text{abs. std.})\ (\text{conc. sample in ug/ml})}$$

Method submitted (summer - ?) 1978 by:

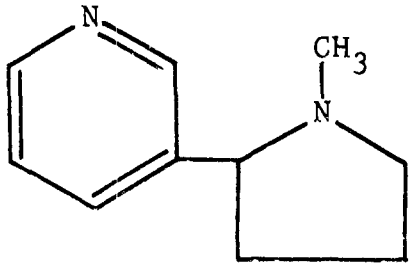
Dr. Gabriele Tartari
Agrochemical Department
Control Laboratory
CIBA-GEIGY S.P.A.
C.P. 88
I-21047 SARONNO (VA)
ITALY

Note: The amount of standard and sample and some dilution factors have been changed to allow more significant figures in the calculations and to reduce errors in weighings and making dilutions. The final concentrations are as in the method as received.

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Nicotine by High Performance Liquid Chromatography

Nicotine is the trivial name for 3-(1-methyl-2-pyrrolidyl) pyridine, a registered insecticide having the chemical structure:



Molecular formula: $C_{10}H_{14}N_2$

Molecular weight: 162.2

Physical state-color-odor: colorless liquid alkaloid

Boiling point: 247°C

Solubility: miscible with water below 60°C (forms a hydrate); miscible with ethanol and ether; readily soluble in most organic solvents

Stability: very hydroscopic; darkens slowly and becomes viscous on exposure to air; forms mono and dibasic salts with many acids and metals

Other names: Black Leaf 40

Reagents:

1. Nicotine standard of known purity
2. Phenol (internal standard) of known purity (make sure that the phenol gives a clean chromatogram with no co-eluting peaks)
3. Aqueous mobile phase - (0.0025M 1-heptane sulfonic acid sodium salt and 0.04M tetramethylammonium chloride adjusted to pH 3.0 with sulfuric acid) Filter through a 0.45 micron filter.
4. Organic mobile phase - (0.06M tetramethylammonium chloride in 200 ml water adjusted to pH 3.0 with sulfuric acid plus 800 ml acetonitrile) Filter through a 0.45 micron filter.

5. Internal standard solution - weigh 1.1 grams phenol into a 500 ml volumetric flask, dissolve in and make to volume with aqueous mobile phase. (conc 2.2 mg/ml)

Equipment:

1. High Performance Liquid Chromatograph with UV detector at 254 nm. If a variable wavelength detector is available, other wavelengths may be used to increase sensitivity or to eliminate interference.
2. Column: MicroPak MCH-10 (30 cm x 4 mm ID) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 85% aqueous mobile phase + 15% organic mobile phase
Column temperature: ambient
Flow rate: 1.5 to 2.0 ml/min
Wavelength: 254 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 95 mg nicotine standard into a 50 ml volumetric flask, make to volume with internal standard solution, and mix well. Dilute 10 ml to 50 ml, mix well, and filter through a 0.45 micron filter. (conc 0.38 mg nicotine and 2.2 mg phenol per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 95 mg nicotine into a 50 ml volumetric flask, dissolve in and make to volume with internal standard solution, and mix well. Dilute 10 ml to 50 ml, mix well, and filter through a 0.45 micron filter. (conc 0.38 mg nicotine and 2.2 mg phenol per ml)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give good convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solutions. Elution order is nicotine then phenol.

Calculation:

Measure the peak heights or areas of the nicotine and the phenol for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area nicotine}}{\text{peak height or area phenol}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area nicotine}}{\text{peak height or area phenol}}$$

Average the standard and sample ratios, and calculate the percent nicotine as follows:

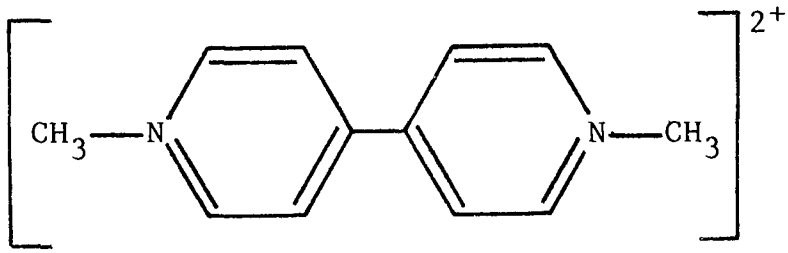
$$\% = \frac{(\text{ratio of sample})\ (\text{weight standard})\ (\%\ \text{purity of standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

Method submitted by EPA - NEIC, Denver, Colorado (G. Thomas Gale)
January 1980

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Paraquat by High Performance Liquid Chromatography

Paraquat is the accepted (ANSI, BSI, ISO, WSSA) name for 1,1'-dimethyl-4,4'-bipyridylium ion; usually present as the dichloride or dimethyl sulfate salt. Paraquat is a registered herbicide and desiccant and has the chemical (cation) structure:



Molecular formula: $C_{12}H_{14}N_2$ (cation); $C_{12}H_{14}N_2Cl_2$ (dichloride salt)

Molecular weight: 186.3 (cation); 257.2 (dichloride salt)

Physical state-color-odor: both the dichloride and the dimethyl sulfate salts are white deliquescent crystalline solids; the technical product is greater than 95% pure

Melting point: both salts - decompose about 300°C

Solubility: both salts are freely soluble in water, sparingly soluble in lower alcohols, insoluble in hydrocarbons

Stability: both salts are stable under acid conditions but are hydrolyzed by alkali; generally compatible with non-alkaline aqueous solutions but may be inactivated by inert clays and anionic surfactants; decompose in UV light; unformulated products are corrosive to metals

Other names: Crisquat; Dextrone X; Dexuron; Esgram; Gramonol; Gramoxone; Gramuron; Herboxone; Para-Col; Pathclear; Pillarquat; Pillarxone; Sweep; Terraklene; TotaCol; Toxer Total; Weedol

Reagents:

1. Paraquat (dichloride) standard of known purity
2. Phenol (internal standard) of known purity (make sure that the phenol gives a clean chromatogram with no co-eluting peaks)
3. Aqueous mobile phase - (0.0025M 1-heptane sulfonic acid sodium salt and 0.04M tetramethylammonium chloride adjusted to pH 3.0 with sulfuric acid) Filter through a 0.45 micron filter.
4. Organic mobile phase - (0.06M tetramethylammonium chloride in 200 ml water adjusted to pH 3.0 with sulfuric acid plus 800 ml acetonitrile) Filter through a 0.45 micron filter.
5. Internal standard solution - weigh 1.5 grams phenol into a 500 ml volumetric flask, dissolve in and make to volume with aqueous mobile phase. (conc 3 mg/ml)

Equipment:

1. High Performance Liquid Chromatograph with UV detector at 254 nm. If a variable wavelength detector is available, other wavelengths may be used to increase sensitivity or to eliminate interference.
2. Column: MicroPak MCH-10 (30 cm x 4 mm ID) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 80% aqueous mobile phase + 20% organic phase
Column temperature: ambient (for excessive tailing, increase organic mobile phase or insulate column at 25°C)
Flow rate: 1.5 to 2.0 ml/min
Wavelength: 254 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 50 mg paraquat (dichloride) standard into a 100 ml volumetric flask, dissolve in and make to volume with internal standard solution; mix well. Filter a portion through a 0.45 micron filter. (conc 0.5 mg paraquat (dichloride) and 3 mg phenol per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 50 mg paraquat (dichloride) into a 125 ml screw-cap flask, add 100 ml internal standard solution by pipette, close tightly, and shake on a mechanical shaker for 30 minutes. Filter a portion through a 0.45 micron filter. (conc 0.5 mg paraquat (dichloride) and 3 mg phenol per ml)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solutions.

Calculation:

Measure the peak heights or areas of the paraquat (dichloride) and the phenol for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area paraquat (dichloride)}}{\text{peak height or area phenol}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area paraquat (dichloride)}}{\text{peak height or area phenol}}$$

Average the standard and sample ratios, and calculate the percent paraquat (dichloride) as follows:

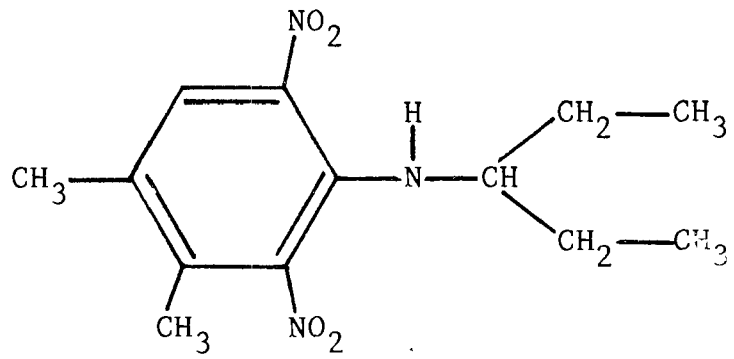
$$\% = \frac{\text{(ratio of sample) (weight of standard) (\% purity of standard)}}{\text{(ratio of standard) (weight of sample)}}$$

Method submitted by EPA - NEIC, Denver, Colorado (G. Thomas Gale)
January 1980

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Pendimethalin by Gas Chromatography (TCD-IS)

Pendimethalin is the accepted (ANSI, WSSA) common name for N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzeamine, a registered herbicide having the chemical structure:



Molecular formula: $C_{13}H_{19}N_3O_4$

Molecular weight: 281.3

Physical state-color-odor: orange-yellow crystalline solid with a faint nutty odor

Melting point: 54 to 58°C

Boiling point: 330°C

Solubility: less than 0.5 ppm in water at 20°C; soluble in chlorinated hydrocarbons and aromatic solvents

Stability: stable to alkaline and acidic conditions; non-corrosive

Other names: AC 92553; Accotab; Cynoff; Go-Go-San; Herbadox; Nicocyan; Pay-off; penoxyn; penoxalin; Prowl; N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine

Reagents:

1. Pendimethalin standard of known purity
2. Pyrene (internal standard) of known purity
   Note: pyrene is available from Sigma Chemical Co. and Aldrich Chemical Co. Pyrene is a possible carcinogen and should be handled accordingly.
3. Chloroform, pesticide grade
4. Internal standard solution - weigh 1.0 gram pyrene into a 100 ml volumetric flask, dissolve in and make to volume with chloroform; mix well. (conc 10 mg/ml)

Equipment:

1. Gas chromatograph with thermal conductivity detector (TCD)
2. Column: 4' x 1/4" glass packed with 3.8% SE-30 on 80 to 100 mesh Diatoport S (or equivalent column)
3. Precision liquid syringe
4. Usual laboratory glassware

Operating conditions for TCD:

Column temperature: 205°C
Injection port temperature: 225°C
Detector temperature: 230°C
Filament current: 200 ma
Carrier gas: Helium - flow adjusted as necessary

Procedure:

(This method is for emulsifiable concentrates but could be adapted to other formulations if and when they become available.)

Preparation of standard:

Weigh 140 mg pendimethalin standard into a small screw-cap flask or bottle, add 20 ml internal standard solution by pipette and 20 ml chloroform by graduated cylinder (or pipette); mix thoroughly. (conc 3.5 mg pendimethalin and 5 mg pyrene per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 140 mg pendimethalin into a small flask or bottle and treat exactly as under preparation of standard as above. Shake thoroughly to insure adequate mixing of sample and solvent.

GC Determination:

Inject 3 to 5 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and to obtain peak heights of 1/3 to 2/3 full scale. Proceed with the determination, making at least three injections each of standard and sample solutions. The elution order is pendimethalin then pyrene.

Calculation:

Measure the peak heights or areas of the pendimethalin and pyrene for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area pendimethalin}}{\text{peak height or area pyrene}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area pendimethalin}}{\text{peak height or area pyrene}}$$

Average the standard and sample ratios, and calculate the percent pendimethalin as follows:

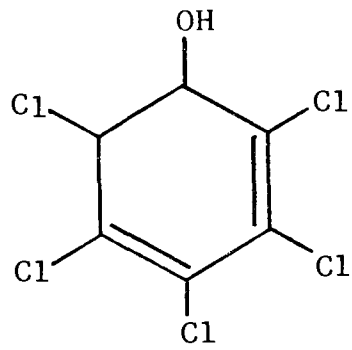
$$\% = \frac{(\text{ratio of sample})\ (\text{weight of standard})\ (\%\ \text{purity of standard})}{(\text{ratio of standard})\ (\text{weight of sample})}$$

Method submitted by EPA (former) Product Analysis Laboratory, Region II, New York, NY
June 1977

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Pentachlorophenol by Gas Chromatography (FID-IS) Using on Column Derivatization with MSFTA

Pentachlorophenol (also commonly known as PCP and penta) is a registered insecticide, fungicide, herbicide, and molluscicide. It has the chemical structure:



Molecular formula: C_6HCl_5O

Molecular weight: 266.34

Physical state-color-odor: colorless crystals with a phenolic odor (crude products are dark grayish flakes or powder)

Melting point: 191°C (pure); 187 to 189°C (crude)

Solubility: 20 ppm in water at 30°C; soluble in most organic solvents; limited solubility in carbon tetrachloride and petroleum oils of low aromatic or olefin content

Stability: non-flammable; non-corrosive except in presence of moisture; aqueous solutions have an alkaline reaction

Sodium salt: forms buff colored flakes with one mole of water of crystallization; solubility in water is 33 grams/100 ml at 25°C; insoluble in petroleum oils

Other names: Antimicrobial; Dowicide; Dowicide G; Dowicide EC-7; Dow Pentachlorophenol DP-2; penchlorol; Pentacon; Penwar; Priltox; Santobrite; Santophen; Sinituho; Weedone

Reagents:

1. Pentachlorophenol standard of known purity
2. Dibutyl phthalate (internal standard) of known purity
3. Acetone, analytical grade or better
4. MFSTA [N-methyl-N-trimethyl-silyltrifluoracetamide] derivatization reagent
5. Internal standard solution - weigh 500 mg dibutyl phthalate into a 100 ml volumetric flask, dissolve in and make to volume with acetone, and mix well. (conc 5 mg/ml)

Equipment:

1. Gas chromatograph with flame ionization detector
2. Column: 6' x 1/4" glass packed with 3% OV-1 on Supelcoport 100/200 (or equivalent column)
3. Precision liquid syringe: 10 ul
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating conditions for FID:

Column temperature: 180°C
Injection port temperature: 225°C
Detector temperature: 300°C
Carrier gas: nitrogen - flow adjusted as necessary (approx. 25 ml/min)
Hydrogen flow: adjusted as necessary (approx. 30 ml/min)
Air flow: adjusted as necessary (approx. 800 ml/min)

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

This method is for liquid formulations but could easily be adapted for solid formulations such as dusts, granules, powders, etc.

Preparation of standard:

Weigh 75 mg pentachlorophenol standard into a 50 ml volumetric flask, add 10 ml internal standard solution, and make to volume with acetone; mix well. (conc 1.5 mg pentachlorophenol and 1 mg dibutyl phthalate per ml)

Preparation of sample:

For liquid samples, weigh a portion of sample equivalent to 75 mg pentachlorophenol into a 50 ml volumetric flask, add 10 ml internal sample, and make to volume with acetone; mix well. (conc as above)
For granular or solid samples, weigh a portion of sample equivalent to 75 mg pentachlorophenol into a small (100/125 ml) screw-cap flask or bottle, add 10 ml internal standard solution and 40 ml acetone by pipette, close tightly and shake for 30 minutes on a mechanical shaker. Allow to settle, centrifuge or filter if necessary to obtain a clear solution. (conc as above)

GC Determination:

Using a 10 ul syringe, fill as follows: 1 ul acetone, 1 ul air, 1 ul MSTFA, and 2 ul standard (or sample) solution. Make an injection of standard and, if necessary, adjust the instrument parameters and the volume injected (keep the same relative amounts as above) to give a complete separation within a reasonable time and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the determination, making at least three injections of sample - each preceeded and followed by an injection of standard.

Calculation:

Measure the peak heights or areas of the pentachlorophenol and dibutyl phthalate for both the standard and sample solutions and calculate the following ratios:

$$\text{ratio of standard} = \frac{\text{peak heights or area pentachlorophenol}}{\text{peak heights or area dibutyl phthalate}}$$

$$\text{ratio of sample} = \frac{\text{peak heights or area pentachlorophenol}}{\text{peak heights or area dibutyl phthalate}}$$

Average the standard and sample ratios, and calculate the percent pentachlorophenol as follows:

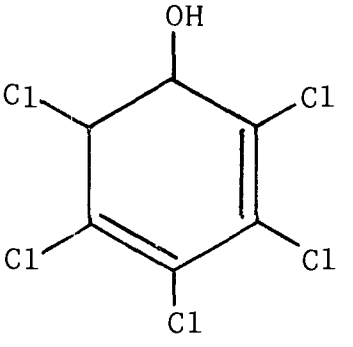
$$\% = \frac{(\text{ratio of sample})\ (\text{weight standard})\ (\%\ \text{purity of standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

Method submitted by EPA - NEIC, Denver, Colorado (Chuck Rzeszutko)
August 1979

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Pentachlorophenol by High Performance Liquid Chromatography

Pentachlorophenol (also commonly known as PCP and penta) is a registered insecticide, fungicide, herbicide, and molluscicide. It has the chemical structure:



Molecular formula: C_6HCl_5O

Molecular weight: 266.34

Physical state-color-odor: colorless crystals with phenolic odor (crude products are dark grayish flakes or powder)

Melting point: 191°C (pure); 187 to 189°C (crude)

Solubility: 20 ppm in water at 30°C; soluble in most organic solvents; limited solubility in carbon tetrachloride and petroleum oils of low aromatic or olefin content

Stability: non-flammable; non-corrosive except in the presence of moisture; aqueous solutions have an alkaline reaction

Sodium salt: forms buff colored flakes with one mole of water of crystallization; solubility in water in 33 grams/100 ml at 25°C; insoluble in petroleum oils

Other names: Antimicrobial; Dowicide; Dowicide G; Dowicide EC-7; Dow Pentachlorophenol DP-2; penchlorol; Pentacon; Penwar; Priltox; Santobrite; Santophen; Sinituho; Weedone

Reagents:

1. Pentachlorophenol standard of known purity
2. Benzyl benzoate (internal standard) of known purity
3. Methanol/PIC A - (1 bottle PIC A in one liter of 90% methanol + 10% water filtered through a 0.45 micron filter)
4. Water/PIC A - (1 bottle PIC A in one liter of water filtered through a 0.045 micron filter)
5. Internal standard solution - weigh 250 mg benzyl benzoate into a 500 ml volumetric flask, dissolve in and make to volume with methanol/PIC A solution. (conc 0.5 mg/ml)

Equipment:

1. High Performance Liquid Chromatograph with a variable wavelength UV detector at 218.5 nm. If a variable wavelength detector is not available, operating parameters and concentrations may have to be changed to obtain the necessary separation and sensitivity
2. Column: MicroPak MCH-10 (30 cm x 4 mm ID) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 70% (90% MeOH/10% water/PIC A) + 30% (water/PIC A)
Column temperature: 32°C
Flow rate: 2 ml/min
Wavelength: 218.5 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg pentachlorophenol into a screw-cap flask, add 100 ml internal standard solution by pipette, and shake to dissolve. Dilute 5 ml to 50 ml with internal standard solution and filter a portion through a 0.45 micron filter. (conc 0.1 mg pentachlorophenol and 0.5 mg benzoate per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 mg pentachlorophenol into a 125 ml screw-cap flask, add 100 ml internal standard solution by pipette, close tightly, and shake for a few minutes then place in an ultrasonic bath about 5 minutes. Shake again for a few minutes and dilute 5 ml to 50 ml with internal standard solution. Filter a portion through a 0.45 micron filter. (conc as above)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making aleternately three injections each of standard and sample solutions.

Calculation:

Measure the peak heights or areas of the pentachlorophenol and the benzyl benzoate for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area pentachlorophenol}}{\text{peak height or area benzyl benzoate}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area pentachlorophenol}}{\text{peak height or area benzyl benzoate}}$$

Average the standard and sample ratios, and calculate the percent pentachlorophenol as follows:

$$\% = \frac{(\text{ratio of sample})\ (\text{weight standard})\ (\%\ \text{purity of standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

Method submitted by EPA - NEIC, Denver, Colorado (Phil Gee and G. Thomas Gale) January 1980

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Propionic Acid by Gas Chromatography (FID)

Propionic acid is a registered fungicide having the chemical structure:

$$CH_3 — CH_2 — COOH$$

Molecular formula: $C_3H_6O_2$

Molecular weight: 74.08

Physical state-color-odor: oily liquid with a slightly pungent, disagreeable, rancid odor

Melting point: -21.5°C

Boiling point: 141.1°C at 760 mm Hg

Solubility: miscible with water; soluble in alcohol, ether, chloroform; can be salted out of water solutions by the addition of calcium chloride or other salts

Stability: stable - (example: propionates are used as mold inhibitors in bread; blends of acetic acid and propionic acid are used as liquid grain preservatives)

Other names: ChemStor; Grain Treat; propanoic acid; Propionic Acid Grain Preserver; Sentry Grain Preserver

Reagents:

1. Propionic acid of known purity
2. Ethanol, pesticide grade

Equipment:

1. Gas Chromatograph with flame ionization detector (FID)
2. Column: 6" x 1/4" glass packed with Porapak Q
3. Precision liquid syringe: 10 ul

4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating conditions:

Column temperature: 200°C
Injection port temperature: 250°C
Detector temperature: 250°C
Carrier gas: Helium (or nitrogen) flow - adjusted as necessary
Hydrogen flow: adjusted as necessary
Air flow: adjusted as necessary

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg propionic acid standard into a 50 ml volumetric flask, dissolve in and make to volume with ethanol; mix well. (conc 2 mg/ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 mg propionic acid into a 125 ml screw-cap flask, add 50 ml ethanol by pipette, close tightly and shake on a mechanical shaker for 30 to 40 minutes. Centrifuge or filter if necessary to obtain a clear solution. (conc 2 mg/ml)

GC Determination:

Inject 2 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the determination, making at least three injections each of standard and sample solutions.

Calculation:

Measure the peak height or peak area for each peak and calculate the average for both standard and sample. Using these averages, calculate the percent Propionic acid as follows:

$$\% = \frac{(\text{peak height or area sample})(\text{weight standard injected})(\% \text{ purity standard})}{(\text{peak height or area standard})\ (\text{weight sample injected})}$$

Method submitted by Martin J. Byrne, EPA, Region XIII, Denver, Colorado
January 1974

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Pyrethrins by High Performance Liquid Chromatography

For description, structure, and technical data on pyrethrins, see Pyrethrins EPA-1.

Reagents:

1. Pyrethrin standard of known purity
2. Acetonitrile, HPLC grade
3. Water, HPLC grade

Equipment:

1. High Performance Liquid Chromatograph with UV detector at 254 nm. If a variable wavelength detector is available, other wavelengths may be used to increase sensitivity or to eliminate interference.
2. Column: MicroPak MCH-10 (30 cm x 4 mm ID) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 75% acetonitrile + 25% water
Column temperature: ambient
Flow rate: 1.5 ml/min
Wavelength: 254 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg pyrethrin standard into a 125 ml screw-cap flask, add 100 ml acetonitrile by pipette, close tightly and shake to dissolve. Filter through a 0.45 micron filter. (conc 1 mg/ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 mg pyrethrin into a 125 ml screw-cap flask, add 100 ml acetonitrile by pipette, close tightly, and shake for 30 minutes. (A few minutes in an ultrasonic bath may help effect solution) Filter through a 0.45 micron filter. (conc 1 mg/ml)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solutions.

Calculation:

Measure the peak height or peak area for each peak and calculate the average for both standard and sample. Using these averages, calculate the percent pyrethrins as follows:

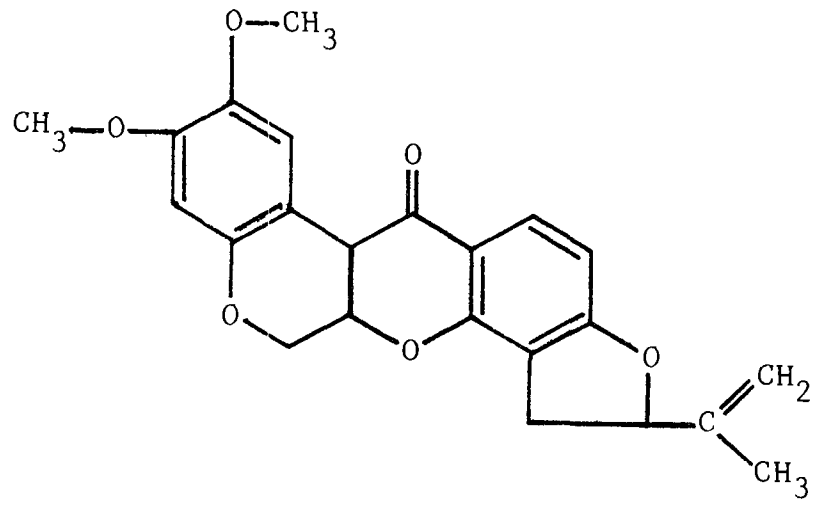
$$\% = \frac{(\text{peak height or area sample})(\text{weight standard injected})(\% \text{ purity standard})}{(\text{peak height or area standard})\ (\text{weight sample injected})}$$

Method submitted by EPA - NEIC, Denver, Colorado (G. Thomas Gale)
January 1980

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Rotenone by High Performance Liquid Chromatography

Rotenone is the trivial name of the main insecticidal component of certain species of "Derris" and "Lonchocarpus". It is a registered insecticide (with some acaricidal properties) and has the chemical structure:



Molecular formula: $C_{23}H_{22}O_6$

Molecular weight: 394.4

Physical state-color-odor: colorless crystals; crystallizes with solvent of crystallization

Melting point: 163°C (a dimorphoric form melts at 181°C)

Solubility: 15 ppm in water at 100°C; slightly soluble in petroleum oils and carbon tetrachloride; soluble in polar organic solvents

Stability: readily oxidized especially in presence of light or alkali

Other names: barbasco; Chem Fish; cube'; derris; haiari; neko; nicouline; Prentox; tubatoxin

Reagents:

1. Rotenone standard of known purity
2. Acetonitrile, HPLC or pesticide grade
3. Methanol, HPLC or pesticide grade

Equipment:

1. High Performance Liquid Chromatograph with a variable wavelength UV detector at 295 nm. If a variable wavelength detector is not available, operating parameters and concentrations may have to be changed to obtain the necessary separation and sensitivity.
2. Column: uBondapak C18 (30 cm x 3.9 mm ID) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 45% acetonitrile + 55% water
Column temperature: 33°C
Flow rate: 3 ml/min
Wavelength: 295 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg rotenone standard into a 125 ml screw-cap flask, add 100 ml methanol by pipette, close tightly, and shake to dissolve. Filter a portion through a 0.45 micron filter. (conc 1 mg/ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 mg rotenone into a 125 ml screw-cap flask, add 100 ml methanol by pipette, close tightly, and shake several minutes. Place in an ultrasonic bath for 2 or 3 minutes and then shake on a mechanical shaker for one hour. Filter a portion through a 0.45 micron filter. (conc 1 mg/ml)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solutions.

Calculation:

Measure the peak height or area for each peak and calculate the average for both standard and sample. Using these averages, calculate the percent rotenone as follows:

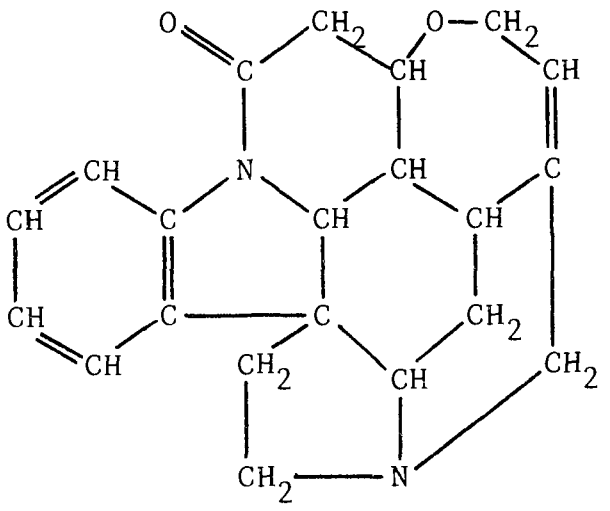
$$\% = \frac{(\text{peak height or area sample})(\text{weight standard injected})(\% \text{ purity standard})}{(\text{peak height or area standard})\ (\text{weight sample injected})}$$

Method submitted by EPA - NEIC, Denver, Colorado (Chuck Rzeszutko)
November 1979

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Strychnine by High Performance Liquid Chromatography

Strychnine is an alkaloid extracted from the seeds of "Strychnos nux-vomica". It is a registered rodenticide and has the chemical structure:



Molecular formula: $C_{21}H_{22}N_2O_2$

Molecular weight: 334.4

Physical state-color-odor: hard white crystals or powder; very bitter taste; very poisonous!

Melting point: 270 to 280°C with decomposition

Solubility: Practically insoluble in water, cold alcohol and cold ether; slightly soluble in benzene and chloroform

Stability: forms salts with acids; precipitated by alkaloid precipitants

Other names: Kwik-kil; Mouse-tox; Ro-Dec

Strychnine hydrochloride: colorless prisms containing water of crystillization (1 1/2 - 2 mol), lost at 100°C; soluble in water and alcohol; insoluble in ether

Strychnine sulfate: white crystallization powder containing water of crystallization lost at 110°C, mp above 199°C; moderately soluble in water and alcohol; insoluble in ether

Reagents:

1. Strychnine standard of known purity
2. Phenol (internal standard) of known purity (make sure that the phenol gives a clean chromatogram with no co-eluting peaks)
3. Aqueous mobile phase - (0.0025M 1-heptane sulfuric acid sodium salt and 0.04M tetramethylammonium chloride adjusted to pH 3.0 with sulfuric acid) Filter through a 0.45 micron filter.
4. Organic mobile phase - (0.06M tetramethylammonium chloride in 200 ml water adjusted to pH 3.0 with sulfuric acid plus 800 ml acetonitrile) Filter through a 0.45 micron filter.
5. Internal standard solution - weigh 1.125 grams phenol into a 500 ml volumetric flask, dissolve in and make to volume with aqueous mobile phase. (conc 2.25 mg/ml)

Equipment:

1. High Performance Liquid Chromatograph with UV detector at 254 nm. If a variable wavelength detector is available, other wavelengths may be used to increase sensitivity or to eliminate interference.
2. Column: MicroPak MCH-10 (30 cm x 4 mm ID) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 30% aqueous mobile phase + 70% organic mobile phase
Column temperature: ambient (may be somewhat sensitive to temperature changes)
Flow rate: 1.5 ml/min
Wavelength: 254 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 87.5 mg strychnine standard into a 50 ml volumetric flask, dissolve in and make to volume with internal standard solution; mix well. Dilute 10 ml to

50 ml with internal standard solution and mix well. Filter a portion through a 0.45 micron filter. (conc 0.35 mg strychnine and 2.25 mg phenol per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 35 mg strychnine into a 125 ml screw-cap flask, add 100 ml internal standard solution by pipette, close tightly, place in an ultrasonic bath for several minutes, then shake on a mechanical shaker for one hour. Filter a portion through a 0.45 micron filter. (conc 0.35 mg strychnine and 2.25 mg phenol per ml)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solutions. Elution order is strychnine then phenol.

Calculation:

Measure the peak heights or areas of the strychnine and the phenol for both standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area strychnine}}{\text{peak height or area phenol}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area strychnine}}{\text{peak height or area phenol}}$$

Average the standard and sample ratios, and calculate the percent strychnine as follows:

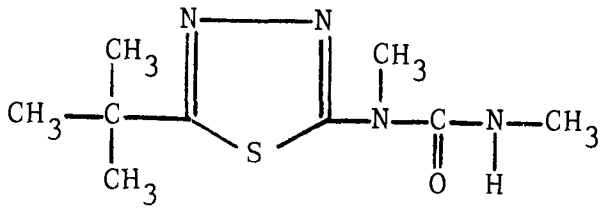
$$\% = \frac{(\text{ratio of sample})\ (\text{weight standard})\ (\%\ \text{purity of standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

Method submitted by EPA - NEIC, Denver, Colorado (G. Thomas Gale)
March 1980

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Tebuthiuron by Ultraviolet Spectroscopy

Tebuthiuron is the accepted (ANSI, BSI, WSSA) common name for N-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]N,N-dimethylurea, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{16}N_4OS$

Molecular weight: 228.31

Physical state-color-odor: colorless, odorless solid

Melting point: 161.5 to 164°C

Solubility: grams per 100 ml solvent at 25°C: chloroform - 25; methanol - 17; acetone - 7; acetonitrile - 6; methyl cellosolve - 6; hexane - 0.6; benzene - 0.37; water - 0.23

Stability: stable under usual storage conditions; non-corrosive; non-flammable; generally compatible with most other herbicides

Other names: EL-103; Graslan; Spike; 1-(5-tert-butyl-1,3,4-thiadiazol-2-yl)-1,3-dimethylurea

Reagents:

1. Tebuthiuron standard of known purity
2. Methanol, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells.
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of standard:

Weigh 80 mg tebuthiuron standard into a 100 ml volumetric flask, dissolve in and make to volume with methanol. Mix thoroughly and pipette a 10 ml aliquot into a second 100 ml volumetric flask, make to volume with methanol and mix thoroughly. Pipette 10 ml into a third 100 ml volumetric flask, make to volume with methanol and mix thoroughly. (final conc 8 ug tebuthiuron/ml).

Preparation of sample:

Weigh a portion of sample equivalent to 80 mg tebuthiuron into a 250 ml glass-stoppered flask or screw-cap bottle, add 100 ml methanol by pipette, close tightly and shake on a mechanical shaker for 30 minutes. Allow to settle, centrifuge or filter if necessary, taking precautions to avoid evaporation of solvent. Dilute 10 ml to 100 ml and then 10 ml to 100 ml as under standard preparation. (final conc 8 ug tebuthiuron/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen at 0 and 100% transmission at 253 nm with methanol in each cell. Scan both standard and sample solutions from 320 to 220 nm with methanol in the reference cell. Measure the absorbance of standard and sample solutions at 253 nm.

Calculations:

From the above absorbances and using the standard and sample concentrations, calculate the percent tebuthiuron as follows:

$$\% = \frac{\text{(abs. sample) (conc. std. in ug/ml) (\% purity)}}{\text{(abs. std.) (conc. sample in ug/ml)}}$$

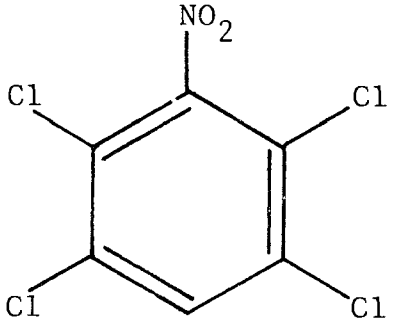
There is a straight line relationship between absorbance and concentration for up to 10 ug/ml.

Method submitted by EPA (former) Product Analysis Laboratory, Region II.
New York, NY
November 1976

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Tecnazene by Gas Chromatography (FID-IS)

Tecnazene is the accepted (BSI, ISO) common name for 1,2,4,5-tetrachloro-3-nitrobenzene, a registered fungicide and plant growth regulator having the chemical structure:



Molecular formula: $C_6HCl_4NO_2$

Molecular weight: 260.9

Physical state-color-odor: colorless, odorless crystalline solid

Melting point: 99°C

Solubility: practically insoluble in water; about 4% in ethanol at 25°C; readily soluble in benzene, carbon disulfide, chloroform

Stability: appreciably volatile at room temperature

Other names: Folosan; Fusarex; TCNB; 2,3,5,6-tetrachloronitrobenzene

Reagents:

1. Tecnazene standard of known purity
2. Orthophenylphenol (internal standard), analytical grade
3. Acetone, pesticide grade
4. Internal standard solution - weigh 250 mg o-phenylphenol into a 500 ml volumetric flask, dissolve in and make to volume with acetone; mix well. (conc 0.5 mg/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 4' x 1/4" glass packed with 3.8% UC-V98 on 80/100 mesh Diatoport S (or equivalent column such as SP-2100 on Chromosorb W HP)
3. Precision liquid syringe: 10 ul
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating conditions for FID:

Column temperature: 150 to 170°C adjusted for best time and separation
Injection port temperature: 200°C
Detector temperature: 230°C
Carrier gas: helium - flow adjusted as necessary
Hydrogen flow: 30 ml/min - adjusted as necessary
Air flow: 55 ml/min - adjusted as necessary

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 90 mg tecnazene standard into a small (100/125 ml) screw-cap flask or bottle, add 50 ml internal standard solution by pipette, and shake to dissolve. (conc 1.8 mg tecnazene and 0.5 mg o-phenylphenol per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 90 mg tecnazene into a small flask or bottle, add 50 ml internal standard solution, close tightly and shake for 30 minutes on a mechanical shaker. Allow to settle, centrifuge or filter if necessary to obtain a clear solution. (conc 1.8 mg tecnazene and 0.5 mg o-phenylphenol per ml)

GC Determination:

Inject 3 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the determination, making at least three injections each of standard and sample solutions. The elution order is o-phenylphenol then tecnazene.

Calculation:

Measure the peak heights or areas of the tecnazene and o-phenylphenol for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area tecnazene}}{\text{peak height or area o-phenylphenol}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area tecnazene}}{\text{peak height or area o-phenylphenol}}$$

Average the standard and sample ratios, and calculate the percent tecnazene as follows:

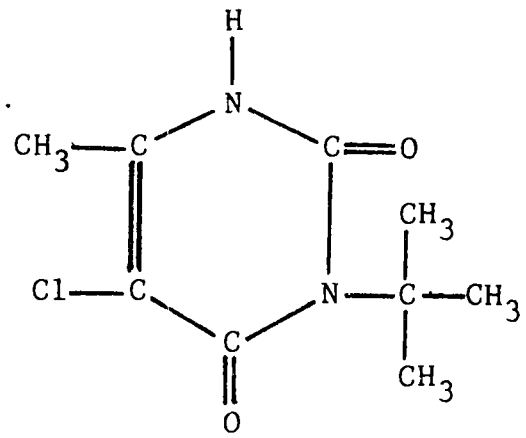
$$\% = \frac{(\text{ratio of sample})\ (\text{weight of standard})\ (\%\ \text{purity of standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

Method submitted by EPA (former) Product Analysis Laboratory, Region II,
New York, NY
March 1976

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Terbacil by Ultraviolet Spectroscopy

Terbacil is the accepted (ANSI, BSI, ISO, WSSA) common name for 3-tert-butyl-5-chloro-6-methyluracil, a registered herbicide having the chemical structure:



Molecular formula: $C_9H_{13}N_2O_2Cl$

Molecular weight: 216.5

Physical state-color-odor: odorless, white crystalline solid

Melting point: 175 to 177°C

Solubility: 710 ppm in water at 25°C; moderately soluble in methyl isobutyl ketone, butyl acetate, xylene; highly soluble in cyclohexane, dimethylformamide

Stability: stable to heat up to mp (below which it sublimes); non-corrosive; non-flammable; stable in water, aqueous bases, and common organic solvents at room temperature

Other names: DuPont Herbicide 732; Sinbar

Reagents:

1. Terbacil standard of known purity
2. Chloroform, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells.
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of standard:

Weigh 150 mg terbacil standard into a 100 ml volumetric flask, make to volume with chloroform and mix thoroughly. Pipette a 10 ml aliquot into a second 100 ml volumetric flask, make to volume with chloroform and mix thoroughly. Pipette 10 ml into a third 100 ml volumetric flask and make to volume with chloroform; mix thoroughly. (final conc 15 ug terbacil/ml)

Preparation of sample:

Weigh a portion of sample equivalent to 150 mg terbacil into a 250 ml glass-stoppered flask or screw-cap bottle, add 100 ml chloroform by pipette, stopper tightly, and shake on a mechanical shaker for 30 minutes. Allow to settle, centrifuge or filter if necessary, taking precaution to avoid evaporation of solvent. Dilute 10 ml to 100 ml and then 10 to 100 ml as under sample preparation. (final conc 15 ug terbacil/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen at 0 and 100% transmission at 275 nm with chloroform in each cell. Scan both standard and sample solutions from 320 to 230 nm with chloroform in the reference cell. Measure the absorbance of standard and sample solutions at 275 nm.

Calculations:

From the above absorbances and using the standard and sample concentrations, calculate the percent terbacil as follows:

$$\% = \frac{\text{(abs. sample) (conc. std. in ug/ml) (\% purity)}}{\text{(abs. std.) (conc. sample in ug/ml)}}$$

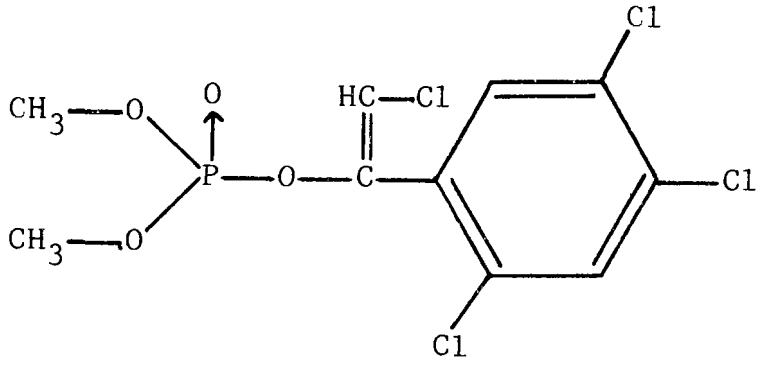
There is a straight line relationship between absorbance and concentration for up to 25 ug/ml.

Method submitted by EPA (former) Product Analysis Laboratory, Region II, New York, NY
November 1976

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Tetrachlorvinphos by Gas Chromatography (FID-IS)

Tetrachlorvinphos is the accepted (BSI, ISO) common name for (cis or Z isomer of) 2-chloro-1-(2,4,5-trichlorophenyl) vinyl dimethyl phosphate, a registered insecticide having the chemical structure:



Molecular formula: $C_{10}H_9Cl_4O_4P$

Molecular weight: 365.96

Physical state-color-odor: off-white crystalline solid

Melting point: technical Gardona (98% minimum cis isomer) 97 to 98°C
technical Rabon (94% by weight active ingredient) 93 to 98°C

Solubility: at 20°C: 11 ppm in water, less than 20% w/w in acetone, 40% w/w in chloroform and methylene chloride, less than 15% w/w in xylene

Stability: stable to 100°C; slowly hydrolyzed by neutral or acid media, more rapidly hydrolyzed in alkaline media

Other names: Appex; CVMP; Dust M; Gardcide; Gardona; Rabon; Rabone; ROL; SD 8447; Stirofos

Reagents:

1. Tetrachlorvinphos standard of known purity
2. n-Docosane (internal standard), practically grade (or better)

3. Methylene chloride, pesticide grade
4. Internal standard solution - weigh 675 mg n-docosane into a 250 ml volumetric flask, dissolve in and make to volume with methylene chloride; mix well. (conc 2.7 mg/ml)

Equipment:

1. Gas chromatograph with a flame ionization detector (FID)
2. Column: 6' x 1/4" glass packed with 10% OV-1 on 80/100 Chromosorb W
3. Precision liquid syringe: 10 ul
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating conditions for FID:

Column temperature: 225°C
Injection port temperature: 235°C
Detector temperature: 240°C
Carrier gas: nitrogen - flow adjusted as necessary
Hydrogen flow: adjusted as necessary
Air flow: adjusted as necessary

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 200 mg tetrachlorvinphos standard into a 125 ml screw-cap flask, add 50 ml internal standard solution by pipette, and shake to dissolve; mix thoroughly. (conc 4 mg tetrachlorvinphos and 2.7 mg n-docosane per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 200 mg tetrachlorvinphos into a 125 ml screw-cap flask, add 50 ml internal standard solution by pipette, close tightly, and shake on a mechanical shaker for one hour. Allow to settle, centrifuge or filter if necessary to obtain a clear solution.
(conc 4 mg tetrachlorvinphos and 2.7 mg n-docosane per ml)

GC Determination:

Inject 3 ul of standard and, if necessary, adjust the instrument parameters and the volume injected to give a complete separation within a reasonable time

and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the determination, making at least three injections each of standard and sample solutions. The elution order is tetrachlorvinphos then n-docosane.

Calculation:

Measure the peak heights or areas of the tetrachlorvinphos and the n-docosane for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area tetrachlorvinphos}}{\text{peak height or area n-docosane}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area tetrachlorvinphos}}{\text{peak height or area n-docosane}}$$

Average the standard and sample ratios, and calculate the percent tetrachlorvinphos as follows:

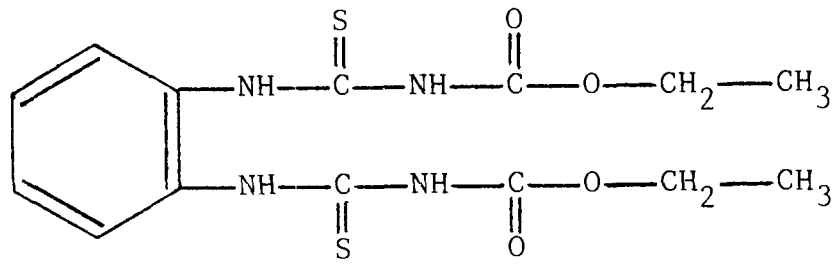
$$\% = \frac{(\text{ratio of sample})\ (\text{weight of standard})\ (\%\ \text{purity of standard})}{(\text{ratio of standard})\ (\text{weight of sample})}$$

Method submitted by E. S. Greer, EPA (formerly) Product Analysis Laboratory, Region IX, San Francisco, CA (Mr. Greer is now at Beltsville, MD) August 1977

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Thiophanate by Ultraviolet Spectroscopy

Thiophanate is the accepted (BSI, ISO) common name for diethyl [1,2-phenylene bis (iminocarbonothioyl)] bis[carbamate], a registered fungicide having the chemical structure:



Molecular formula: $C_{14}H_{18}N_4O_4S_2$

Molecular weight: 370.4

Physical state-color-odor: colorless, crystalline solid

Melting point: 190°C with decomposition

Solubility: very slightly soluble in water; soluble in acetone, methanol, chloroform, acetonitrile, cyclohexane, ethyl acetate

Stability: stable in neutral or acidic aqueous solutions, but unstable in alkaline aqueous solutions; forms chelates with calcium, copper, and sodium ions

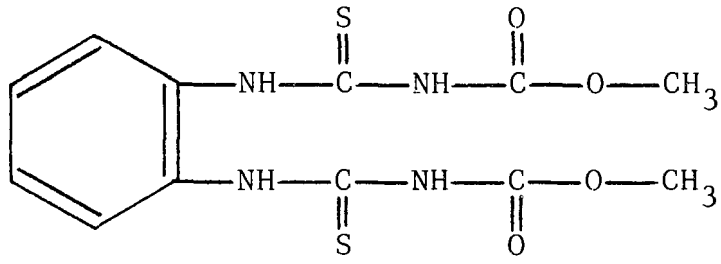
Other names: 3336; Cercobin; NF-35; Topsin; Topsin E; 1,2-bis (3-ethoxycarbonyl-2-thioureido) benzene; diethyl 4,4- o-phenylenebis[3-thioallophanate]; thiophanate-ethyl

Analytical method: see thiophanate-methyl and use the same method

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Thiophanate-methyl by Ultraviolet Spectroscopy

Thiophanate-methyl is the accepted (ANSI, BSI, ISO) common name for dimethyl [(1,2-phenylene) bis-(iminocarbonothioyl)] bis [carbamate], a registered fungicide having the chemical structure:



Molecular formula: $C_{12}H_{14}O_4N_4S_2$

Molecular weight: 342.4

Physical state-color-odor: colorless, crystalline solid; odorless to slightly sulfurous

Melting point: 178°C (decomposes)

Solubility: practically insoluble in water; slightly soluble in common organic solvents

Stability: stable in solid state when kept below 160°C; stable in acid aqueous solutions, slowly decomposes in neutral aqueous solutions, rapidly decomposes in alkaline aqueous solutions

Other names: Cercobin-M; Fungitox; Labilite; Mildothane; Sigma; Topsin-M

Reagents:

1. Thiophanate-methyl standard of known purity
2. Chloroform, pesticide or spectro grade

Equipment:

1. Ultraviolet spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Centrifuge or filtration apparatus
4. Usual laboratory glassware

Procedure:

Preparation of standard:

Weigh 80 mg thiophanate-methyl standard into a 100 ml volumetric flask, dissolve in and make to volume with chloroform. Mix thoroughly, and pipette 10 ml into a second 100 ml volumetric flask. Make to volume with chloroform and mix thoroughly. Pipette 10 ml into a third 100 ml volumetric flask, make to volume with chloroform, and mix thoroughly.
(final conc 8 ug/ml).

Preparation of sample:

Weigh a portion of sample equivalent to 80 mg thiophanate-methyl into a 250 ml glass-stoppered flask or screw-cap bottle, add 100 ml chloroform by pipette, and shake on a mechanical shaker for one hour. Allow to settle, centrifuge or filter if necessary, taking precautions to avoid evaporation of solvent. Dilute 10 ml to 100 ml and then 10 ml to 100 ml as under sample preparation.
(final conc 8 ug thiophanate-methyl/ml)

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen at 0 and 100% transmission at 269 nm with chloroform in each cell. Scan both standard and sample solutions from 360 to 230 nm with chloroform in the reference cell. Measure the absorbance of standard and sample solutions at 269 nm.

Calculations:

From the above absorbances and using the standard and sample concentrations, calculate the percent thiophanate-methyl as follows:

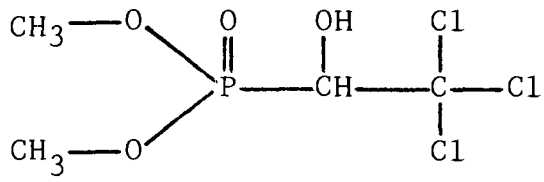
$$\% = \frac{\text{(abs. sample) (conc. std. in ug/ml) (\% purity)}}{\text{(abs. std.) (conc. sample in ug/ml)}}$$

Method submitted by EPA (former) Product Analysis Laboratory, Region II, New York, NY
July 1975

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Trichlorfon by Gas Chromatography (FID-IS) Using on Column Derivization with BSFTA

Trichlorfon is the accepted (ISO) common name for dimethyl (2,2,2-trichloro-1-hydroxyethyl) phosphonate, a registered insecticide having the chemcial structure:



Molecular formula: $C_4H_8Cl_3O_4P$

Molecular weight: 257.44

Physical state-color-odor: white crystalline solid

Melting point: 83 to 84°C

Solubility: 15.4 grams in 100 ml water at 25°C; soluble in benzene, ether, ethanol, and most chlorinated solvents; slightly soluble in petroleum oils, and in carbon tetrachloride

Stability: stable at room temperature, but is decomposed by water at higher temperatures and at pH 5.5 to form dichlorvos

Other names: Bayer 15922; Bovinox; Briten; Cekufon; chlorofos; Ciclosom; Crinex; Danex; Dipterex; Dylox; Equino-Aid; Leivasom; metrifonate; Neguvon; Proxol; trichlophon; Trinex; Tugon

Reagents:

1. Trichlorfon standard of known purity
2. Benzyl benzoate (internal standard) of known purity
3. Acetone, analytical, dry

4. BSTFA [N,O-bis(trimethylsilyl)-trifluoroacetamide] silylation reagent for derivization
5. Internal standard solution - weigh 850 mg benzyl benzoate into a 100 ml volumetric flask, dissolve and make to volume with acetone, and mix well. (conc 8.5 mg/ml)

Equipment:

1. Gas chromatograph with flame ionization detector (FID)
2. Column: 6' x 2 mm ID glass packed with 3% OV-17 on Chromosorb W HP (or other suitable column)
3. Precision liquid syringe: 10 ul
4. Mechanical shaker
5. Centrifuge or filtration apparatus
6. Usual laboratory glassware

Operating conditions:

Column temperature: 150°C
Injection port temperature: 225°C
Detector temperature: 260°C
Carrier gas: nitrogen - flow adjusted as necessary
Hydrogen flow: adjusted as necessary
Air flow: adjusted as necessary

Operating parameters (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 110 mg trichlorfon standard into a 125 ml screw-cap flask, add 10 ml internal standard solution by pipette and 40 ml acetone by pipette, close tightly and mix well. (conc 2.2 mg trichlorfon and 1.7 mg benzyl benzoate per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 110 mg trichlorfon into a 125 ml screw-cap flask, add 10 ml internal standard solution by pipette and 40 ml acetone by pipette, close tightly and shake for 30 minutes on a mechanical shaker. Allow to settle, and if necessary centrifuge or filter to clarify. (conc 2.2 mg trichlorfon and 1.7 mg benzyl benzoate per ml)

GC Determination:

Using a 10 ul syringe, fill as follows: 1 ul acetone, 1 ul air, 1 ul BSTFA, and 2 ul standard (or sample) solution. Make an injection of standard and, if necessary, adjust the instrument parameters and the volume injected (keep the same relative amounts as above) to give a complete separation within a reasonable time and to obtain peak heights of 1/2 to 3/4 full scale. Proceed with the determination, making at least three injections of sample - each preceeded and followed by an injection of standard. Elution order is trichlorfon then benzyl benzoate.

Calculation:

Measure the peak heights or areas of the trichlorfon and benzyl benzoate for both the standard and sample solutions and calculate the following ratios:

$$\text{ratio of standard} = \frac{\text{peak height or area trichlorfon}}{\text{peak height or area benzyl benzoate}}$$

$$\text{ratio of sample} = \frac{\text{peak height or area trichlorfon}}{\text{peak height or area benzyl benzoate}}$$

Average the standard and sample ratios, and calculate the percent trichlorfon as follows:

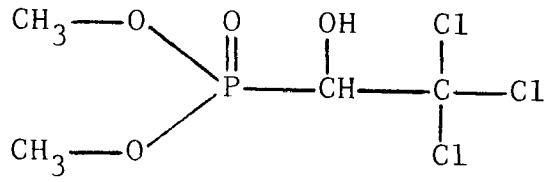
$$\% = \frac{(\text{ratio of sample})\ (\text{weight standard})\ (\%\ \text{purity of standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

Method submitted by EPA - NEIC, Denver, Colorado (G. Thomas Gale)
September 1980

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Trichlorfon by High Performance Liquid Chromatography

Trichlorfon is the accepted (ISO) common name for dimethyl (2,2,2-trichloro-1-hydroxyethyl) phosphonate, a registered insecticide having the chemical structure:



Molecular formula: $C_4H_8Cl_3O_4P$

Molecular weight: 257.44

Physical state-color-odor: white crystalline solid

Melting point: 83 to 84°C

Solubility: 15.4 grams in 100 ml water at 25°C; soluble in benzene, ether, ethanol, and most chlorinated solvents; slightly soluble in petroleum oils, and in carbon tetrachloride

Stability: stable at room temperature, but is decomposed by water at higher temperatures and at pH 5.5 to form dichlorvos

Other names: Bayer 15922; Bovinox; Briten; Cekufon; chlorofos; Ciclosom; Crinex; Danex; Dipterex; Dylox; Equino-Aid; Leivasom; metrifonate; Neguvon; Proxol; trichlorphon; Trinex; Tugon

Reagents:

1. Trichlorfon standard of known purity
2. Phenol (internal standard) of known purity (make sure that the phenol gives a clean chromatogram with no co-eluting peaks)
3. Acetonitrile, HPLC grade
4. Water, HPLC grade

5. Internal standard solution - weigh 125 mg phenol into a 100 ml volumetric flask, dissolve in and make to volume with acetonitrile; mix well. Dilute 10 ml to 100 ml. (conc 0.125 mg/ml)

Equipment:

1. High Performance Liquid Chromatograph with a variable wavelength UV detector at 224 nm. If a variable wavelength detector is not available, operating parameters and concentrations may have to be changed to obtain the necessary separation and sensitivity.
2. Column: uBondapak C18 (30 cm x 3.9 mm ID) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 30% acetonitrile + 70% water
Column temperature: 33°C
Flow rate: 2 ml/min
Wavelength: 224 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 100 mg trichlorfon standard into a 10 ml volumetric flask, add 2 ml internal standard solution by pipette, and make to volume with acetonitrile. Mix thoroughly and filter a portion through a 0.45 micron filter. (conc 10 mg trichlorfon and 0.025 mg phenol per ml)

Preparation of sample:

Weigh a portion of sample equivalent to 100 mg trichlorfon into a 10 ml volumetric flask, add 2 ml internal standard solution by pipette, and make to volume with acetonitrile. Stopper tightly and place in an ultrasonic bath for 10 minutes. Filter a portion through a 0.45 micron filter. (conc as above)

HPLC Determination:

Inject 10 ul of standard solution and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solutions.

Calculation:

Measure the peak heights or areas of the trichlorfon and the phenol for both the standard and sample solutions and calculate the following ratios:

$$\text{Ratio of standard} = \frac{\text{peak height or area trichlorfon}}{\text{peak height or area phenol}}$$

$$\text{Ratio of sample} = \frac{\text{peak height or area trichlorfon}}{\text{peak height or area phenol}}$$

Average the standard and sample ratios, and calculate the percent trichlorfon as follows:

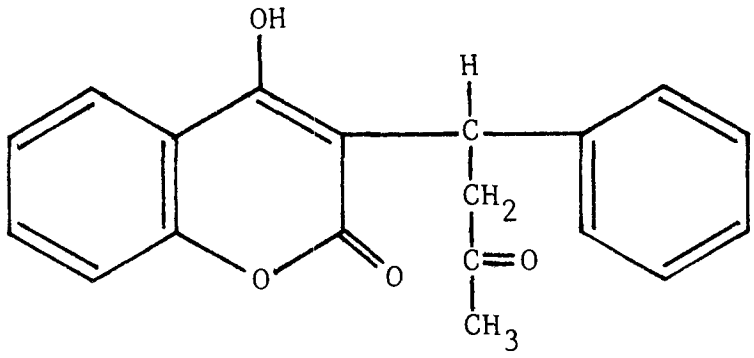
$$\% = \frac{(\text{ratio of sample})\ (\text{weight standard})\ (\%\ \text{purity of standard})}{(\text{ratio of standard})\ (\text{weight sample})}$$

Method submitted by EPA - NEIC, Denver, Colorado (G. Thomas Gale)
September 1980

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Warfarin by High Performance Liquid Chromatography

Warfarin is the accepted (BSI,ISO) common name for 3-(alpha-acetonylbenzyl)-4-hydroxycoumarin, a registered rodenticide having the chemical structure:



Molecular formula: $C_{19}H_{16}O_4$

Molecular weight: 308.3

Physical state-color-odor: colorless, odorless, tasteless crystals (dl form)

Melting point: 159 to 161°C (dl form)

Solubility: practically insoluble in water and benzene; moderately soluble in alcohols; readily soluble in acetone and dioxane; forms water soluble salts with sodium

Stability: stable under normal conditions

Other names: coumafene (France); zoocoumarin (Netherlands and USSR); Co-Rax; Cov-R-Tox; Kypfarin; Ratox; RAX; Rodex; Rodex Blox; Tox-Hid; Warfarin Plus; Warfarin Q

Reagents:

1. Warfarin standard of known purity
2. Methanol/PIC A - (1 bottle PIC A in one liter of 90% methanol + 10% water filtered through a 0.45 micron filter)

3. Water/PIC A - (1 bottle PIC A in one liter water filtered through a 0.45 micron filter)

Equipment:

1. High Performance Liquid Chromatograph with a variable wavelength UV detector at 312 nm. If a variable wavelength detector is not available, operating parameters and concentrations may have to be changed to obtain the necessary separation and sensitivity.
2. Column: MicroPak MCH-10 (30 cm x 4 mm ID) or equivalent column
3. High pressure liquid syringe or sample injection loop: 10 ul
4. Mechanical shaker and/or ultrasonic bath
5. 0.45 micron filtering apparatus
6. Usual laboratory glassware

Operating conditions:

Mobile phase: 50% (90%/10% water/PIC A) + 50% (water/PIC A)
Column temperature: 32°C
Flow rate: 2 ml/min
Wavelength: 312 nm

Operating conditions (above) as well as attenuation and chart speed should be adjusted by the analyst to obtain optimum response and reproducibility.

Procedure:

Preparation of standard:

Weigh 110 mg warfarin standard into a 125 ml screw-cap flask, add 100 ml methanol/PIC A solution by pipette, close tightly, and shake to dissolve. Dilute 5 ml to 50 ml with methanol/PIC A solution and filter through a 0.45 micron filter. (conc 0.11 mg/ml)

Preparation of sample:

Weigh a portion of sample equivalent to 110 mg warfarin into a 125 ml screw-cap flask, add 100 ml methanol/PIC A solution, close tightly, and shake for several minutes. Place in an ultrasonic bath 2 or 3 minutes, then shake again for several minutes. Dilute 5 ml to 50 ml with methanol/PIC A solution and filter through a 0.45 micron filter. (conc 0.11 mg/ml)

HPLC Determination:

Inject 10 ul of standard and, if necessary, adjust the flow rate and/or mobile phase composition to give good separation in a reasonable time. Adjust the attenuation or the amount injected to give convenient size peaks. Proceed with the determination making alternately three injections each of standard and sample solution.

Calculation:

Measure the peak height or area for each peak and calculate the average for both standard and sample. Using these averages, calculate the percent warfarin as follows:

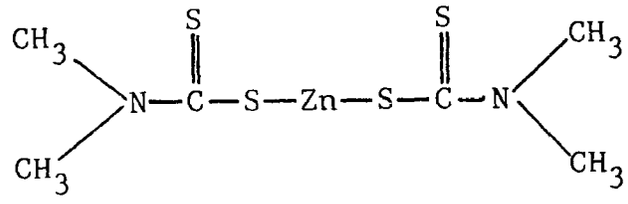
$$\% = \frac{(\text{peak height or area sample})(\text{weight standard injected})(\% \text{ purity standard})}{(\text{peak height or area standard})\ (\text{weight sample injected})}$$

Method submitted by EPA - NEIC, Denver Colorado (Phil Gee & G. Thomas Gale)

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

Determination of Ziram by Ultraviolet Spectroscopy

Ziram is the accepted (BSI, ISO) name for zinc dimethyldithiocarbamate, a registered fungicide having the chemical structure:



Molecular formula: $C_6H_{12}N_2S_4Zn$

Molecular weight: 305.79

Physical state-color-odor: odorless, white powder

Melting point: 240°C (pure), 240 to 244°C (technical)

Solubility: 65 ppm in water at 25°C; slightly soluble in ethanol, ether; moderately soluble in acetone; soluble in dilute alkali, chloroform, carbon disulfide

Stability: stable under normal conditions, but is decomposed by acids; compatible with other pesticides except copper and mercury compounds

Other names: Antene; Carbazinc; Corozate; Cuman; Drupina 90; Fuclasin Ultra; Fuklasin; Fungostop; Hexazir; Mezene; Pomarsol Z Forte; Prodaram; Tricarbamix Z; Triscabol; Vancide MZ-96; Z-C Spray; Zerlate; Zincmate; Ziramvis; Zirasan 90; Zirberk; Zirex 90; Ziride; Zitox

Reagents:

1. Ziram standard of known purity
2. Chloroform, pesticide or spectro grade

Equipment:

1. Ultraviolet Spectrophotometer, double beam ratio recording with matched 1 cm cells
2. Mechanical shaker
3. Water bath
4. Filtration apparatus with anhydrous sodium sulfate
5. Usual laboratory glassware

Procedure:

Preparation of standard:

Weigh 100 mg ziram standard into a 100 ml volumetric flask, dissolve in and make to volume with chloroform. Mix thoroughly and pipette 10 ml into a second 100 ml volumetric flask. Make to volume with chloroform, mix thoroughly, and pipette 5 ml into a third 100 ml volumetric flask. Make to volume with chloroform and mix thoroughly. (final conc 5 ug/ml).

Preparation of sample (liquid-viscous formulations):

Weigh a portion of sample equivalent to 100 mg ziram into a 100 ml round-bottom flask, add 40 ml chloroform, and reflux for 30 minutes on a boiling water bath. Filter through anhydrous sodium sulfate into a 100 ml volumetric flask and make to volume with chloroform. Mix thoroughly and pipette 10 ml into a second 100 ml volumetric flask. Make to volume with chloroform, mix thoroughly and pipette 5 ml into a third 100 ml volumetric flask; make to volume with chloroform and mix thoroughly. (final conc 5 ug ziram/ml).

Preparation of sample (powder formulations):

Weigh a portion of sample equivalent to 100 mg ziram into a 250 ml glass-stoppered or screw-cap flask, add 100 ml chloroform by pipette, and shake on a mechanical shaker for 15 minutes. Allow to settle, filter and pipette 10 ml into a 100 ml volumetric flask. Make to volume with chloroform, mix thoroughly, and pipette 5 ml into another 100 ml volumetric flask; make to volume with chloroform and mix thoroughly. (final conc 5 ug ziram/ml).

UV Determination:

With the UV spectrophotometer at the optimum quantitative settings for the particular instrument being used, balance the pen at 0 and 100% transmission at 261 nm with chloroform in each cell. Scan both the standard and sample solutions from 300 to 200 nm with chloroform in the reference cell. Measure the absorbance of standard and sample at 261 nm.

Calculations:

From the above absorbances and using the standard and sample concentrations, calculate the percent ziram as follows:

$$\% = \frac{\text{(abs. sample) (conc. std. in ug/ml) (\% purity)}}{\text{(abs. std.) (conc. sample in ug/ml)}}$$

Method submitted (summer - ?) 1978 by:

Dr. Gabriele Tartari
Agrochemical Department
Control Laboratory
CIBA-GEIGY S.p.A.
C.P. 88
I-21047 SARONNO (VA)
ITALY

Note: The amount of standard and sample and some dilution factors have been changed to allow more significant figures in the calculations and to reduce errors in weighings and making dilutions. The final concentrations are as in the method as received.

Any criticisms, suggestions, or data concerning the use of this method will be appreciated.

TLC Systems for Identification of Pesticides*

To facilitate the process of pesticide identification, laboratory-prepared aluminum oxide and silica gel TLC plates were spotted with pesticide standards, developed in a series of mobile solvents, the spots visualized, and the R_F values recorded in tables (TLC Systems 1 and 2). The objective of this work was to speed up the identification of a suspect pesticide by means of a rapid screening technique which would eliminate unlikely candidates, while allowing the selection of likely ones for further study. The suspect pesticide sample is subjected to the same TLC systems as for the pesticide standards, and the elimination-selection process proceeds after comparison of R_F values of the unknown with those of the standards previously obtained. Owing to changes in R_F values resulting from change in humidity, temperature, layer thickness, pesticide purity, etc., some discretion must be used in the selection process. It is advisable to spot several known pesticides (preferably technical materials) along with the unknown to enable compensation for these variables. For example, if the R_F values of the known are elevated from the recorded data, the unknown spots may be similarly elevated (this is somewhat empirical because there is no assurance that the R_F values of different pesticides will change to the same degree). The change in R_F resulting from change in mobile solvent is a better criterion for the selection process than is dependence on absolute R_F values for a given solvent system.

The data are presented, therefore, only as a general guide, with emphasis on the need for additional solvent systems and closer control of variable conditions affecting spot movement. Pesticides which do not exhibit movement in the mobile solvents listed require different layers and/or more polar solvents. TLC is used only for initial identification and semi-quantitation with subsequent confirmation required by at least one other means (GLC, GC-MS, etc.).

Preparation of TLC Plates

TLC System 1 (organochlorine pesticides) - Forty grams Aluminum Oxide G Type E (EM Laboratories, Inc., 500 Exec Blvd., Elmsford, N.Y. 10523) is slurried with 75 ml of a methanol solution containing 130 mg of silver nitrate. This will coat five 8 x 8" plates or twenty 2 x 8" plates using a DeSaga applicator set for a .38 mm layer. Plates are air-dried about 5 minutes, dried in a 100°C oven for about 1/2 hour,

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*Developed by B. M. Olive, CBIB, Residue & Special Projects Unit

cooled, and stored in a desiccator shielded from light. The larger plates (accommodating 12-13 spots) were normally used for spotting the reference pesticides (5-10 micrograms) to develop the data, and the smaller plates for the unknown and a couple of references as a check on R_F variation. Plates were developed to a 10 cm penciled line, air-dried a few minutes, and exposed to unfiltered UV light (UV sterilizer) until the spots (typically black on white background) reach maximum intensity (usually 30-60 min.).

TLC System 2 (organophosphorus and fungicide pesticides) - Forty grams of MN-Silica Gel G-HR/UV (distributed by Brinkman Instruments, Inc., Cantiague Road, Westbury, N.Y. 11590) is slurried with 85 ml distilled water and applied in a layer .38 mm thick to coat five 8 x 8" plates or twenty 2 x 8" plates. Plates are air-dried until the layer is set, then dried in a 100 -105°C oven for about 1/2 hour, cooled and stored. The spotting and development is the same as for the chlorinated insecticides (hexane was omitted as a mobile solvent in TLC System 2 because few pesticides of this type move in it). After air-drying a few minutes, plates are viewed under long and/or short wave UV light in a UV viewing box. The location of any spots is marked with a pencil indentation (usually spots appear dark blue on fluorescent yellow background). The plate is next sprayed with a 2% acetone solution of 4-(p-nitrobenzyl)-pyridine (NBP), heated at 110°C for ca 10 minutes, and then sprayed with a 10% acetone solution of tetraethylenepentamine (TEPA). This chromogenic treatment was developed for detection of organophosphorus pesticides and produces blue spots on a yellowish background (JAOAC, 47, No. 6, 1964, p. 1094).

TLC System 1

Aluminum Oxide G and Silver Nitrate Layer
Spots Visualized by Exposure to UV Lamp (unfiltered)

Acceptable[1]		Mobile Solvents[2]				
Name	No.	Hexane	Benzene	Chloroform	Cyclohexane+ Benzene+HAC+ Paraffin Oil (200+30+20+11)	Ethyl Acetate
(Herbicides)		R_F Values[3]				
Lasso	11	0	.14	.47	0, .66	.72
Tordon, Methyl Ester	39A	0	0---.13	0---.35	0, .13	0, .63
Aminotriazole	40	0	0	0	0	0
Atrazine	63	0	.04	.23	0, .60	.60
Barban	68	0	0---.28	0---.50	0, .35	0, .73
Prometone	96	No data (ND)	ND	ND	0----.53	ND
Prometryne	97	ND	ND	ND	0----.59	ND
Bromacil	111	0	0	.02	0, .45	.02---.07
Chlorbromuron	173A	0	.23	.57	.40	.72
Propazine	184	0	.08	.33	.70	.60, .70
Chloroxuron	217B	0	.03	.22	.14	.63
Dursban	219AA	0	0---.07	0	0----.33	0----.08
Dalapon	273	0	0	0	0	0

Acceptable[1]		Mobile Solvents[2]				
Name	No.	Hexane	Benzene	Chloroform	Cyclohexane+ Benzene+HAC+ Paraffin Oil (200+30+20+11)	Ethyl Acetate
(Herbicides)		R_F Values[3]				
Banvel D	295	0	0	0	0----.05	0
2,4-D Acid	315	0	0	0	0----.02	0
2,4-D Butyl Ester	315 AL	0	0, .57	0, .72	0, .73	0, .77
2,4-D Ethyl Ester	315 AP	0	0---.53	0, .70	0, .72	0, .75
2,4-D Ethyl Hexyl	315 AS	0	0, .65	0, .77	0, .80	0, .80
2,4-D IOE	315 AU	0	0, .60	0, .75	ND	0, .77
2,4-D Isopropyl	315 AV	0	0, .55	0, .75	0, .75	0, .80
2,4-D Prop. Gly. But. Ether	315 BA	0	0, .45	.72	0, .75	0, .77
2,4-DB Acid	316	0	0	0	0----.30	0
2,4-DB IOE	316D	0	0, .62	.83	.85	.79
TOK	323D	ND	.67	.77	.80	.82
Stam	325	ND	.12	.42	.07	.67
Dacthal	382	0	.60	.75	.80	.77

Acceptable[1]		Mobile Solvents[2]				
Name	No.	Hexane	Benzene	Chloroform	Cyclohexane+ Benzene+HAC+ Paraffin Oil (200+30+20+11)	Ethyl Acetate
(Herbicides)		R_F Values[3]				
Diuron	410	0	0	.27	0----.03	.59
Linuron	528	ND	.25	.53	0, .55	.69
MCPA	557C	0	0	0	0----.07	0
MCPA dimethyl amine	557G	ND	0	0	0----.12	0
MCPA IOE	557I	ND	0, .80	0---.72	0----.12	.80
MCPB	558	ND	0	0	0----.47	0
MCPP	559	ND	0	0	0----.24	0
Monuron	583	0	.02	.22	0, .07	.55
Monuron TCA	583A	ND	0, .05	0---.04	0----.12	0, .42, .57
Neburon	594	ND	.12	0, .40	0, .45	.72
Paraquat	634	0	0	0	0	0
Fenuron TCA	655	ND	.02	.15	.07	.52
Tordon	663AA	0	0	0	0, .52	0
Siduron	733A	0	0	.04	.37	.65
Silvex	739	0	0	0	0----.09, .30	0
Silvex IOE	739I	ND	0, .85---.92	0, .77	0----.20---.45---.97	0, .80

Acceptable[1]		Mobile Solvents[2]				
Name	No.	Hexane	Benzene	Chloroform	Cyclohexane+ Benzene+HAC+ Paraffin Oil (200+30+20+11)	Ethyl Acetate
(Herbicides)		R_F Values[3]				
Silvex P.G.B. E.E.	739M	ND	0---.55---.72	0---.60---.72	0---.22---.45---.95	0, .80
Simazine	740	ND	.05	0, .10	0, .75	.50
TCBA	873AA	ND	0	0	0---.03	0
2,4,5-T Acid	881	0	0	0	0---.06, .30	0
2,4,5-T Butoxy Ethyl Ester	881N	ND	0---.55	0---.65	0---.07---.95	0, .72
2,4,5-T Butyl Ester	881P	ND	0---.55---.80	0---.67---.75	0---.06---.47---.95	0, .77
2,4,5-T IOE	881SS	0---.03	0, .57	0, .72	0---.06, .30, .75	0, .77
2,4,5-T P.G.B. E.E.	881U	ND	0---.45---.62	0---.62---.68	0---.07---.97	0, .72
Fenac	882	0	ND	ND	0, .20, .23, .27	ND
(Chlorinated Insecticides)[3]						
Aldrin	12	.54	.77	.87	.92	.82
BHC, Tech	79	0, .22	.68	.79, .84	.87	.82
Kelthane	93	.07	.62, .79	.39, .84	.87	.82
Alpha-chlordane	174AA	.30	.77	.87	.87	.82

Acceptable[1]		Mobile Solvents[2]				
Name	No.	Hexane	Benzene	Chloroform	Cyclohexane+ Benzene+HAC+ Paraffin Oil (200+30+20+11)	Ethyl Acetate
(Chlorinated Insecticides)[3]		R_F Values[3]				
Gamma-chlordane	174AB	.27	.77	.87	.80	.82
Kepone	275	ND	0, .82	0, .89	0---.04	.09, .85
DDD	307	.24	.77	.87	.82	.85
DDE	307A	.55	.79	.87	.90	.85
DDT	308	0, .02, .42, .50	.67, .79	.87	.90	.85
DDVP	328	0	0	0	0	0
Dieldrin	333	.09	.67	.84	.87	.82
Dipterex	385	0	0	0	0---.08	0---.09
Mirex	411	.62	.79	ND	ND	ND
Thiodan	420	0---.14	0, .57, .69	ND	ND	ND
Endrin	423	0---.04, .12	0, .52, .67	ND	ND	ND
Heptachlor	474	.02---.50	0, .02, .77	ND	ND	ND
Heptachlor Epoxide	474AA	.12	.69	ND	ND	ND
Lindane	527	.17, .45	.72	ND	ND	ND
Methoxychlor	550	0, .05	0, .67	ND	ND	ND

Acceptable[1]		Mobile Solvents[2]				
Name	No.	Hexane	Benzene	Chloroform	Cyclohexane+ Benzene+HAC+ Paraffin Oil (200+30+20+11)	Ethyl Acetate
(Chlorinated Insecticides)[3]			R_F Values[3]			
Ovex	624	.03	.65	ND	ND	ND
Oxychlordane	627AB	.04, .27	.77	ND	ND	ND
Phenothiazine	652	0	0---.17, .75	ND	ND	ND
Strobane	822	0---.50	0, .77	ND	ND	ND
Tedion	836	0---.07	0, .60	ND	ND	ND
Toxaphene	861	0---.52	.77	ND	ND	ND

TLC System 2

Silica Gel GHR/UV Layer. Spots Visualized by Inspection in UV View Box and/or by Nitrobenzylpyridine/Tetraethylene Pentamine Sprays

Acceptable[1]		Mobile Solvents[2]			
Name	No.	Benzene	Chloroform	Cyclohexane + Benzene + HAC + Paraffin Oil (200 + 30 + 20 + 11)	Ethyl Acetate
(Organophosphate Pesticides)		R_F Values[3]			
Acephate	2A	0°	0°	0°	0°
Gophacide	91A	.05*	.14*	0*	.75*
Bromophos	114E	.65*°	.72*°	.50°	.80*°
Phosdrin, Tech.	160B	0*°	0*°---.07*°	.02*°	.45°, .55*°
Trithion	165	.75*°	.82*°	.10*---.50*----.65*	.86*°
Cmpd. 4072	187	0*°---.02*°	.25*°	.10*°	.75*°
Akton	187A	.67*°	.75*°	.52*°	.85*°
Methyl Trithion	212	.72*°	.80*°	.10*---.42*°---.65*	.82*°
Ruelene	263A	0*°	.07*°, .92*	.10*°	.60°
Demeton	279	ND	.15°	.10°	.65°
Dicapthon	296	.62*°	.10*, .75*°	.25*°	.82*°
VC-13	321	ND	.92*	ND	ND
DDVP	328	.05°	.27°, .85*	.10°	.65°

Acceptable[1]		Mobile Solvents[2]			
Name	No.	Benzene	Chloroform	Cyclohexane + Benzene + HAC + Paraffin Oil (200 + 30 + 20 + 11)	Ethyl Acetate
(Organophosphate Pesticides)		R_F Values[3]			
Co-Ral	335	0*, .25*	0*, .60*°	0, .10	.80
Disyston	341	ND	ND	ND	.82°
Diazinon	342	0°, .15*	0°, .42*°	.15*°	.77*°
Dasanit	343	0*°	.02*°	0*°	.40*°
Dimethoate	358	0°	.05°	0°	.45°
Bomyl	367	0*°, .05°	.02°---.12*	0*°	.52*°, .60*
Methyl Parathion	372	.02*°, .55*°	.25*°, .70*°	.02*°, .20*	.65*°, .77*°
Guthion	374	.10*°	.30*°	.07*°	.70*°
Guthion Oxygen Analog	---	0*°	0*°	0*°	.42*°
Ciodrin	378	0*°---.02*	.09*°	.02*°	.57°
Dipterex	385	0°	0°	.02°	.30°
Delnav	393	.30°, .40°	.60°, .90°	.12°	.80°
Ethion	427	.62°	.75*°	.30°	.80°
Bay 68138	453A	0*°	.02*°	.02*	.55*
Baytex	456F	.02*°, .60*°	.20*°, .70*°	.02*°, .27*°	.62°, .80*°

Acceptable[1]		Mobile Solvents[2]			
Name	No.	Benzene	Chloroform	Cyclohexane + Benzene + HAC + Paraffin Oil (200 + 30 + 20 + 11)	Ethyl Acetate
(Organophosphate Pesticides)		R_F Values[3]			
Malathion	535	.12°	.40°	.02°, .10°	.77°
Bay 93820	574B	.04*°	.27*°	.05*°	.80*°
Dibrom	586	0°	.32°	.07°	.67°
Parathion	637	0*---.02*,.20*,.30*,.55*°	0*°,.42*,.52*,.67*°	0*°,.02*°,.07*,.17*,.25°	.65*,.72*,.82*°
Nellite, Tech.	654B	0*	ND	0*	.10*
Thimet	660	.65*°	.75*°	.47*	ND
Phosalone	660A	.30*°	.55*°	.05*°	.82*°
Phosphamidon	661	0°	0*°	0*°	.25*°, .45°
Ronnel	724	.30*, .72°	.77°	.52°	.80°
Sulfotepp	837	.57°	.70°	0-------.40°	.80°
Tepp	838	ND	0°--.07°--.27°--.67°	.02°	ND
Abate	845	.07*°----.45*°	0°-----.22°---.67*°	.02*°----.07*°	.67°, .82*°

Acceptable[1]		Mobile Solvents[2]			
Name	No.	Benzene	Chloroform	Cyclohexane + Benzene + HAC + Paraffin Oil (200 + 30 + 20 + 11)	Ethyl Acetate
(Fungicides)		R_F Values[3]			
Santophen 1	83	0*---.07*	0*---.11*	0*, .50*	0*---.55*
Captan	159	0*---.07*	0*---.05*	0*, .70*	0*
Chloranil	171	0*---.62*	0*---.48*	0*---.30*---.42*---.82*	0*---.26*
Daconil	215B	0*, .67*	0*---.06*, .72*	0*---.05*, .80*	0*, .35*, .79*
Dichlone	298	0*, .62*	0*, .72*	0*, .81*	0*, .77*
Dyrene	302	0*, .32*	0*---.55*	0, .82	0----.57
Botran	311	0*, .50*°	0*, .62*°	0*, .55*	0*, .69*°
Karathane	391D	0*°, .65*°, .75*°	0*°, .72*°, .77*°	0*, .77*°, .87*°	0*°, .78*°
Phaltan	464	0*---.25*	0*---.70*	0*, .76*	0*, .75*
Hexachloro-benzene	477	.84*	.79*	0*------.95*	.79*
Maneb	539	0*°	0*°	0*	0*°
Dichlorophene	563	0*	0*	0*------.05*	0*
Hexachlorophene	566	0*	0*	.50*	0*
PCNB	640	.82*	.80*	0*	.82*
Salicylanilide	730	ND	0*°	.30*°	0*°---.15*°

Acceptable[1]		Mobile Solvents[2]			
Name	No.	Benzene	Chloroform	Cyclohexane + Benzene + HAC + Paraffin Oil (200 + 30 + 20 + 11)	Ethyl Acetate
(Fungicides)		R_F Values[3]			
3,3',4,5 Tetrachlorosalicylanilide	833	0*	0*---.11*	0*------.47*	0*
Thiram	856	0*°---.06*°	0*°	0*, .09*°	0*---.11*°
Zineb	930	ND	ND	0*	ND

[1] Acceptable Names & Numbers refers to the compendium: "Acceptable Common Names and Chemical Names for the Ingredient Statement on Pesticide Labels," 2nd Ed., June 1972. Pesticide Regulation Division, OPP, EPA, Washington, D. C. 20250. The common or trade names are used here for convenience, but the numbers refer to the preferred name.

[2] Mobile solvent tanks were lined with filter paper for vapor saturation.

[3] R_F = distance spot moved from origin/distance traveled by solvent (10 cm).

A line (----) signifies a streak between indicated R_F values.

Asterisk (*) signifies positive to viewing in long and/or short wave UV light (UV View Box).

Degree sign (°) signifies positive to NBP/TEPA chromogenic treatment.

ND - not detectable

PESTICIDE FORMULATION BIBLIOGRAPHY

This bibliography is intended to provide the pesticide formulation analyst a fairly complete reference list of published material related to the field of pesticides. The references have been limited to "book" or "manual" types of sources for the sake of brevity, with no effort having been made to include specific journal articles; however, individual journals concerned with pesticides are given in Section E. Industrial methodology and technical data material have also been excluded.

Descriptive notes for individual references were limited to those sources dealing specifically with pesticide product analysis and some of the more important residue and technical reference sources. Enough description of some of the instrumental methods was given so an analyst without the specified source could possibly complete a needed analysis, if necessary. The information would also enable one to cross-reference certain quoted methods with industrial or other methods that may be available in the laboratory.

Some references are dated and are probably available only through a library. They were included, however, for the sake of completeness--some of them offering interesting reading, if only from a historical standpoint.

The bibliography is by no means considered to be complete. Further additions for any of the sections would certainly be welcome for a later edition. Please address correspondence or comments to either:

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PESTICIDE BIBLIOGRAPHY

A. PESTICIDE FORMULATION ANALYSIS

1. Official Methods of Analysis of the Association of Official Chemists, 12th Edition, 1975. Published by the Association of Official Analytical Chemists, P. O. Box 540, Benjamin Franklin Station, Washington, D. C. Supplements issued annually.

   The methods described in the A.O.A.C. have been subjected to interlaboratory collaboration and shown to be statistically reliable. These methods are the most official methods available from an enforcement standpoint and should be used, if possible, to substantiate any suspected violations.

   Chapter 6 deals with pesticide formulations. Unfortunately, the scope of coverage is severely limited in terms of the types and mixtures of pesticides being currently used, and one must resort to other methods.

   Other potentially useful methods to the pesticide formulation chemist are:

   1. Acetone (GLC, 36.011)
   2. Benzocaine (Colorimetric, 38.134)
   3. Dichlorophene (UV, 39.120)
   4. Ethanol (GLC, 36.011)
   5. Glycerol (Titrimetric, 35.075)
   6. Griseofulvin (UV, 42.273)
   7. Hexachlorophene (UV, 35.023)
   8. Isopropanol (GLC, 36.011)
   9. Nicotine (UV, 42.087)
   10. Paraldehyde (GLC, 37.105)
   11. Phenothiazine (GLC, 38.178)
   12. Phenothiazine (Colorimetric, 42.121)
   13. Propylene Glycol (GLC, 35.007)
   14. Propylene Glycol (Titrimetric, 19.006)
   15. Ronnel (GLC, 42.141)
   16. Ronnel (UV, 42.144)
   17. Sulfaquinoxaline (Colorimetric, 42.168)
   18. Thiabendazole (Colorimetric, 42.180)
   19. Thymol (Titrimetric, 37.143)

   Other pertinent sections are Ch. 2 (Fertilizers), Ch. 3 (Plants), Ch. 29 (Pesticide Residues), and Ch. 20 (Food Additives). Chapters 49, 50, and 51 deal with Spectroscopic Methods, Standard Solutions, and Laboratory Safety, respectively.

2. Manual of Chemical Methods for Pesticides and Devices, Environmental Protection Agency, Office of Pesticide Programs, Technical Services Division, Chemical and Biological Investigations Branch. Issued 1975 and will be updated as needed.

   The manual contains standard and generally accepted methods for pesticide product analysis which have not yet been subjected to interlaboratory collaboration. The methods are usually accepted by enforcement authorities, but should be checked by two or more different methods, whenever possible, for suspected violative samples. There are also sections on representative IR spectra for many of the agricultural pesticides, techniques of analysis, TLC procedures, NMR spectra, and cross-reference method index.

3. Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives, Ed. Gunter Zweig, Academic Press, N. Y. Vols. I-VII; Vols. VI and VII also edited by Joseph Sherma.

   Volume I (1963), Principles, Methods and General Applications
   Chapters 2 and 23 concern formulation analysis; however, both are somewhat dated and should be read with this in mind. Other sections of general interest are Chapter 8 (Spectrophotometric Methods), Chapter 11 (Total Halide Analysis), and Chapters 15-17 on bioassay techniques. Most of the other material in Volume I has been updated in later volumes, or has little application to the formulation chemist.

   Volume II (1964), Insecticides
   Individual insecticides are covered by review articles giving information on names, producers, and chemical, physical, and biological properties. In addition, methods for formulation and residue analysis are presented, and one or several of each type are given in detail for each insecticide discussed. The formulation methods are primarily derived from industrial sources, as most of the articles have been written by representatives of the companies that manufacture the different insecticides.

   Volume III (1964), Fungicides, Nematocides and Soil Fumigants, Rodenticides, and Food and Feed Additives
   Review articles with the same format as Volume II but covering pesticides from the classes listed in the above title.

Volume IV (1964), Herbicides
A continuation of the individual pesticide series but covering herbicides only.

Volume V (1967), Additional Principles and Methods of Analysis
Chapter 1 contains an introduction to gas chromatographic detectors, although the material is primarily oriented toward pesticide residue analysis. Other general chapters of interest cover thin-layer chromatography, polarography, and residue analysis for water, fish, and wildlife samples. There is also an introduction to techniques used in metabolism studies of pesticides.

Volume VI (1972), Gas Chromatographic Analysis
Chapter 4 pertains specifically to the application of GLC techniques to pesticide formulation analysis. Detectors, columns, and sample preparation techniques are discussed, as well as the precision to be expected for different types of peak measurements. References are also presented for the gas chromatographic analysis of different classes of pesticide compounds by liquid phase. Standard deviations to be expected from GLC procedures as well as other typical analytical methods are given.

Other general chapters in Volume VI pertain to residue sample preparation, detectors, and qualitative analysis. In addition, the different chemical classes of pesticides are covered, primarily from the residue standpoint, such as chlorinated hydrocarbons and organophosphates, with the remainder grouped together in a chapter on miscellaneous compounds.

Volume VII (1974), Thin-layer and Liquid Chromatography and Analysis of Pesticides of International Importance

4. Infra-red Analysis of Pesticide Formulations, by S. W. Goza, Virginia Department of Agriculture and Commerce, Division of Technical Services, Richmond, Virginia 23219

This loose-leaf volume contains many useful methods for the infra-red analysis of agricultural pesticide formulations. Although some of the methods are identical or similar to those given elsewhere, there are many that are unique to this collection. Both dry and liquid formulation methods are described. Different sample preparation techniques are referred to in each method according to the type of formulation. Many of the methods are applicable in the presence of other co-formulated pesticides.

The VDA IR methods, not listed as tentative, are well recognized by enforcement authorities; however, alternative methods should be used to substantiate any suspected violative samples, whenever possible. Many of these methods will be part of "EPA Manual of Chemical Methods for Pesticides and Devices."

5. CIPAC Handbook, Volume I, Analysis of Technical and Formulated Pesticides. Compiled by R. D. Ashworth, J. Henriet, and J. F. Lovett; edited by G. R. Law. Collaborative International Pesticides Analytical Council Limited, 1970. Published by W. H. Heffer and Sons Ltd., Cambridge, England.

   This handbook is a compilation of assay methods and other testing procedures for examining pesticidal technical materials and formulated products. The methods are those adopted by the CIPAC, and are used primarily in Europe. The assay methods are mainly wet chemical and spectrophotometric; however, individual procedures are described in detail for technical materials, dusts, granulars, wettable powders, and emulsifiable concentrates. The methods are classified as: "CIPAC Methods," which have been investigated collaboratively, "CIPAC Provisional Methods," which have found wide usage but lack collaboration, and "CIPAC Draft Methods," which should be considered tentative at best.

   Of equal value to the assay methods described in the CIPAC Handbook are the miscellaneous physical, stability, and by-product determinations that are presented. Flash point, viscosity, moisture content, suspendibility, flowability, particle size distribution, and wettability are covered in Chapter 7 (Miscellaneous Techniques) and referred to in the main text under the individual pesticides. Solubility measurements, hydrolyzable and total chlorine determinations, dye removal, and accelerated storage tests are also described. Chapter 7 also covers preparation and criteria for purity of chemicals and reagents used in pesticide analysis.

   Chapter 8 covers the preparation of pure pesticides for use as analytical standards. Purification steps and purity criteria are described for: 2,4-D, MCPA, Dieldrin, Aldrin, Endrin, Rotenone, DNBP, Ovex, Fenson, Diquat, and Paraquat.

   Among the various chemical assay procedures described, the following may be of use to the formulation analyst. It must be kept in mind, however, that these methods have no official status in the U. S. Some methods have been jointly adopted by both CIPAC and AOAC; however, these methods are described in the AOAC. Official "CIPAC Methods" have been designated with an asterisk.

1. ANTU (Titrimetric), p. 16
2. Captan (IR, 1264 $cm^{-1}/CHBr_3$), p. 172*
3. Captan (IR, 1130 $cm^{-1}/CHCl_3$), p. 174*
4. CIPC (Hydrolysis/Titration), p. 223*
5. 2,4-D Esters (Hydrolysis/Titration), p. 249-56*
6. Dalapon-Na (Colorimetric), p. 274*
7. Dalapon-Na (Titrimetric), p. 276
8. Dimefox (Differential Hydrolysis), p. 329
9. DNBP (UV), p. 337*
10. Endosulfan (Chromatography/IR), p. 361
11. Endothion (Hydrolysis/Titration), p. 373*
12. Fenson (Hydrolysis/Titration), p. 392*
13. Ferbam (UV, 410 mμ/$CHCl_3$), p. 397*
14. Gamma BHC (Hydrolyzable Chlorine), p. 986
15. Gamma BHC (Polarography), p. 37*
16. IPC (Hydrolysis/Titration), p. 593
17. MCPA (Extraction/Titration), p. 475*/477
18. MCPA (IR, 808 cm^{-1}/acetone), p. 482*
19. MCPA Esters (Hydrolysis/Titration), p. 499*
20. Methyl Guthion (Colorimetric), p. 24
21. Ovex (Hydrolysis/Titration), p. 213*
22. Petroleum Oils (Gravimetric - Neutral Oil Content), p. 582
23. Rotenone (Colorimetric), p. 610
24. Schradan (Differential Hydrolysis), p. 621
25. Sodium Chlorate (Titrimetric/Iodimetric), p. 626*
26. Sodium Chlorate (Titrimetric/$K_2Cr_2O_7$), p. 628*
27. Sodium Trichloroacetate (Decarboxylation/Titration), p. 691*
28. Sulfur (Titrimetric), p. 632*
29. 2,4,5-T (Extraction/Titration), p. 642*
30. 2,4,5-T Esters (Hydrolysis/Extraction/Titration), p. 646*& 651*
31. TCNB (Polarography), p. 663*
32. TEPP (Selective Hydrolysis/Titration), p. 667
33. Thiram (Dimethylamine Distillation), p. 677
34. Trichloroacetic Acid (Decarboxylation/Titration), p. 691*
35. Warfarin (UV, 305 mμ in $CHCl_3$), p. 698 & 699*

The following infra-red procedures are described in general terms in Chapter 5 (p. 730-733). The extraction procedure used for dusts and wettable powders is diethyl ether/Büchner funnel rinsing. <u>These methods should be considered strictly as tentative</u>.

1. Allyl Alcohol (920 cm^{-1}/CS_2)
2. Bromophos (715 cm^{-1}/CS_2)
3. Chlorbenside (818 cm^{-1}/CS_2)
4. 2,4-D (720 cm^{-1}/acetone)
5. Difolatan (1732 $cm^{-1}/CHCl_3$
6. Diuron (822 cm^{-1}/acetone)
7. 2,4-DP (799 cm^{-1}/CS_2)

8. Fenson (749 cm^{-1}/CS_2)
9. Kelthane (532 cm^{-1}/CS_2)
10. Linuron (806 cm^{-1}/CS_2)
11. MCPP (801 cm^{-1}/CS_2)
12. Methoxychlor (618 cm^{-1}/CS_2)
13. Monuron (835 cm^{-1}/acetone)
14. Ovex (768 cm^{-1}/CS_2)
15. Pentachlorophenol (767 cm^{-1}/CS_2 - in presence of 2,3,4,6-Tetrachlorophenol)
16. Piperonyl Butoxide (940 cm^{-1}/CS_2)
17. Pyrazon (825 cm^{-1}/DMF)
18. Ronnel (962 cm^{-1}/CS_2)
19. Tetradifon (582 cm^{-1}/CS_2)
20. 2,3,4,6-Tetrachlorophenol (751 cm^{-1}/CS_2 - in presence of Pentachlorophenol)
21. Thiometon (658 cm^{-1}/CS_2)
22. Thiram (981 or 858 cm^{-1}/CS_2)
23. Toxaphene (1299 cm^{-1}/CCl_4)

6. Standard Methods of Chemical Analysis, 6th Edition, N. Howell Furman, Ed., (Volume I), Frank J. Welcher, Ed., (Volumes II and III), D. Van Nostrand and Co., Inc., Princeton, N. J., 1962 (3 volumes)

Volume IIB, Chapter 39 specifically deals with pesticide formulation analysis. However, most of the methods presented are wet chemical or spectrophotometric methods available from the first three references. The methods are quite dated, the A.O.A.C. references being from the 1960 edition.

Other chapters of interest to the formulation chemist are: Chapter 37 (Paint, Varnish, and Lacquer), Chapter 40 (Petroleum and Petroleum Products), and Chapter 45 (Soaps and Detergents).

Volume I covers the analysis of individual elements in a variety of chemical forms. There are several specific methods, not quoted elsewhere, that can be useful to the pesticide product analyst, among which are:

1. Available Chlorine (Iodimetric titration), p. 341
2. Chlorate ($KBrO_3$/As +++ titration), p. 343
3. Chromate (Soluble), p. 360
4. Titratable Iodine (Thiosulfate & As titration), p. 451
5. Manganese (Gravimetric), p. 643
6. Silver (with Potentiometric modification), p. 982
7. Tin (Dithiol reaction), p. 1082

In addition, there is a useful section in the back of Volume I on the preparation of different laboratory reagents and solutions.

Volume IIA covers noninstrumental methods for industrial and natural products. Sections of interest include chapters on laboratory apparatus (p. 3), specific and selective precipitants (p. 101), and the analysis of acids and bases (p. 534). There is also an interesting chapter on titration methods (p. 254).

Volume IIIA gives an introduction to the theory and application of most of the common instrumental techniques of analysis.

Volume IIIB covers specific instrumental techniques for various types of compounds, classified by usage. Topics of conceivable interest to the pesticide formulation chemist are: Fertilizers (p. 1102), Organic Functional Groups (p. 1162), Paints, Varnish, and Lacquer (p. 1265), and Petroleum and Petroleum Products (p. 1506). There is also a specific chapter on pesticide residue analysis (p. 1464); however, it also is rather dated, as most of the techniques have been supplanted.

7. Analysis of Insecticides and Acaricides, by F. A. Gunther and R. C. Blinn, Interscience Publishers, Inc., New York, 1955.

This reference is quite dated, there being no material relating to thin-layer, gas, or liquid chromatography. There is some good background material on residue loss and decomposition after field treatment, particularly for chlorinated hydrocarbons. Sampling and sample preparation for residue analysis are covered, but primarily for colorimetric and other methods now obsolete.

There is a section in the appendix giving UV and IR spectra for a group of pesticides that may be of value to the formulation chemist, although the selection is pretty much limited to chlorinated hydrocarbons, natural products, etc.

Chapter 15 gives formulation and residue methods for quite a large number of compounds. Most of the formulation methods, however, are elemental in nature and have since been replaced by more specific means of analysis. There are some methods in this source, though, not mentioned in previous references that may be of some use to the pesticide product analyst in certain situations. Among these are:

1. Acrylonitrile (Cyanoethylation/Titration), p. 264
2. D-D (Bromination/Titration), p. 404
3. Ethylene Oxide (Precipitation/Titration), p. 451
4. Metaldehyde (Depolymerization/Titration), p. 479
5. Methoxychlor (Hydrolyzable chlorine), p. 347
6. Perthane (Hydrolyzable chlorine), p. 347
7. Schradan (Hydrolysis/Titration), p. 577
8. Sodium Selenate (Gravimetric), p. 582
9. TDE (Hydrolyzable chlorine), p. 347

8. Reagent Chemicals and Standards, 5th Edition, Joseph Rosin, D. Van Nostrand Company, Inc., Princeton, N. J., 1967

This volume contains many impurity tests and analytical assays for common laboratory reagent chemicals to determine their purity. There are also volumetric tables in the back that can be very useful in determining what equivalent weight to use for a particular titration.

Among the assay procedures, there are a number that may be of use to the formulation chemist, particularly for technical materials. Most of those listed below are titrimetric procedures.

1. Benzaldehyde, p. 78
2. Benzoic Acid, p. 82
3. Chloramine T, p. 129
4. Cupric Oxide, p. 157
5. Ferrous Ammonium Sulfate, p. 203
6. Ferrous Sulfate, p. 206
7. Hydrochloric Acid, p. 224
8. Hydrogen Peroxide, p. 228
9. Phosphoric Acid, p. 346
10. Potassium Bisulfate, p. 361
11. Potassium Chromate, p. 372
12. Potassium Permanganate, p. 393
13. Potassium Persulfate, p. 394
14. Silver, precipitated, p. 427
15. Sodium Bisulfate, p. 443
16. Sodium Bisulfite, p. 445
17. Sodium Borate, p. 448
18. Sodium Carbonate, p. 452
19. Sodium Chlorate, p. 453
20. Sodium Fluoride, p. 460
21. Sodium Hydrosulfite, p. 463
22. Sodium Hydroxide, p. 464
23. Sulfuric Acid, p. 509
24. Trichloroacetic Acid, p. 531

9. American Wood-Preserver's Association Standards, Published by the American Wood-Preserver's Association, 1012 Fourteenth Street, N.W., Washington, D. C. 20005 (Revised periodically)

Section A of this manual contains methods specifically applicable to the analysis of wood preservatives, both in formulations and treated surfaces. The methods, derived mainly from ASTM sources, have been adopted by the AWPA as official, but their application in pesticide enforcement situations is virtually untested, except for those that are similar to those in previously quoted sources.

Results derived from the use of these methods should be confirmed, whenever possible, by the use of alternate methods for suspected violative samples. Most of the methods are wet chemical in nature, with very little in the way of modern instrumentation involved; thus much of the material presented may be of historical interest only.

The following topic areas are covered:

1. Creosote (Water content, petroleum oil content, specific gravity, etc.)
2. Waterborne Preservatives
   a. Ammoniacal Copper Arsenite (NH_3, As, & Cu determination)
   b. Chromated Copper Arsenate (NH_3, As,& Cr determination)
   c. Chromated Zinc Chloride (Cl, Zn,& Cr determination)
   d. Copperized Chromated Zinc Arsenate (Cu, Cr, Zn,& As determination)
   e. Fluor Chrom Arsenate Phenol (F, DNP, PCP-Na, Cr,& As determination)
3. Oil-borne Preservatives
   a. Pentachlorophenol (Total acidity, total chlorine, and a colorimetric assay)

B. ADDITIONAL REFERENCE SOURCES FOR CHEMICAL INFORMATION ON PESTICIDES AND THEIR ANALYSIS

(Later editions of some of these sources may be available.)

1. Acceptable Common Names and Chemical Names for the Ingredient Statement on Pesticide Labels, 3rd Edition, prepared by R. L. Caswell et al, Office of Pesticide Programs, EPA, Washington, D. C. 20460 (1975).

2. Advances in Pest Control Research, Ed. R. L. Metcalf, Interscience Publishers, Inc., New York, 1957.

3. Agricultural Chemicals, W. R. Thomson, Thomson Publications, P. O. Box 989, Davis, California, 1967 revision. Issued in 4 volumes.

4. Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd Ed., L.M. Jackman and S. Sternhell, Pergamon Press, New York, 1969.

5. Atomic Absorption Spectroscopy, G. Christian and F. Feldman, Wiley Interscience, New York, 1970.

6. Basic Gas Chromatography, H. M. McNair and E. J. Bonelli, Consolidated Printers, Berkeley, Calif.

7. Catalog of Pesticide Standards for Pesticide Formulation Analysis, Environmental Protection Agency, TSD-CBIB, Beltsville, Md.

8. Chem Sources--U.S.A. 1974, Directories Publishing Company, Inc., Flemington, New Jersey.

9. Chemicals for Pest Control, G. S. Hartley and T. F. West, Pergamon Press, New York, 1966.

10. The Chemistry and Action of Insecticides, H. H. Shepard, McGraw-Hill Book Co., New York, 1951.

11. Chemistry and Mode of Action of Herbicides, A. S. Crafts, Interscience Publishers, New York, 1961.

12. The Chemistry of Organophosphorus Pesticides, K. J. Schmidt and C. Fest, Springer-Verlag, New York, 1973.

13. Chemistry of the Pesticide, Donald E. Frear, 3rd Edition, D. Van Nostrand Co., Inc., New York, 1955.

14. Chemistry of the Pesticides, N. M. Melnikov, Edited by F. A. Gunther and J. D. Gunther, Translated by R. L. Busbey, Springer-Verlag, New York, 1971.

    This is one of the best contemporary books available on the overall chemistry of pesticides, even though it is basically a Russian translation.

15. Degradation of Herbicides, P. C. Kearney and D. D. Kaufman, Marcel Dekker, Inc., 1969, New York.

16. Detergents and Emulsifiers Annual, North American Division, Published by McCutcheon's Division, Allured Publishing Corporation, 45 North Broad Street, Ridgewood, New Jersey.

17. Disinfection, Sterilization, and Preservation, C. A. Lawrence and S. S. Block, Lea and Febiger, Philadelphia, 1968.

18. EPA Compendium of Registered Pesticides, Issued by the Office of Pesticide Programs, Technical Services Division, Environmental Protection Agency. Available from: Superintendent of Documents, U. S. Government Printing Office (Stop No. 550-1), Washington, D. C. 20402.

    Issued in 5 volumes:
    Volume I - Herbicides and Plant Growth Regulators
    Volume II - Fungicides and Nematocides
    Volume III- Insecticides, Acaricides, Molluscicides, and Anti-Fouling Compounds
    Volume IV - Rodenticides and Mammal, Bird, and Fish Toxicants
    Volume V - Disinfectants

19. Farm Chemicals Handbook, Published annually by Farm Chemicals. Available from Meister Publishing Co., 37841 Euclid Avenue, Willoughby, Ohio, 44094.

20. Gas Chromatographic Analysis of Drugs and Pesticides, Vol. 2, Benjamin J. Gudzinowicz, 1967, Marcel Dekker, Inc., New York.

21. Gas Liquid Chromatography, S. V. Nogare, R. S. Juvet, Jr., 1962, Interscience Publishers, a division of John Wiley & Sons, New York.

22. Guide to the Chemicals Used in Crop Protection, 1973, E. Y. Spencer, University of Western Ontario, Information Canada, Ottawa.

23. Guide to Stationary Phases for Gas Chromatography, 1973, Analabs, Inc., North Haven, Conn.

24. Herbicide Handbook of the Weed Science Society of America, 3rd Ed., 1974, Weed Science Society of America.

25. Herbicides, Fungicides, Formulation Chemistry, Pesticide Chemistry, Vol. V, edited by A. S. Tahori, Gordon and Breach Science Publishers, New York, 1972.

26. Industrial Production and Formulation of Pesticides in Developing Countries - Volume I: General Principles and Formulation of Pesticides. Prepared by the Industrial Development Organization, Vienna, Austria, 1972.

27. Insecticides, Fungicides, and Weed Killers, E. Bourart, 2nd Ed., Revised and enlarged by T. R. Burton, D. Van Nostrand Company, 250 Fourth Avenue, New York, 1925.

28. Manual of Methods for Chemical Analysis of Water and Wastes, U. S. Environmental Protection Agency, Office of Technology Transfer, Washington, D. C. 20460.

29. The Merck Index, P. G. Stecher (Ed.), Published by Merck & Co., Inc., Rahway, New Jersey (Latest Edition).

30. Modern Practice of Liquid Chromatography, edited by J. J. Kirkland, Wiley-Interscience, a division of John Wiley & Sons, New York, 1971.

31. National Formulary XIV, 1975, Prepared by the National Formulary Board, Published by the American Pharmaceutical Association, Washington, D. C. Supplements issued annually.

32. Natural Pest Control Agents, Advances in Chemistry Series 53, American Chemical Society, Washington, D. C., 1966.

33. Organic Insecticides, Their Chemistry and Mode of Action, R. L. Metcalf, Interscience Publishers, New York, 1955.

34. Pesticide Chemicals Official Compendium, Published by the Association of American Pesticide Control Officials, Inc., 1966. May be available from: Control Division, Kansas State Board of Agriculture, 1032-S State Office Building, Topeka, Kansas, 66606.

35. Pesticide Formulations, W. Van Valkenburg, Ed., Marcel Dekker, Inc., New York, 1973.

36. Pesticide Identification at the Residue Level, Division of Pesticide Chemistry, ACS Symposium - May 26-27, 1970, Toronto, Canada; Francis J. Giros, Symposium Chairman, Advances in Chemistry Series 104, American Chemical Society, Washington, D. C., 1971.

37. Pesticide Index, 4th Ed., Donald Frear, College Science Publishers, State College, Pa., 16801, 1965.

38. Pesticide Manual, H. Martin, Ed., Issued by British Crop Protection Council, 3rd Edition (1972), Available from: Mr. A. W. Billitt, Clacks Farm, Borely, Ombersley, Droitwich, Worcester, England.

Probably the best handy reference source for general information on agricultural pesticides. Although the headings are based on British nomenclature, there is a good index to cross-reference into American names. A brief page description for each pesticide includes:

Chemical, common, and trade names
Manufacturing process
Stability
Chemical and physical properties
Uses
Toxicity
Types of formulations
References to formulation and residue analytical methods

39. Pyrethrum; The Natural Insecticides, J. E. Casida, Academic Press, Inc., New York, 1974.

40. Quantitative Organic Analysis via Functional Groups, 3rd Ed., Sidney Siggia, John Wiley & Sons, New York, 1963.

41. Residue Reviews, F. A. Gunther, Residues of Pesticides and Other Chemicals in Foods and Feeds, Springer-Verlag, New York.

42. The Sadtler Commercial Infra-red Spectra - Agricultural Chemicals, Available from the Sadtler Research Laboratories, 3314-20 Spring Garden St., Philadelphia, Pa., 19104.

Includes KBr, neat, and mull spectra of acaricides, bactericides, defoliants, fungicides, herbicides, insecticides, nematocides, repellants and attractants, rodenticides, and miscellaneous pesticides.

43. The Sadtler Guide to NMR Spectra, W. W. Simons, M. Zanger, Sadtler Research Laboratories, Inc., Philadelphia, Pa.

44. Specifications for Pesticides, 2nd Ed., World Health Organization, Geneva, Switzerland, 1961.

45. Spectrometric Identification of Organic Compounds, 3rd Ed., R. Silverstein and G. Bassler, John Wiley & Sons, New York, 1975.

46. Spot Tests in Organic Analysis, Fritz Feigl, in collaboration with Vinzenz Anger, translated by Ralph E. Oesper, 7th Ed., Elsevier Publishing Co., New York, 1966.

47. The United States Dispensatory, 24th Ed., A. Osol, R. Pratt, and G. Farrar, Jr., J. B. Lippincott Co., Philadelphia and Toronto.

48. The United States Pharmacopeia, U.S.P. XIX (1975) By Authority of the U. S. Pharmacopeial Convention, Inc., 12601 Twinbrook Parkway, Rockville, Md. 20852. Supplements issued.

49. Thin Layer Chromatography, edited by Egon Stahl, 1965, Springer-Verlag, New York.

C. JOURNALS USEFUL TO THE PESTICIDE FORMULATION ANALYST

Only the Journal of the Association of Official Analytical Chemists publishes articles concerning pesticide formulation analysis on a sustained basis. The other journals listed have occasional articles on pesticide product analysis, but are generally more oriented toward residue analysis, photo- and metabolic decomposition, toxicity, or general analytical chemistry.

1. The Analyst, Published monthly by the Society for Analytical Chemistry, 9/10 Savile Row, London, W1X 1AF.

2. Analytical Abstracts, Published monthly by the Society for Analytical Chemistry, 9/10 Savile Row, London. Printed by Heffers Printers, Ltd., Cambridge, England.

3. Analytical Chemistry, Published monthly by the American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036.

4. Bulletin of Environmental Contamination and Toxicology, Published monthly by Springer-Verlag, Inc., 175 Fifth Avenue, New York, N. Y. 10010.

5. Chemical and Engineering News, Published weekly by the American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036.

6. Environment, Published monthly by the Scientists' Institute for Public Information, 438 N. Skinker Blvd., St. Louis, Missouri 63130.

7. Environmental Science and Technology, Published monthly by the American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036.

8. Journal of Agricultural and Food Chemistry, Published bimonthly by American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036.

9. Journal of the Association of Official Analytical Chemists, Published bimonthly by the Association of Official Analytical Chemists, Inc., Box 540, Benjamin Franklin Station, Washington, D. C. 20044.

10. Journal of Chromatographic Science (Formerly Journal of Gas Chromatography), Published monthly by Preston Technical Abstracts Company, P. O. Box 312, Niles, Illinois, 60648.

11. Journal of Chromatography, Published fortnightly by Elsevier Publishing Company, Amsterdam, Netherlands.

12. Pesticide Abstracts (Formerly Health Aspects of Pesticides Abstract Bulletin), Published monthly by the Environmental Protection Agency, Office of Pesticides Programs, Technical Services Division, Rm. EB-49, 401 M Street, S. W., Washington, D. C. 20460.

13. Pesticide Chemical News, Published weekly by Louis Rothschild, Jr., 420 Colorado Building, 1341 G Street, N. W., Washington, D. C. 20005.

14. Pesticides Monitoring Journal, Published quarterly under the auspices of the Federal Working Group on Pest Management by the U. S. Environmental Protection Agency, Office of Pesticides Programs, Technical Services Division, Room B49, East Waterside Mall, 401 M Street, S. W., Washington, D. C. 20460.

15. Science, Published weekly by the American Association for the Advancement of Science, 1515 Massachusetts Avenue, N. W., Washington, D. C. 20005.

D. PESTICIDE RESIDUE ANALYSIS

Methods of multi-residue and specific pesticide residue analysis in different media are given in references quoted in Section I as noted. The following sources may also be of value to the pesticide residue analyst:

1. Pesticide Analytical Manual, U. S. Department of Health, Education and Welfare, Food and Drug Administration, 2nd Edition (1968), revised periodically. Issued in two volumes.

   Volume I - Methods Which Detect Multiple Residues
   Organochlorine (both ionic and nonionic) and organophosphate pesticide extraction procedures and clean-ups are described. GLC, TLC, PC, and confirmatory tests are given treatment with respect to multi-residue analysis.

   Volume II- Methods of Individual Pesticide Residues
   These methods are primarily those derived from commodity tolerance applications and petitions, although others are also included. The methods may or may not have had collaborative testing, but most are referenced to published or available literature.

2. Analysis of Pesticide Residues in Human and Environmental Samples, Ed. J. F. Thompson; Prepared by The Primate & Pesticides Effect Laboratory, Perrine, Florida (now located at Research Triangle Park, North Carolina). Revised November 1972 and December 1974.

   This valuable manual contains general information on sampling, laboratory procedures, gas chromatography, and confirmatory procedures. Chlorinated hydrocarbon and organophosphate pesticide analyses in human tissue and excreta are covered, along with urine analysis for some of the ionic pesticides. Air, water, soil, and dust procedures are given for pesticide analysis. PCB analysis is covered, including typical chromatograms of different Aroclors. Mercury analysis in water, blood, urine, and fish samples is presented along with the specific analysis for methyl mercury.

3. Methods for Organic Pesticides in Water and Wastewater, Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio, 1971. Revisions and additions issued periodically.

   Primarily covers laboratory practices and analytical methodology for analysis of chlorinated hydrocarbons in water and wastewater.

4. Guide to the Analysis of Pesticide Residues, Prepared by H. P. Burchfield and Donald W. Johnson for U. S. Department of Health, Education, and Welfare, Public Health Service, Bureau of State Services (Environmental Health), Office of Pesticides, Washington, D. C., under contract with Southwest Research Institute, San Antonio, Texas 78206. Available from the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20402 (issued in 2 volumes)

   Volume I - Contains a compilation of methods which are recommended for the analysis of pesticide residues in water, soil, plant tissues, animal tissues, body fluids, dairy products, and related environments. General principles, extraction, clean-up, and gas chromatography are covered for a variety of classes of compounds.

   Volume II- Covers non-chromatographic techniques, infra-red identification, and a compilation of chemical and physical properties for a number of individual pesticides. There are a number of infra-red spectra for different compounds, most being KBr disks, however.

5. Analysis of Organic Pollutants in Water and Wastewater, W. Leithe, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1973

E. SOURCES ON PESTICIDE USAGE, TOXICITY, AND CONTROVERSY

1. Agricultural Applications of Petroleum Products, Advances in Chemistry Series No. 7, Published by the American Chemical Society, Washington, D. C., 1952.

2. Chlorodioxins - Origin and Fate, Advances in Chemistry Series No. 120, Published by the American Chemical Society, Washington, D. C., 1973.

3. Organic Pesticides in the Environment, Advances in Chemistry Series No. 60, Published by the American Chemical Society, Washington, D. C., 1966.

4. Pesticidal Formulations Research, Advances in Chemistry Series No. 86, Published by the American Chemical Society, Washington, D. C., 1969.

5. Pesticides in Tropical Agriculture, Advances in Chemistry Series No. 13, Published by the American Chemical Society, Washington, D. C., 1955.

6. Scientific Aspects of Pest Control, Symposium conducted by the National Academy of Sciences, National Research Council, Washington, D. C., Feb. 1-3, 1966 (Publication 1402 NAS/NRC).

7. Beatty, R. G., The DDT Myth: Triumph of the Amateurs, John Day Co., New York, 1973.

8. Beirne, B., Pest Management, CRC Press, Cleveland, Ohio, 1966.

9. Bicknell, F., Chemicals in Your Food and in Farm Produce: Their Harmful Effects, Emerson Books, Inc., 1961.

10. Brown, A. W. A., Insect Control by Chemicals, John Wiley and Sons, New York, 1951.

11. Burgess, H. D. and Hussey, N. W., Microbial Control of Insects, Academic Press, New York, 1971.

12. Busvine, J. P., A Critical Review of the Techniques for Testing Insecticides, Commonwealth Agricultural Bureau, 1971.

13. Carson, Rachel, Silent Spring, Houghton Mifflin Co., Boston, 1962. (Available in paperback)

14. deOng, E. R., Insect, Fungus, and Weed Control, Chemical Publishing Co., New York, 1953.

15. Dethier, V. G., Chemical Insect Attractants and Repellents, Blakiston Co., Philadelphia, 1947.

16. Edwards, C., Persistent Pesticides in the Environment, CRC Press, Cleveland, Ohio, 1970.

17. Epstein, S. S. and Legator, M. S., The Mutagenicity of Pesticides, Concepts and Evaluations, MIT Press, Cambridge, Mass., 1971.

18. Gerard, H. W. and Deichmann, U. B., Toxicology of Drugs and Chemicals, Academic Press, New York, 1969.

19. Graham, F. Jr., Since Silent Spring, Houghton Mifflin Co., Boston, 1970. (Available in paperback)

20. Gunther, F. A. and Jeppson, L. R., Modern Insecticides and World Food Production, John Wiley and Sons, New York, 1960.

21. Headley, J. C. and Lewis, J. N., The Pesticide Problem: An Economic Approach to Public Policy, Resources for the Future, Inc., Washington, D. C., Distributed by Johns Hopkins Press, Baltimore, Maryland, 1967.

22. Henkin, H. et al, The Environment, the Establishment, and the Law, Houghton Mifflin Co., Boston, 1971.

23. Herber, L., Our Synthetic Environment, Alfred E. Knopf, New York, 1962.

24. Hunter, B. T., Gardening without Poisons, 2nd Ed., Houghton Mifflin Co., Boston, 1971.

25. Jacobson, M., Naturally Occurring Insecticides, Marcel Dekker, New York, 1971.

26. Kilgore, W. and Doutt, R., Pest Control; Biological, Physical, and Selected Chemical Methods, Academic Press, New York, 1967.

27. Lehman, A. J., Summaries of Pesticide Toxicity, Published by the Association of Food and Drug Officials, P. O. Box 4267, Springfield, Illinois 62708, 1965.

28. Mallis, A., Handbook of Pest Control, 5th Ed., MacNair-Dorland Company, New York, 1969.

29. Martin, H., Scientific Principles of Crop Protection, 5th Ed., Edward Arnold Ltd., London, 1964.

30. Matsumura, F. et al. (Eds.), Environmental Toxicology of Pesticides, Academic Press, 1972.

31. McMillen, W., Bugs or People, Appleton-Century, New York, 1967.

32. Meltzer, Y., Hormonal and Attractant Pesticide Technology, Noyes Data Corporation, Park Ridge, N. J., 1971.

33. Miller, M. W. and Berg, G. G., Eds., Chemical Fallout, Charles C. Thomas Publishers, Springfield, Illinois, 1969.

34. Montague, K. and Montague, P., Mercury, Sierra Club, San Francisco, 1971.

35. Muirhead-Thomson, R. C., Pesticides and Freshwater Fauna, Academic Press, New York, 1971.

36. Pfadt, R. (Ed.), Fundamentals of Applied Entomology, 2nd Edition, MacMillan Company, New York, 1971.

37. Rodale, J. I. and Staff, Our Poisoned Earth and Sky, Rodale Books, Inc., Emmaus, Pennsylvania, 1964.

38. Rolsten, L. and McCoy, C. E., Introduction to Applied Entomology, The Ronald Press Company, New York, 1966.

39. Rudd, R. L., Pesticides and the Living Landscape, University of Wisconsin Press, Madison, Wisconsin, 1964. (Available in soft cover)

40. Sondheimer, E. and Simeone, J. B., Chemical Ecology, Academic Press, New York, 1970.

41. Sunshine, I. (Ed.), Handbook of Analytical Toxicology, CRC Company, Cleveland, Ohio, 1969.

42. Swann, L., Beneficial Insects, Harper and Row, New York, 1964.

43. Wellford, H., Sowing the Wind, Grossman Publishers, New York, 1972.

44. Whiteside, T., Defoliation, Ballantine/Friends of the Earth Book, New York, 1970. (Available in paperback)

45. Whiteside, T., The Withering Rain, America's Herbicidal Folly, E. P. Dutton and Co., New York, 1971.

46. Whitten, J., That We May Live, D. Van Nostrand Co., Princeton, New Jersey, 1966.

47. Wood, D. L. et al, Control of Insect Behavior by Natural Products, Academic Press, New York, 1970.

Infrared Spectra -- Introduction

Infrared spectroscopy is one of the most definitive ways of characterizing a chemical compound. The infrared absorption band pattern is analogous to a "fingerprint." With very few exceptions, positive identification of a chemical compound can be made by comparing the IR spectrum of the substance in question to the IR spectrum of known pure compounds. Small differences in the spectra will differentiate between compounds of similar structure and also will indicate the presence of impurities.

Infrared spectroscopy is a very useful tool for the analysis of pesticide formulations. Quite frequently, quantitative measurements can be made without elaborate extraction procedures just by using an absorption band at a wavelength where no interference is present. A linearity curve made at this chosen wavelength will determine a working range of useful concentrations. Only this short section of the IR spectrum is needed for quantitative calculation; however, a full scan will provide a qualitative identification.

The infrared spectra in this section were scanned on a Perkin-Elmer Model 521 double beam spectrophotometer using KBr disks, Nujol mull cells, and internal reflectance attachments. The samples of pesticides were obtained directly from the manufacturers. Samples from other sources were purified or recrystallized when necessary. Scans were made from 4000 cm^{-1} to 200 cm^{-1} (2.5 μ to 50 μ) using instrument settings as follows: attenuator speed 11, amplifier gain 5, slit program 10, scan time 32, speed suppression 5, beam source current 0.8 amp., and filter automatic.

The spectra of samples prepared using KBr disks, solutions, mulls, or internal reflectance will differ in the shape and intensity of the absorption bands. For this reason it is advisable for each lab to accumulate spectra scanned on their own instruments using concentrations, solvents or other matrices, cells or sample holders, in accordance with their analytical needs and interest.

The names used in the following index and table and on the individual spectra are a combination of common, trade, and accepted proper names. They are arranged alphabetically and the same name is used throughout. Cross reference to other names may be made using the "Pesticide Cross Reference Index to the Methods" section under "Methods of Analysis" or by using the "Other Names" section under each method.

The Environmental Protection Agency expresses its gratitude to Dr. Paul A. Giang of the Analytical Chemistry Laboratory, Agricultural Environmental Quality Institute, United States Department of Agriculture, Beltsville, MD 20705 for his expertise in preparing these infrared spectra. E.P.A. also wishes to thank the U.S.D.A. for permitting use of this material.

Mention of a pesticide or a proprietary product in this manual does not constitute a recommendation or an endorsement of this product by the U. S. Department of Agriculture or the U. S. Environmental Protection Agency.

In the table of "Pesticide and IR Data," the following key is used to indicate the type of pest control provided by compounds listed in the table:

(A) Acaricide

(B) Bactericide

(D) Disinfectant

(Fum) Fumigant

(F) Fungicide

(H) Herbicide

(I) Insecticide

(IR) Insect Repellent

(M) Molluscicide

(N) Nematocide

(PGR) Plant Growth Regulator

(R) Rodenticide

(S) Synergist

(VP) Vertebrate Poison

The analytical bands in the table indicate areas where (for single compounds) quantitation is most feasible; however, for several compounds present in a formulation, these peaks may not necessarily be the best. It may be necessary to choose another absorption band where only the component of interest absorbs, or to extract the component of interest free from any interfering compounds.

Infrared Spectra -- Pesticide and IR Data

Pesticide			IR Sample Matrix	Analytical Bands	
Name	Use	% Purity		Wave number (cm^{-1})	Microns (μ)
Abate	I	99.0	KBr disk	930, 778	10.74, 12.87
Acaralate	A	98.6	KBr disk	1022, 760	9.78, 12.20
Acritet	Fum	44.0	Nujol mull	2220, 864	4.52, 11.58
Akton	I	90.5	IRA plate	1224, 720	8.16, 13.94
alachlor	H	99.0	KBr disk	1180, 894	8.46, 11.18
aldicarb	I,A,N	92.4	KBr disk	1330, 988	7.51, 10.16
aldicarb sulfone	I,A,N	90.0	KBr disk	1158, 760	8.64, 13.14
aldicarb sulfoxide	I,A,N	92.2	KBr disk	1360, 515	7.35, 19.42
aldrin	I	99.5	KBr disk	1320, 720	7.55, 13.64
Alice Ketone	R,S	99.4	KBr disk	1029, 696	9.72, 14.34
allethrin	I	94.8	KBr disk	910, 850	11.00, 11.76
Alodan	I,A	97.8	KBr disk	1196, 846	8.36, 11.82
ametryne	H	95.0	KBr disk	1224, 808	8.16, 12.84
Amiben	H	tech. gr.	KBr disk	1214, 774	8.24, 12.88
Amical-48	D	tech. gr.	KBr disk	1068, 815	9.36, 12.27
amidithion	I,A	88.2	IRA plate	1114, 574	8.96, 17.50
aminocarb	I	94.2	KBr disk	1084, 826	9.22, 12.08
4-Amino-pyridine	Avi-repel.	100.0	KBr disk	1436, 1224	6.96, 8.16
amitrole	H	98.7	KBr disk	1426, 876	7.01, 11.40
Ammate	H	98.6	Nujol mull	792, 364	12.64, 27.48
ancymidol	PGR	tech. gr.	KBr disk	1298, 824	7.70, 12.12
antimycin	B	tech. gr.	Nujol mull	1516, 746	6.59, 13.42
Anti-resist-ant/DDT	I	tech. gr.	KBr disk	1150, 758	8.69, 13.22

Pesticide			IR Sample	Analytical Bands	
Name	Use	% Purity	Matrix	Wave number (cm^{-1})	Microns (μ)
ANTU	R	tech. gr.	KBr disk	1338, 764	7.47, 13.07
Aramite	A	90.0	IRA plate	1506, 826	6.64, 12.12
arsenic trioxide	R	100.0	KBr disk	1252, 1040	7.99, 9.54
Aspon	I	94.3	KBr disk	1458, 746	6.86, 13.48
asulam	H	98.6	KBr disk	1082, 676	9.24, 14.78
atrazine	H	99.0	KBr disk	978, 798	10.22, 12.52
azinphos-ethyl	I	98.4	KBr disk	1380, 894	7.25, 11.26
azinphos-methyl	I	99.9	KBr disk	896, 540	11.16, 18.50
azinphos-methyl oxygen analog	I	98.0	KBr disk	896, 826	11.16, 12.06
Azobenzene	A	98.6	KBr disk	1446, 772	6.92, 12.94
Azodrin	I,A	99.0	KBr disk	1262, 808	7.92, 12.37
Bandane	H	99.9	KBr disk	1260, 856	7.94, 11.68
Banol	I	99.5	KBr disk	1096, 930	9.12, 10.75
Banomite	A	98.6	KBr disk	1126, 740	8.88, 13.54
Banvel M	H	99.8	KBr disk	1176, 692	8.52, 14.47
barban	H	tech. gr.	KBr disk	1160, 896	8.62, 11.18
barium carbonate	R	100.0	KBr disk	854, 690	11.72, 14.48
Barthrin	I	tech. gr.	IRA plate	1032, 926	9.69, 10.80
Baygon	I	99.2	KBr disk	1365, 1034	7.33, 9.67
benefin	H	90.0	IRA plate	906, 710	11.06, 14.08
benomyl	F	97.0	KBr disk	1136, 792	8.82, 12.67
bensulide	H	97.7	IRA plate	878, 684	11.38, 14.56

Pesticide			IR Sample	Analytical Bands	
Name	Use	% Purity	Matrix	Wave number (cm^{-1})	Microns (μ)
bentazon	H	99.9	KBr disk	1230, 744	8.14, 13.44
benzadox	H	99.9	KBr disk	1158, 790	8.63, 12.62
BHC, Alpha Isomer	I	98.4	KBr disk	1096, 948	9.12, 10.56
BHC, Delta Isomer	I	97.8	KBr disk	1026, 920	9.74, 10.90
BHC, Epsilon Isomer	I	98.8	KBr disk	1298, 716	7.70, 13.96
BHC, Gamma Isomer	I	100.0	KBr disk	1100, 778	9.09, 12.85
BHC (tech. grade)	I	tech. gr.	KBr disk	1340, 850	7.46, 11.76
bifenox	H	98.7	KBr disk	970, 822	10.31, 12.17
binapacryl	I,F	99.0	KBr disk	740, 796	10.64, 12.58
Black Copper Oxide	F	100.0	KBr disk		
BNOA	PGR	99.0	KBr disk	1072, 840	9.33, 11.90
bomyl	I	92.0	KBr disk	916, 808	10.92, 12.38
bromacil	H	tech. gr.	KBr disk	1074, 760	9.31, 13.14
bromophos	I,A	94.4	KBr disk	1338, 716	7.47, 13.94
bromoxynil	H	96.4	KBr disk	2260, 1578	4.42, 6.34
bromoxynil octanoate	H	97.0	KBr disk	1546, 748	6.47, 13.44
Bulan	I	96.4	KBr disk	1404, 682	7.12, 14.68
butonate	I	95.0	KBr disk	1762, 922	5.68, 10.84
butylate	H	99.5	KBr disk	1224, 724	8.17, 13.82
Bux	I	tech. gr.	KBr disk	948, 698	10.54, 14.32
cacodylic acid	H	98.8	KBr disk	748, 650	13.44, 15.38

Pesticide			IR Sample	Analytical Bands	
Name	Use	% Purity	Matrix	Wave number (cm^{-1})	Microns (μ)
cadmium chloride	F	99.4	KBr disk	1878,	5.34
captafol	F	99.6	KBr disk	996, 816	10.06, 12.26
captan	F	99.6	KBr disk	1378, 880	7.26, 11.35
carbaryl	I	99.0	KBr disk	932, 770	10.68, 13.02
carbophenothion	I,A	92.4	KBr disk	1470, 1090	6.80, 9.17
carboxin	F	100.0	KBr disk	1278, 780	7.82, 12.82
CDAA	H	98.0	KBr disk	984, 788	10.16, 12.68
CDEC	H	97.5	KBr disk	1200, 826	8.33, 12.12
cetyl pyridinium bromide	D	98.2	KBr disk	966, 770	10.36, 13.00
chinothionate	A,F	94.0	KBr disk	1116, 758	8.96, 13.18
Chloranil	F	96.8	KBr disk	1098, 748	9.11, 13.37
chlorbenside	I,A	98.0	KBr disk	1002, 748	9.98, 13.38
chlorbromuron	H	94.0	KBr disk	1226, 872	8.16, 11.45
chlordane, alpha isomer	I	100.0	KBr disk	1160, 826	8.62, 12.11
chlordane, gamma isomer	I	100.0	KBr disk	1250, 820	8.00, 12.18
chlordane (tech. grade)	I	tech. gr.	KBr disk	1434, 748	7.03, 13.38
chlordene	I	98.8	KBr disk	1596, 1178	6.26, 8.49
chlordimeform	I,A	86.4	Nujol mull	1094, 808	9.14, 12.36
chlorfenvinphos	I	92.0	KBr disk	1576, 920	6.34, 10.84
Chlorflurecol	PGR	tech. gr.	KBr disk	1140, 420	8.77, 23.36
chlormequate chloride	PGR	99.8	KBr disk	1288, 450	7.76, 22.20

Pesticide			IR Sample	Analytical Bands	
Name	Use	% Purity	Matrix	Wave number (cm^{-1})	Microns (μ)
chlorobenzilate	A	100.0	KBr disk	1010, 752	9.90, 13.30
chloroneb	F	98.6	KBr disk	1082, 860	9.24, 11.62
chlorophacinone	R	100.0	KBr disk	1008, 580	9.92, 17.24
chlorothalonil	F	94.6	KBr disk	976, 690	10.24, 14.49
chloroxuron	H	96.4	KBr disk	1300, 748	7.69, 13.36
chlorpropham	H	99.9	KBr disk	1278, 878	7.82, 11.38
Chlorthion	I	98.9	KBr disk	1346, 748	7.43, 13.36
Ciodrin	I	89.0	Nujol mull	906, 698	11.04, 14.32
Citronella	IR	100.0	IRA plate	1378, 1226	7.25, 8.16
copper arsenate	I,F	99.4	IRA plate	828, 438	12.07, 22.84
copper sulfate pentahydrate	F	100.0	IRA plate	968, 652	10.34, 15.34
coumachlor	R	98.6	KBr disk	1070, 760	9.34, 13.14
coumaphos	I	98.9	KBr disk	1336, 1142	7.48, 8.75
Counter	I	94.4	KBr disk	1154, 650	8.66, 15.40
cyanamide	H,F	100.0	KBr disk	2074, 664	4.82, 15.10
cycloate	H	99.0	KBr disk	1226, 848	8.16, 11.78
cyclohexamide	F	98.2	Nujol mull	1032, 450	9.69, 22.36
Cyolane	I	98.2	KBr disk	1240, 866	8.06, 11.54
cyprazine	H	99.6	IRA plate	888, 800	11.26, 12.50
2,4-D	H	100.0	KBr disk	1300, 792	7.69, 12.68
2,4-D, butoxyethyl ester	H	98.9	KBr disk	1196, 868	8.36, 11.52
2,4-D, butyl ester	H	98.4	KBr disk	1476, 798	6.77, 12.54

Pesticide			IR Sample	Analytical Bands	
Name	Use	% Purity	Matrix	Wave number (cm^{-1})	Microns (μ)
2,4-D, ethyl-hexyl ester	H	97.4	KBr disk	1078, 718	9.27, 13.92
2,4-D, iso-octyl ester	H	99.6	KBr disk	870, 646	11.52, 15.47
2,4-D, iso-propyl ester	H	97.0	KBr disk	800, 646	12.50, 15.48
dalapon	H	98.0	IRA plate*	1254, 1074	7.97, 9.31
dalapon-Na	H	85.4	IRA plate*	1442, 872	6.93, 11.46
daminozide	PGR	100.0	KBr disk	1012, 788	9.88, 12.68
Dasanit	I,N	tech. gr.	KBr disk	1210, 532	8.27, 18.80
Dasanit (O-Analog)	I,N	tech. gr.	KBr disk	1480, 1154	6.76, 8.66
Dasanit (O-Sulfone)	I,N	tech. gr.	KBr disk	1142, 754	8.76, 13.26
Dasanit Sulfone	I,N	tech. gr.	KBr disk	1102, 750	9.07, 13.34
dazomet	N	99.4	KBr disk	1220, 870	8.20, 11.48
2,4-DB	H	98.2	KBr disk	1022, 738	9.78, 13.55
DCPA	H	tech. gr.	KBr disk	1398, 836	7.15, 11.94
DDA	I	99.4	KBr disk	1086, 732	9.21, 13.64
DDE	I	100.0	IRA plate	1380, 502	7.24, 19.93
DDT	I	100.0	KBr disk	1096, 716	9.01, 13.96
p,p'-$D_{Br}DT$	I	100.0	IRA plate	1078, 836	9.27, 11.97
Deet	IR	98.0	KBr disk	1160, 744	8.62, 13.44
DEF	I	95.2	KBr disk	1200, 574	8.32, 17.43
demeton-O, sulfone	I,A	90.0	KBr disk	1324, 560	7.55, 17.84
demeton-O, sulfoxide	I,A	94.4	KBr disk	1246, 556	8.02, 17.96

Pesticide			IR Sample	Analytical Bands	
Name	Use	% Purity	Matrix	Wave number (cm^{-1})	Microns (μ)
demeton-S sulfone	I,A	92.6	KBr disk	1308, 1136	7.10, 8.80
demeton-S sulfoxide	I,A	88.6	IRA plate	886, 610	11.28, 16.40
demeton, tech. grade	I,A	tech. gr.	KBr disk	1136, 600	8.80, 16.44
demeton (thiol isomer)	I,A	91.6	KBr disk	1250, 620	8.00, 16.14
demeton (thiono isomer)	I,A	94.0	KBr disk	1162, 824	8.61, 12.14
desmedipham	H	99.0	KBr disk	1060, 688	9.43, 14.54
Dexon	F	98.0	KBr disk	1160, 718	8.62, 13.92
diallate	H	99.0	KBr disk	1034, 822	9.67, 12.14
diazinon	I	96.2	KBr disk	1584, 1154	6.31, 8.66
diazoben	F	96.8	KBr disk	1160, 718	8.62, 13.92
dibromochloro-propane	N	tech. gr.	Nujol mull	962, 496	10.38, 20.14
3,5-dibromo-salicylanilide	F	100.0	KBr disk	1162, 752	8.60, 13.30
4,5-dibromo-salicylanilide	F	99.8	KBr disk	1000, 500	10.00, 20.00
dibutalin	H	98.6	Nujol mull	1184, 760	8.44, 13.14
dicamba	H	99.6	KBr disk	1176, 690	8.50, 16.94
dicapthon	I	99.8	KBr disk	1296, 724	7.72, 13.84
dichlobenil	H	97.8	KBr disk	1198, 722	8.35, 13.82
dichlone	F	99.2	KBr disk	1136, 714	8.80, 14.02
dichloran	F	92.0	KBr disk	1148, 898	8.71, 11.16
Dichlofen-thion	I,N	96.4	KBr disk	1160, 560	8.62, 17.84
p-dichloro-benzene	Fum	100.0	IRA plate*	1880, 1016	5.32, 9.84

Pesticide			IR Sample	Analytical Bands	
Name	Use	% Purity	Matrix	Wave number (cm^{-1})	Microns (μ)
dichlorprop	H	98.8	KBr disk	1056, 796	9.47, 12.58
dichlorvos	I	99.6	IRA plate*	1276, 848	7.84, 11.78
Dicoumarol	R	97.4	KBr disk	1104, 1100	9.06, 9.09
dicrotophos	I	97.2	KBr disk	1280, 920	7.81, 10.86
dieldrin	I	99.2	KBr disk	1368, 480	7.31, 20.08
Dilan	I	tech. gr.	KBr disk	1008, 748	9.92, 13.37
dimefox	I,A	98.6	KBr disk	1306, 834	7.66, 11.98
dimethoate	I	99.3	KBr disk	1224, 496	8.17, 20.18
dimethoate, oxygen analog	I	92.6	KBr disk	1250, 836	8.00, 11.97
dimethyl phthalate	IR	94.6	Nujol mull	1070, 740	9.34, 13.52
dimetilan	I	99.4	KBr disk	1262, 750	7.92, 13.32
dinitramine	H	94.6	KBr disk	1196, 722	8.36, 13.83
dinobuton	A,F	99.4	KBr disk	1138, 766	8.79, 13.05
dinoseb	H	99.0	KBr disk	1250, 1068	8.00, 9.36
dioxacarb	I	tech. gr.	IRA plate	1212, 750	8.25, 13.34
dioxathion	I	tech. gr.	KBr disk	864, 650	11.57, 15.38
dioxathion	I	94.0	KBr disk	956, 822	10.46, 12.17
diphacinone	R	98.8	KBr disk	1142, 800	8.75, 12.50
diphenamid	H	100.0	KBr disk	1140, 748	8.77, 13.36
Diphenatrile	H	99.9	KBr disk	1076, 556	9.29, 17.98
diphenyl	F	97.9	KBr disk	1340, 802	7.46, 12.47
diphenylamine	I	99.9	KBr disk	1170, 874	8.55, 11.44
Dipropalin	H	98.6	KBr disk	976, 766	10.27, 13.04
diquat dibromide	H	99.9	KBr disk	1340, 706	7.46, 14.16

Pesticide			IR Sample	Analytical Bands	
Name	Use	% Purity	Matrix	Wave number (cm^{-1})	Microns (μ)
disulfoton	I	96.8	KBr disk	790, 656	12.64, 15.24
dithianon	I	97.4	KBr disk	1154, 698	8.66, 14.34
diuron	H	100.0	KBr disk	816, 524	12.26, 19.12
DN-111	A,I	98.0	KBr disk	1194, 842	8.37, 11.87
DNBP	I,H	98.4	KBr disk	1615, 1256	6.19, 7.96
DNOC	I,H,F	99.0	KBr disk	1010, 926	9.90, 10.78
dodine	F	100.0	KBr disk	1364, 706	7.33, 14.16
Dow ET-15	I	98.6	KBr disk	1124, 878	8.89, 11.42
DSMA	H	100.0	IRA plate	-- --	-- --
Dursban	I	99.0	KBr disk	1156, 677	8.65, 14.78
Dyfonate	I	99.3	IRA plate	942, 624	10.64, 16.02
Dyrene	F	98.4	KBr disk	1036, 790	9.65, 12.63
endosulfan	I	99.4	KBr disk	1598, 750	6.26, 13.34
endothall	H	99.2	KBr disk	1062, 788	9.41, 12.68
endothion	I,A	tech. gr.	KBr disk	1062, 746	9.41, 13.42
endrin	I	99.6	KBr disk	1180, 804	8.47, 12.46
EPN	I,A	98.8	KBr disk	1340, 686	7.46, 14.57
Eptam	H	97.0	KBr disk	1224, 716	8.17, 13.96
erbon	H	tech. gr.	KBr disk	1346, 870	7.43, 11.48
ethephon	PGR	98.0	KBr disk	1308,	7.64
ethion	I,A	100.0	KBr disk	1378, 1148	7.26, 8.71
ethohexadiol	IR	tech. gr.	Nujol mull	1374, 968	7.33, 10.33
ethoxyquin	F	100.0	KBr disk	1148, 800	8.71, 12.50
ethyl dimethoate	I	99.0	KBr disk	910, 494	11.00, 20.16
ethyl formate	Fum	96.0	KBr cell	990, 740	10.10, 13.52

Pesticide			IR Sample	Analytical Bands	
Name	Use	% Purity	Matrix	Wave number (cm^{-1})	Microns (μ)
ethyl hexanediol	IR	tech. gr.	IRA plate	1456, 1370	6.87, 7.30
ethyl trichlorfon	I	94.8	KBr disk	1152, 550	8.68, 18.14
famphur	I	99.2	KBr disk	1232, 704	8.12, 14.22
fenac	H	98.0	KBr disk	1338, 1094	7.47, 9.14
fenitrothion	I,A	97.8	KBr disk	1340, 754	7.46, 13.26
fenson	A	99.0	KBr disk	1010, 496	9.90, 20.17
fenthion O-analog	I	tech. gr.	KBr disk	1154, 794	8.66, 12.58
fenthion sulfone	I	tech. gr.	KBr disk	1228, 768	8.14, 13.02
fenthion sulfoxide	I	tech. gr.	KBr disk	1220, 720	9.20, 13.89
fenthion (tech. gr.)	I	tech. gr.	KBr disk	1220, 960	8.20, 10.45
fentin hydroxide	F	94.6	Nujol mull	1316, 748	7.60, 13.36
fenuron	H	99.4	KBr disk	1300, 686	7.69, 14.56
fenuron	H	90.0	Nujol mull	872, 746	11.46, 13.40
ferbam	F	98.5	KBr disk	1386, 976	7.22, 10.24
Ficam	I	97.0	KBr disk	1154, 930	8.66, 10.71
fluometuron	H	98.8	KBr disk	1329, 790	7.53, 12.66
fluorodifen	H	98.0	KBr disk	906, 748	11.04, 13.36
folpet	F	99.4	KBr disk	866, 526	11.55, 19.04
formetanate	I,A	95.0	KBr disk	1084, 918	9.22, 10.88
Fumarin	R	tech. gr.	Nujol mull	872, 746	11.46, 13.40
Furadan	I,N	98.4	KBr disk	1336, 1058	7.48, 13.02
Furadan (-3-Keto)	I,N	98.0	KBr disk	1024, 758	9.76, 13.19

Pesticide			IR Sample	Analytical Bands	
Name	Use	% Purity	Matrix	Wave number (cm^{-1})	Microns (μ)
Furadan (-3-OH)	I,N	98.6	KBr disk	1126, 886	8.86, 11.26
Gardona	I	99.0	KBr disk	892, 578	11.12, 17.31
Genite	A	100.0	KBr disk	1050, 740	9.52, 13.52
gibberellic acid	PGR	97.6	KBr disk	966, 770	10.35, 12.98
Glytac	H	96.2	IRA plate	1788, 834	5.59, 11.97
Gophacide	R	tech. gr.	IRA plate	1008, 584	9.92, 17.12
heptachlor	I	99.2	KBr disk	1250, 768	8.00, 13.02
heptachlor epoxide	I	96.8	KBr disk	1166, 818	8.58, 12.22
xachloro-acetone	H	95.0	IRA plate	644, 440	15.56, 22.60
exachloro-cyclopenta-diene	Fum	100.0	KBr disk	1142, 708	8.76, 14.16
Hormodin	PGR	99.2	KBr disk	1272, 742	7.86, 13.48
Imidan	I	99.0	KBr disk	906, 714	11.04, 14.02
Indalone	IR	89.2	KBr disk	1076, 768	9.29, 13.04
ioxynil	H	tech. gr.	KBr disk	1246, 896	8.02, 11.17
ioxynil octanoate	H	tech. gr.	KBr disk	1529, 712	6.54, 14.04
IPX	H	97.6	KBr disk	1000, 790	10.00, 12.66
isobanzan	I	99.5	KBr disk	984, 862	10.16, 11.61
isodrin	I	99.0	KBr disk	824, 588	12.14, 17.0
isolan	I	98.5	IRA plate	1154, 838	8.66, 11.92
Isoval	I,R	tech. gr.	Nujol mull	744, 540	13.44, 18.52
Karathane	A,F	tech. gr.	Nujol mull	952, 716	10.47, 13.96
karbutilate	H	99.0	KBr disk	1184, 994	8.45, 10.07

Pesticide			IR Sample	Analytical Bands	
Name	Use	% Purity	Matrix	Wave number (cm^{-1})	Microns (μ)
Kelthane	A	98.8	KBr disk	1014, 504	9.86, 19.84
Kepone	I	85.0	Nujol mull	1054, 504	9.48, 19.84
Landrin, 2,3,5-Isomer	I	99.8	KBr disk	932, 686	10.72, 14.57
Landrin, 3,4,5-Isomer	I	99.2	KBr disk	968, 856	10.32, 11.67
Largon	I	tech. gr.	Nujol mull	1016, 774	9.84, 12.92
lead arsenate	I	100.0	IRA plate		
lenacil	H	99.6	KBr disk	1096, 556	9.12, 17.98
Lethane-384	I	53.0	KBr disk	2180, 1114	4.59, 8.97
linuron	H	98.6	KBr disk	1178, 880	8.49, 11.36
Malachite	F	99.8	IRA plate	1048, 814	9.54, 12.28
malaoxon	I	tech. gr.	Nujol mull	1258, 826	7.95, 12.11
malathion	I	98.4	KBr disk	762, 652	13.18, 15.34
maleic hydrazide	PGR	100.0	KBr disk	1024, 820	9.76, 12.18
maneb	F	98.4	KBr disk	1128, 460	8.86, 21.76
MCPA	H	98.0	KBr disk	1186, 796	8.43, 12.57
MCPA, Iso-octyl Ester	H	tech. gr.	KBr disk	1150, 642	8.69, 15.58
MCPB	H	99.2	KBr disk	1124, 806	8.90, 12.41
MCPP	H	100.0	KBr disk	1046, 552	9.56, 18.13
Memmi	F	99.8	KBr disk	1068, 824	9.36, 12.14
mercuric chloride	I,F	96.8	KBr disk	1600,	6.25
mercury oxide (yellow)	F	100.0	IRA plate	574, 464	17.42, 21.55
Mesurol	I	100.0	KBr disk	1102, 864	9.08, 11.58

Pesticide			IR Sample	Analytical Bands	
Name	Use	% Purity	Matrix	Wave number (cm^{-1})	Microns (μ)
metaldehyde	M	100.0	KBr disk	1332, 548	7.51, 18.22
Metasystox-R	I,A	tech. gr.	KBr disk	834, 576	11.97, 17.36
methazole	H	100.0	KBr disk	1270, 816	7.87, 12.26
methidathion	I,A	99.9	KBr disk	1578, 644	8.34, 15.53
methomyl	I,N	99.0	KBr disk	1090, 556	9.17, 17.98
methoxychlor	I	100.0	KBr disk	1176, 782	8.50, 12.76
methyl demeton	I,A	94.6	KBr disk	1440, 564	6.94, 17.77
methyl parathion	I	99.2	KBr disk	1240, 764	8.06, 13.14
Methyl Trithion	I,A	92.2	KBr disk	1096, 650	9.12, 15.38
metobromuron	H	98.0	KBr disk	1068, 446	9.36, 22.41
metribuzin	H	99.2	KBr disk	1052, 904	9.50, 11.06
MGK-264	S	tech. gr.	IRA plate	1172, 718	8.53, 13.92
mipafox	I	tech. gr.	KBr disk	1370, 476	7.30, 21.02
mirex	I	100.0	KBr disk	882, 532	11.34, 18.78
Mobam	I	96.4	KBr disk	944, 700	9.50, 11.06
molinate	H	99.3	KBr disk	1152, 660	8.68, 15.18
Monitor	I	98.8	KBr disk	1200, 760	8.33, 13.17
monuron	H	98.4	KBr disk	1010, 830	9.90, 12.06
Morestan	I,A,F	99.4	KBr disk	1174, 576	8.52, 17.36
naled	I,A,Fum	99.0	KBr disk	1284, 806	7.79, 12.42
naphthalaphos	I,D	100.0	KBr disk	1082, 544	9.24, 18.37
naphthalene	Fum	100.0	KBr disk	1200, 1000	8.33, 10.00
naphthalene acetamide	PGR	96.4	KBr disk	1380, 774	7.25, 12.92
naphthalene acetic acid	PGR	97.4	KBr disk	1502, 534	6.66, 18.72

Pesticide			IR Sample	Analytical Bands	
Name	Use	% Purity	Matrix	Wave number (cm^{-1})	Microns (μ)
naptalam	H	98.8	KBr disk	1346, 700	7.43, 14.28
N-butyl acetanilide	IR	98.8	KBr disk	1210, 700	8.26, 14.27
neburon	H	96.4	KBr disk	1032, 504	9.69, 19.82
Nellite	N	100.0	Nujol mull	1018, 752	9.82, 13.30
Nemacur	N	97.5	KBr disk	804, 538	12.44, 18.58
norbormide	R	100.0	KBr disk	1482, 1036	6.75, 9.65
norea	H	98.8	IRA plate	1636, 1376	6.11, 7.27
N-Serve	B	99.0	KBr disk	1140, 700	10.28, 11.27
Omite	A	92.0	KBr disk	1506, 874	6.64, 11.44
Orthene	I	99.9	Nujol mull	946, 556	10.64, 17.92
ovex	A	tech. gr.	KBr disk	1020, 768	9.80, 13.02
Oxycarboxin	F	100.0	KBr disk	-- --	-- --
parathion	I	98.5	KBr disk	1160, 682	8.62, 14.66
PCP	H	38.0	IRA plate*	1440, 978	6.94, 10.24
Pentac	A	99.5	KBr disk	1014, 900	9.86, 11.14
pentachloro-benzene	H	99.9	KBr disk	1410, 760	7.09, 13.15
Perthane	I	90.0	KBr disk	1120, 850	8.92, 11.76
Piperalin	F	99.6	KBr disk	1032, 752	9.65, 13.30
piperonyl butoxide	S	100.0	IRA plate*	1044, 942	9.57, 10.62
pival	R	98.0	KBr disk	1136, 704	8.80, 14.21
prometone	H	99.2	KBr disk	1018, 814	9.82, 12.27
pronamide	H	99.4	KBr disk	1094, 660	9.14, 15.15
propachlor	H	96.8	KBr disk	1160, 772	8.62, 12.94
propanil	H	99.2	KBr disk	1196, 844	8.36, 12.04

Pesticide			IR Sample	Analytical Bands	
Name	Use	% Purity	Matrix	Wave number (cm^{-1})	Microns (μ)
pyrethrin concentrate	I	40.0	IRA plate*	1104, 984	9.05, 10.16
Randox-T	H	92.0	KBr disk	1096, 778	9.12, 12.88
rotenone	I	100.0	KBr disk	1304, 1090	7.66, 9.17
Ruelene	I,A	98.6	KBr disk	1356, 798	7.37, 12.58
sesamex	S	tech. gr.	IRA plate*	1182, 1036	8.46, 9.17
sesone	H	99.0	KBr disk	1448, 866	6.91, 11.56
siduron	H	98.8	KBr disk	1442, 1312	6.93, 7.62
Simazine	H	99.1	KBr disk	1298, 798	7.70, 12.52
Sirmate	H	98.6	KBr disk	946, 804	10.58, 12.42
streptomycin sulfate	B	98.0	KBr disk	-- --	-- --
strychnine nitrate	VP	99.2	KBr disk	1270, 758	7.87, 13.18
strychnine sulfate	VP	98.0	KBr disk	1592, 764	6.28, 13.08
Sustar	H	tech. gr.	IRA plate	1300, 466	7.69, 21.46
2,4,5-T	H	100.0	KBr disk	1134, 764	8.81, 13.12
2,4,5-T (butoxyethyl ester)	H	98.4	KBr disk	870, 734	11.49, 13.62
2,4,5-T (butyl ester)	H	100.0	KBr disk	870, 734	11.49, 13.62
2,4,5-T (isooctyl ester)	H	95.5	KBr disk	870, 734	11.49, 13.62
2,4,5-T (isopropyl ester)	H	98.8	KBr disk	830, 770	12.03, 13.01
2,4,5-T (methyl ester)	H	98.2	KBr disk	862, 678	11.60, 16.74

Pesticide			IR Sample	Analytical Bands	
Name	Use	% Purity	Matrix	Wave number (cm^{-1})	Microns (μ)
Tabatrex	IR	100.0	KBr disk	1722, 1106	5.81, 13.34
TEPP	I	40.0	IRA cell*	-- --	-- --
terbacil	H	99.9	Nujol mull	1398, 746	7.15, 13.40
terbutol	H	97.0	KBr disk	1250, 850	8.00, 11.76
thiabenda-zole	F	99.5	KBr disk	1304, 900	7.67, 11.12
thiram	F	tech. gr.	KBr disk	1240, 848	8.06, 11.79
Torak	I,A	97.8	KBr disk	864, 586	11.56, 17.06
triallate	H	99.6	KBr disk	1034, 810	9.67, 12.34
3,4,5-tribromo-salicyl-anilide	F,B	100.0	KBr disk	1002, 735	9.99, 13.58
tricamba	H	98.8	KBr disk	1014, 584	9.86, 17.12
trichloro-carbanilide	D	98.6	KBr disk	1080, 812	9.26, 12.31
trifluralin	H	99.8	KBr disk	904, 704	11.06, 14.19
Tritac	H	99.0	Nujol mull	992, 810	10.17, 12.36
Warfarin	R	100.0	KBr disk	952, 702	11.50, 14.26
Zectran	I,A	92.0	IRA plate	1094, 870	9.14, 11.48
zineb	F	97.4	KBr disk	1384, 974	7.22, 10.37
Ziram	F	91.4	KBr disk	1238, 560	8.08, 17.84

* Internal Reflectance Attachment

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TRIFLURALIN	
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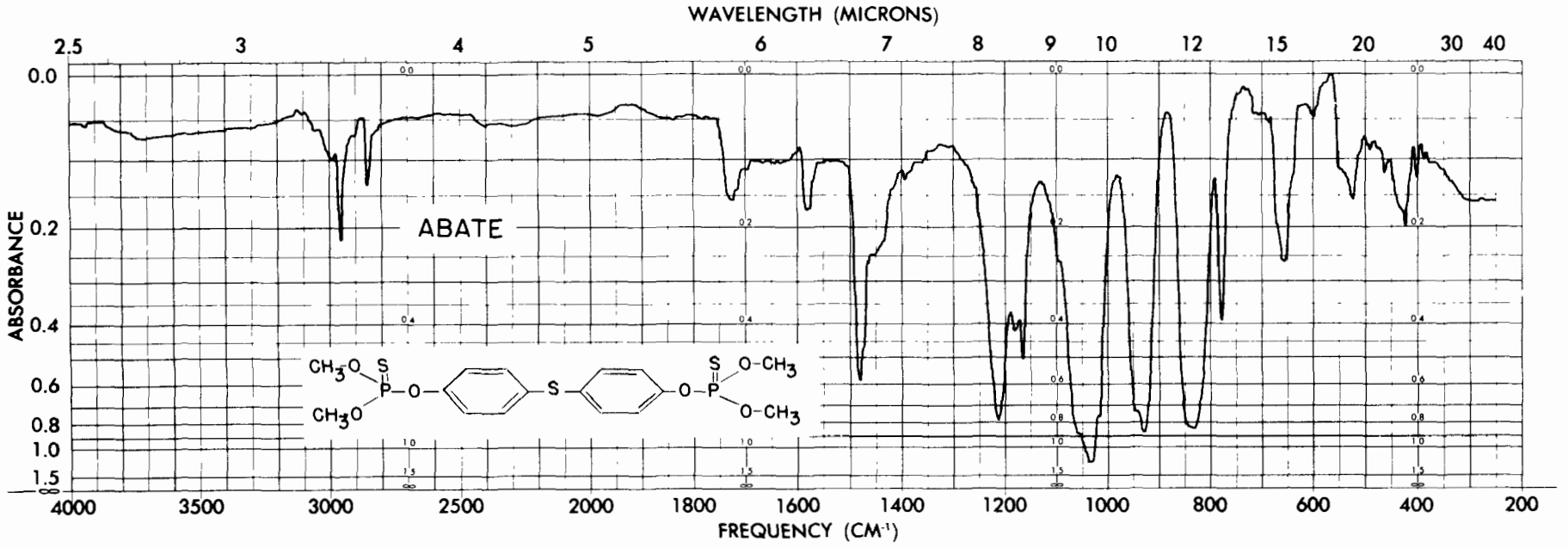
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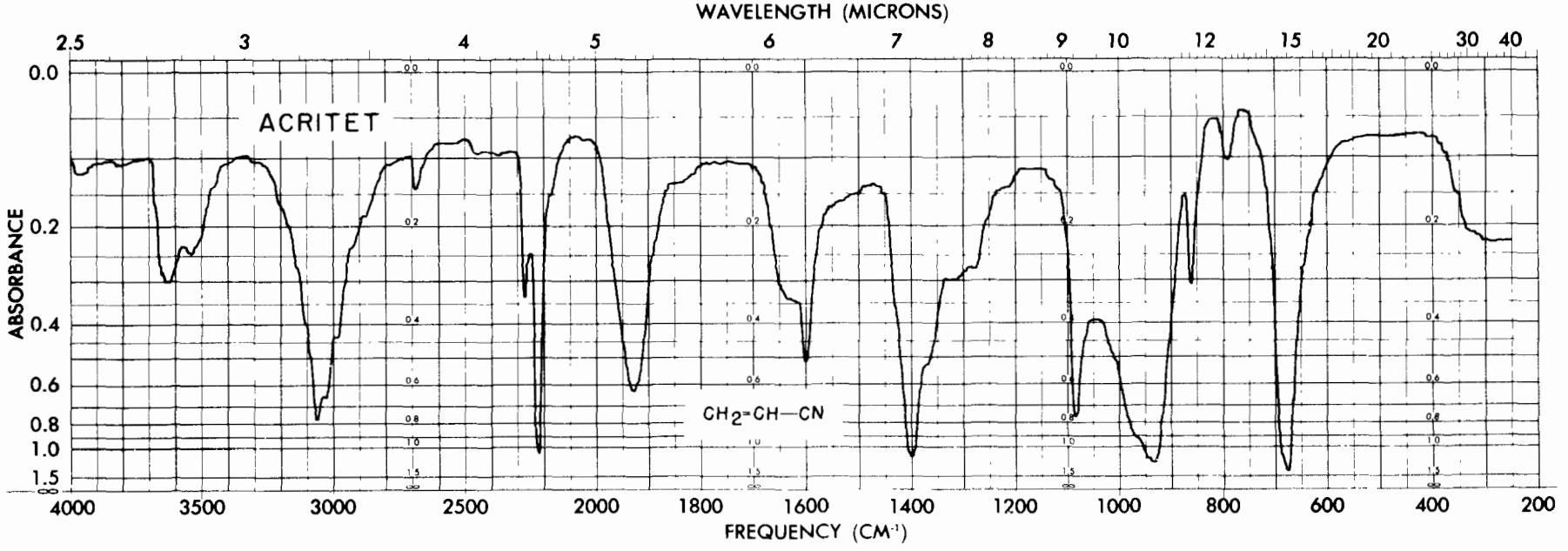
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CH2=CH—CN
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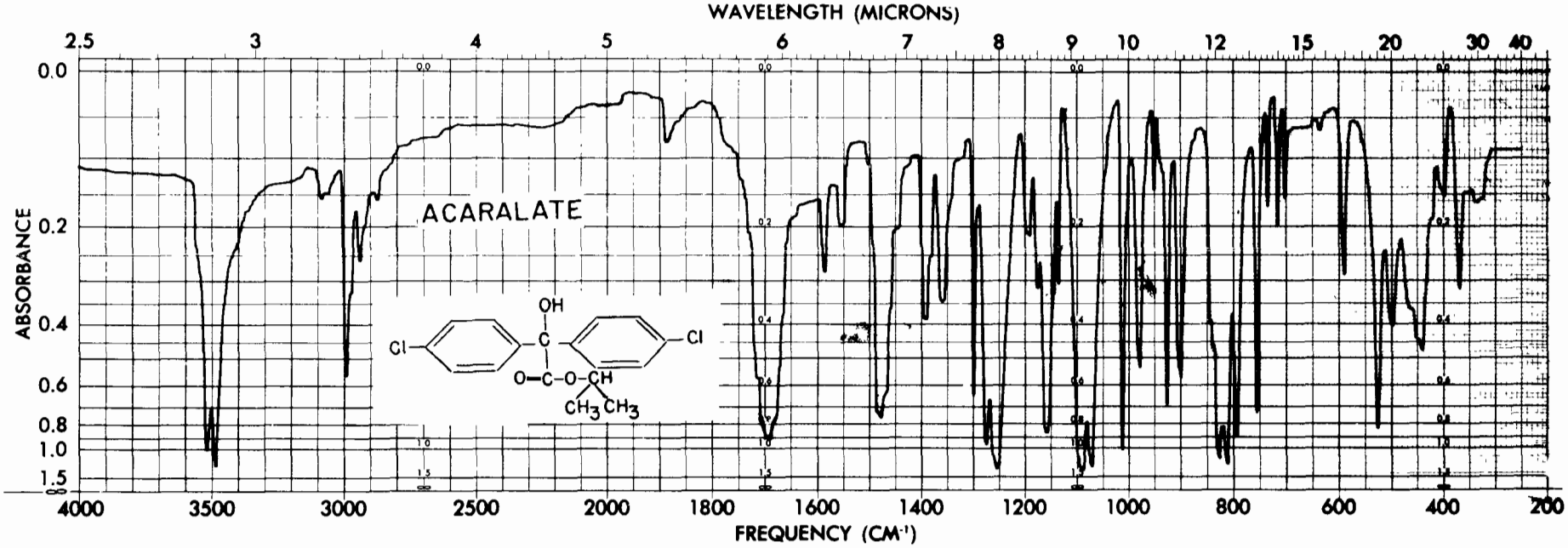
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0.2
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0.6
0.8
1.0
1.5
ACARALATE
OH
Cl
C
Cl
O—C—O—CH
CH3 CH3
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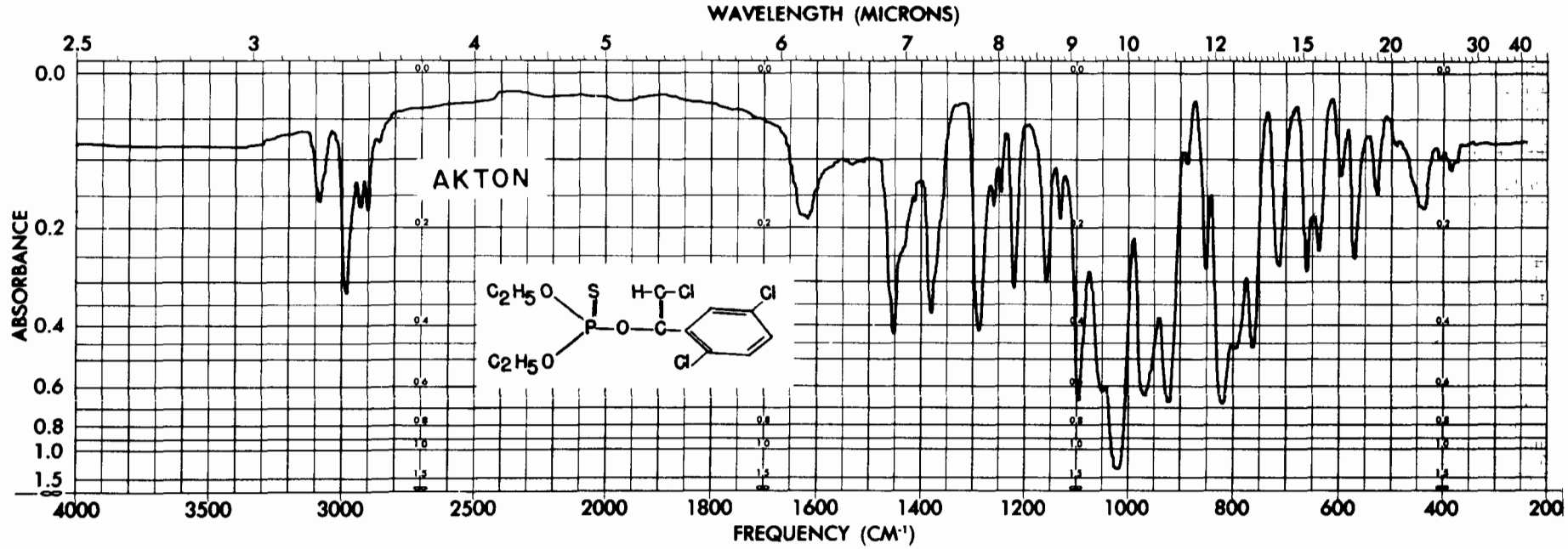
WAVELENGTH (MICRONS)
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1.5
AKTON
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S
H-C-Cl
Cl
P
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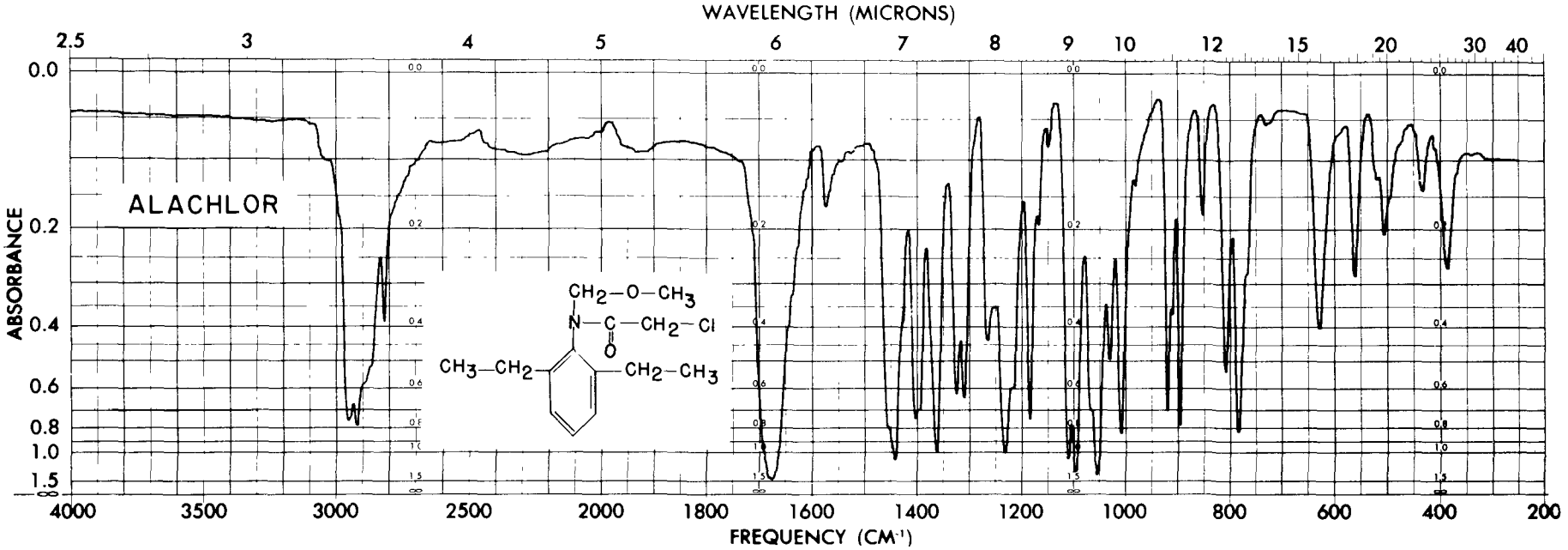
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0.8
1.0
1.5
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3000
2500
2000
1800
1600
1400
1200
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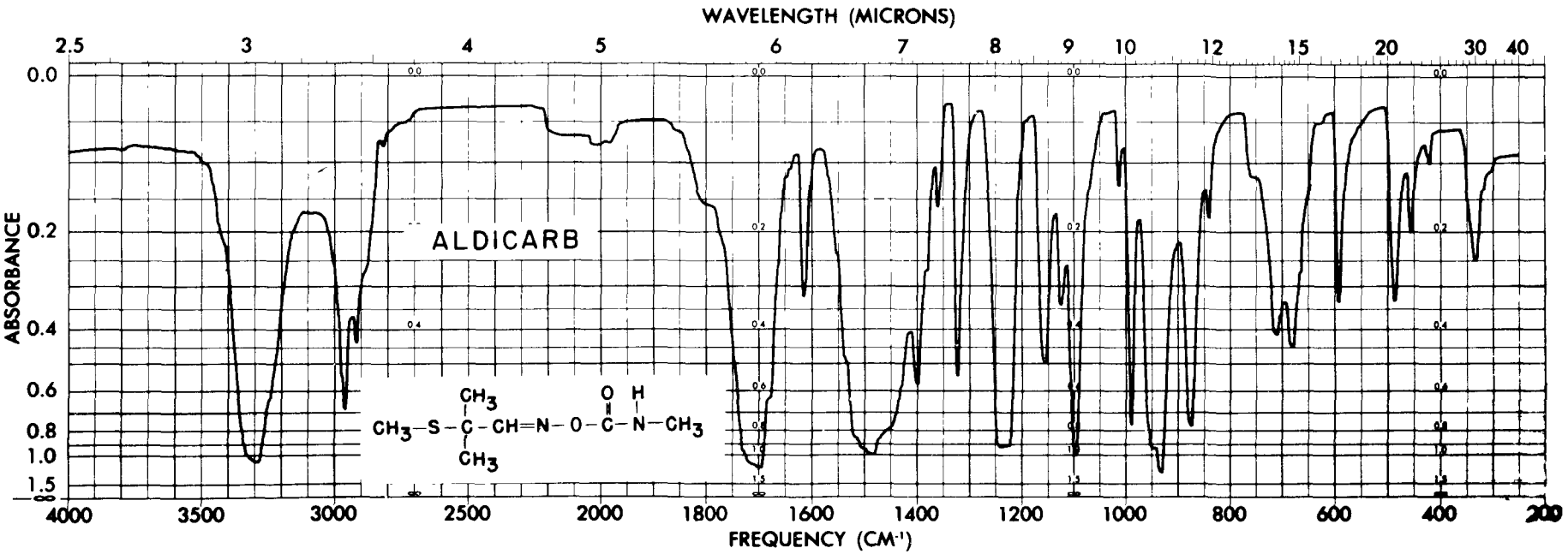
CH3—CH2
CH2—CH3


WAVELENGTH (MICRONS)
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ABSORBANCE
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0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
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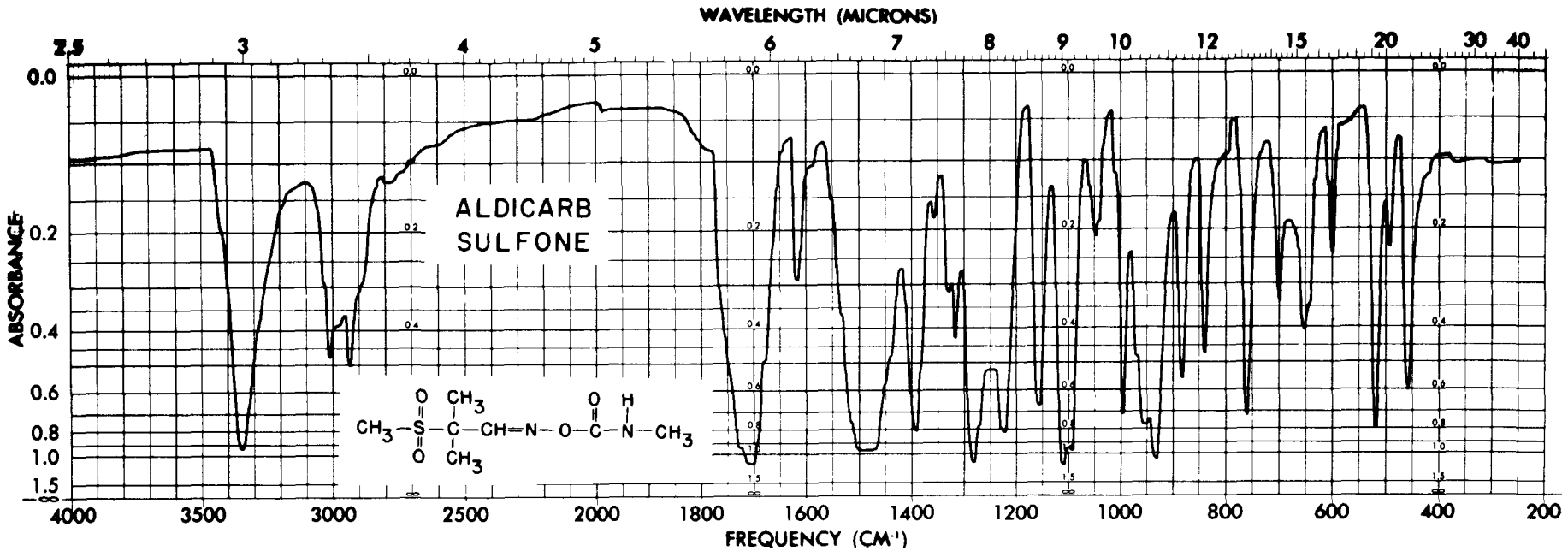
WAVELENGTH (MICRONS)
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0.2
0.4
0.6
0.8
1.0
1.5
ALDICARB
SULFONE
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2500
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1800
1600
1400
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600
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200
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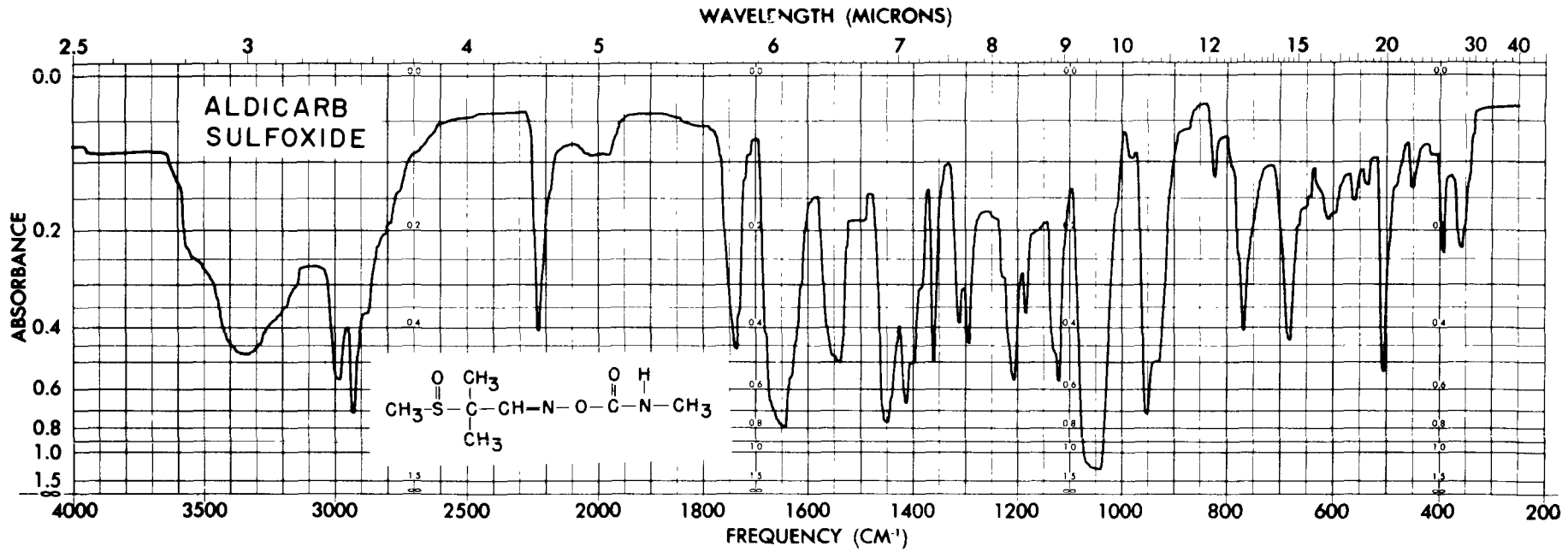
WAVELENGTH (MICRONS)
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ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ALDICARB
SULFOXIDE
4000
3500
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2500
2000
1800
1600
1400
1200
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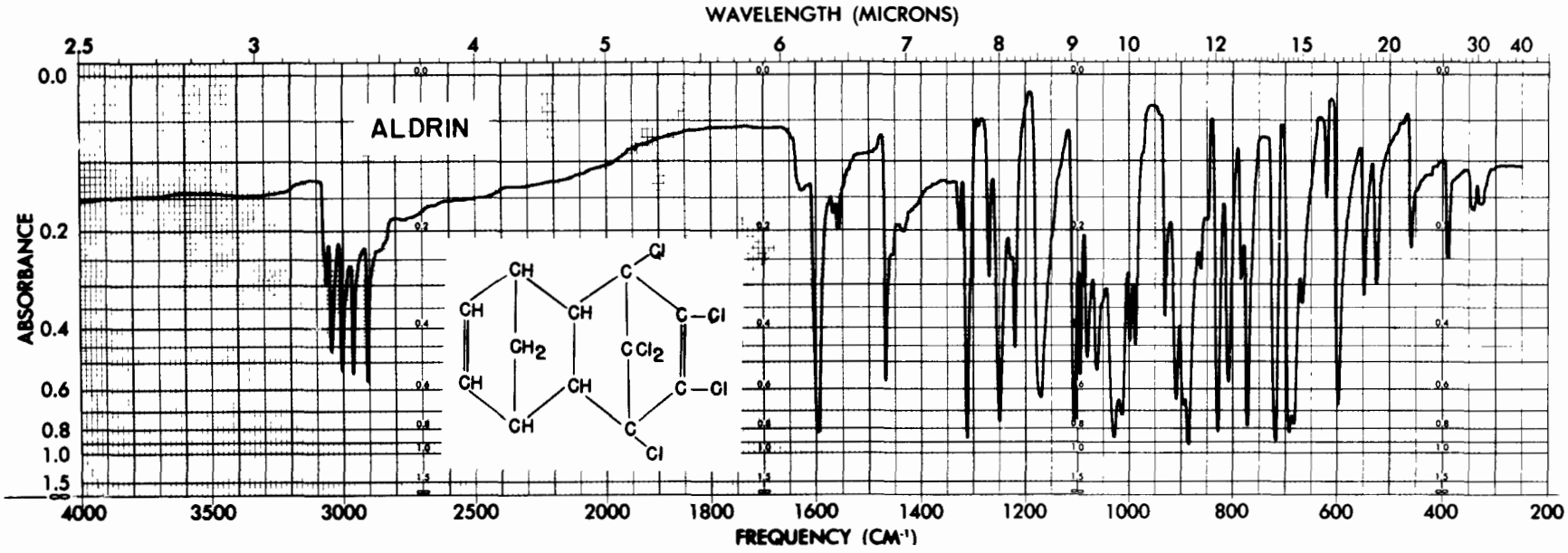
800
600
400
200
FREQUENCY (CM⁻¹)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ALDRIN
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
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2500
2000
1800
1600
1400
1200
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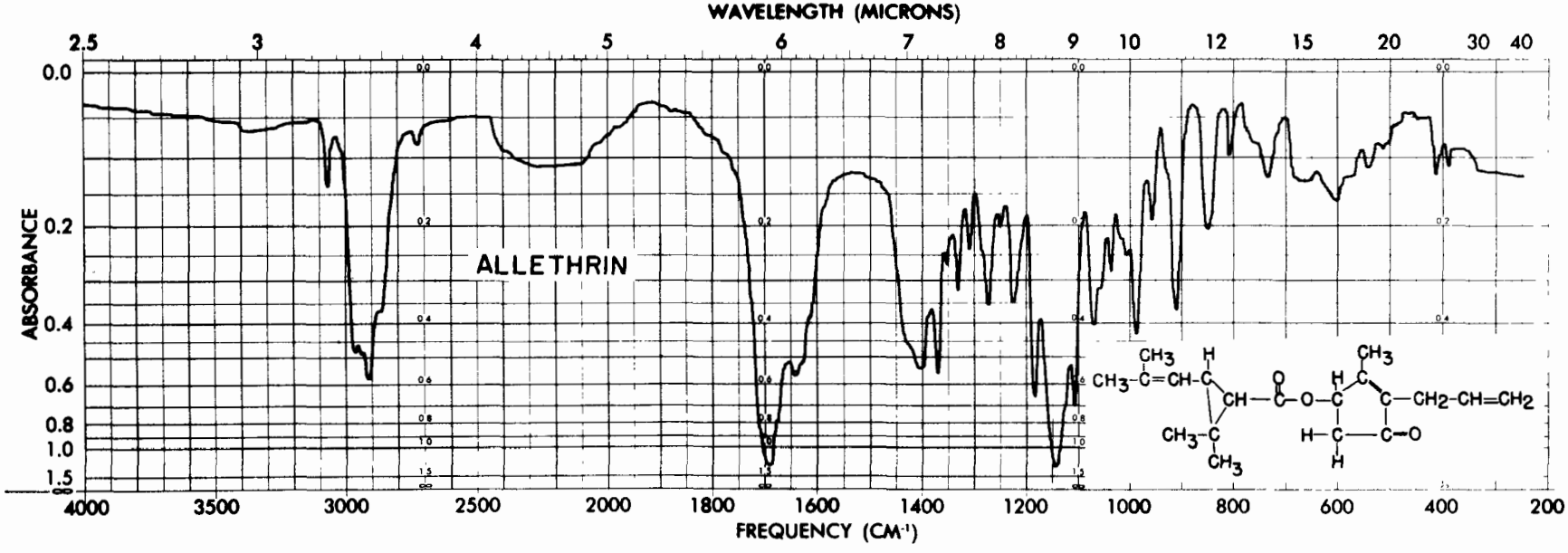
800
600
400
200
FREQUENCY (CM⁻¹)


WAVELENGTH (MICRONS)
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3
4
5
6
7
8
9
10
12
15
20
30
40
ALLETHRIN
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
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2500
2000
1800
1600
1400
1200
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800
600
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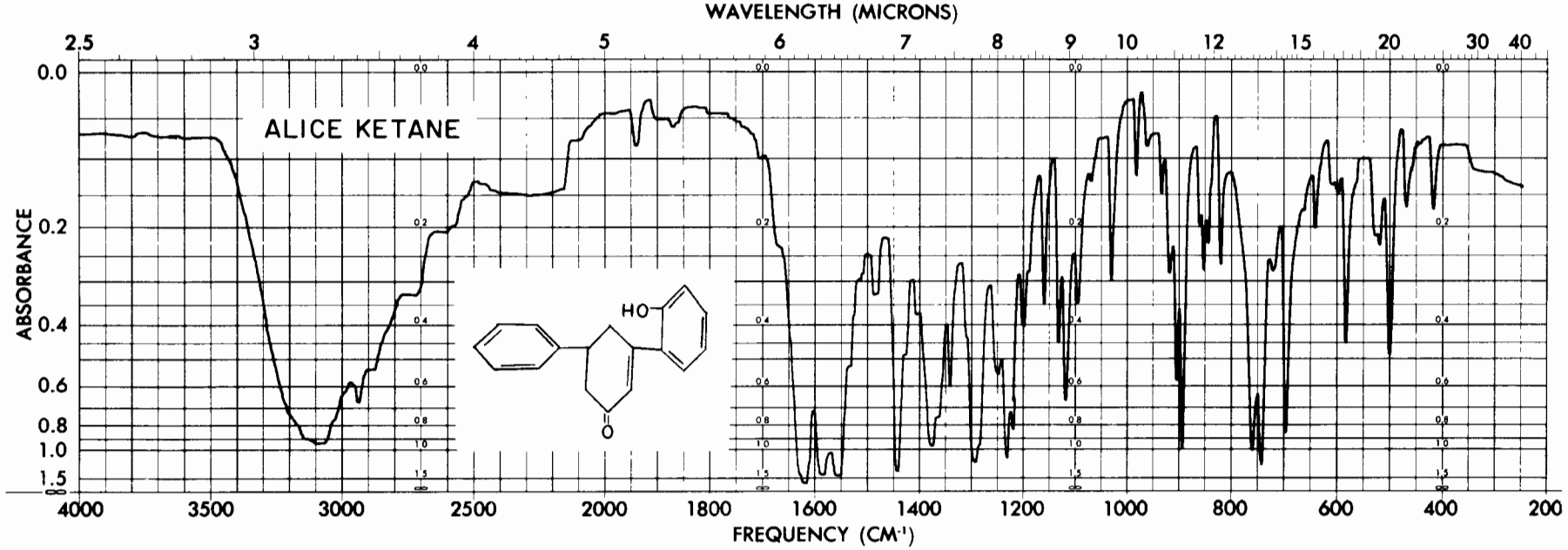
200
FREQUENCY (CM⁻¹)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ALICE KETANE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
HO
O
4000
3500
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2500
2000
1800
1600
1400
1200
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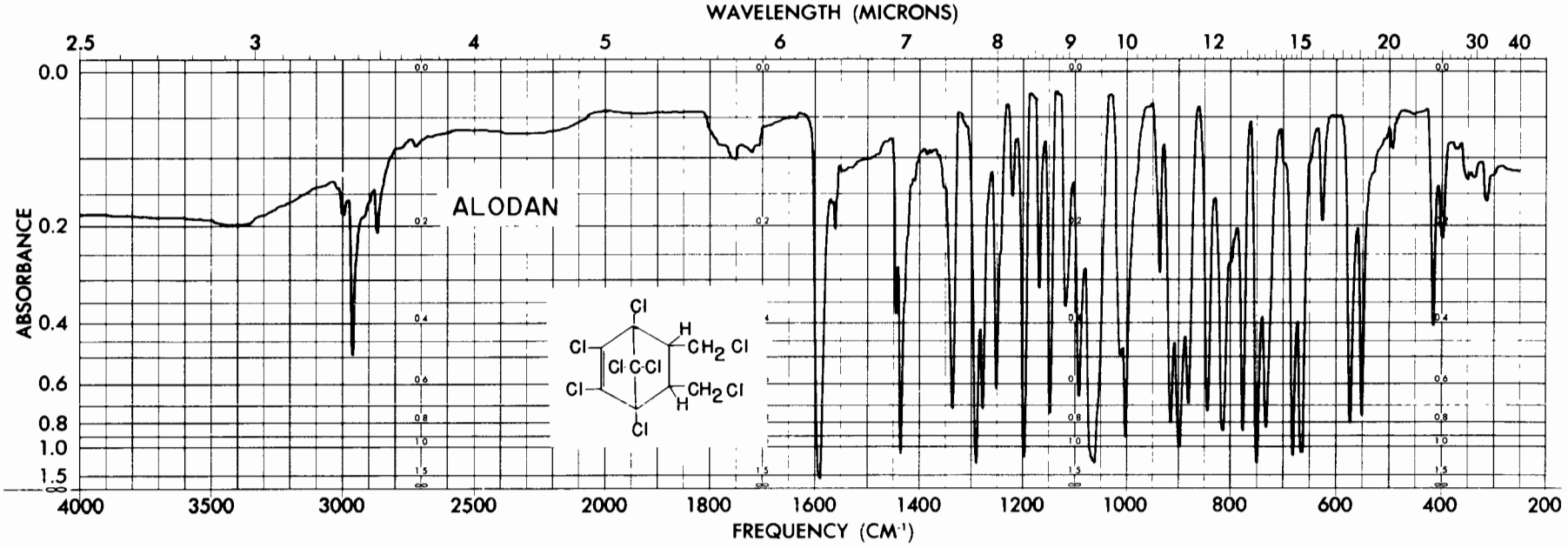
800
600
400
200
FREQUENCY (CM⁻¹)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ALODAN
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
Cl
H
CH2 Cl
Cl
Cl C Cl
Cl
CH2 Cl
H
Cl
4000
3500
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2500
2000
1800
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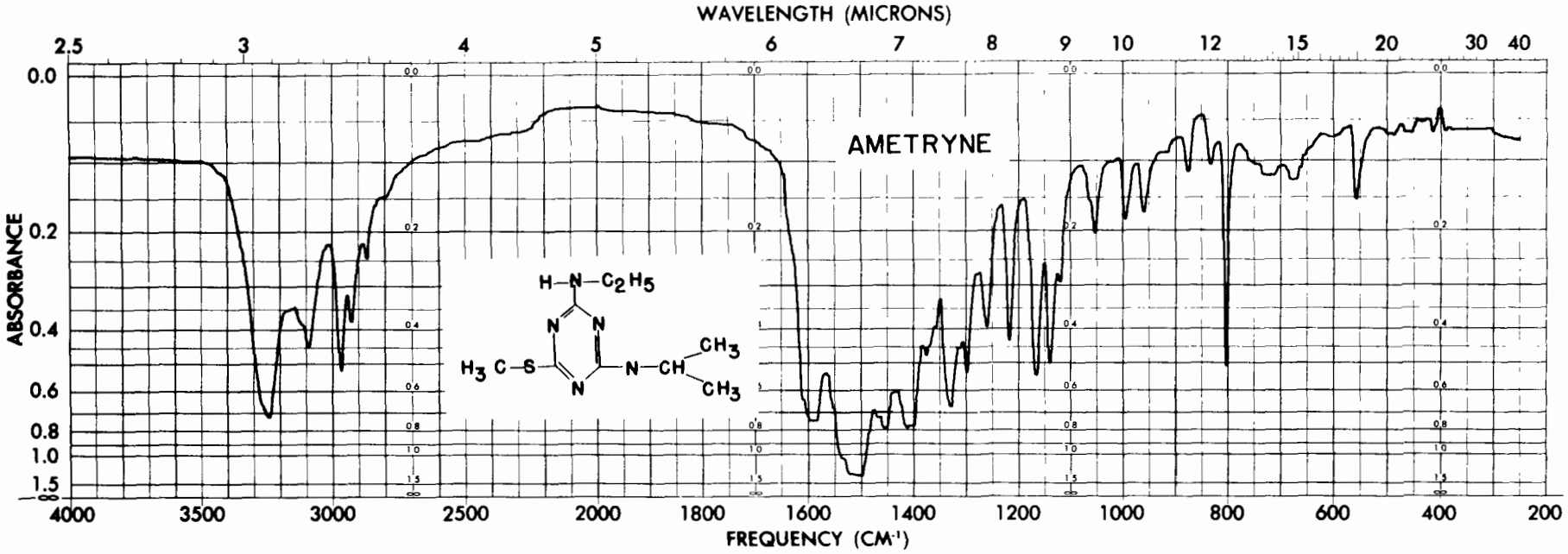
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
AMETRYNE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
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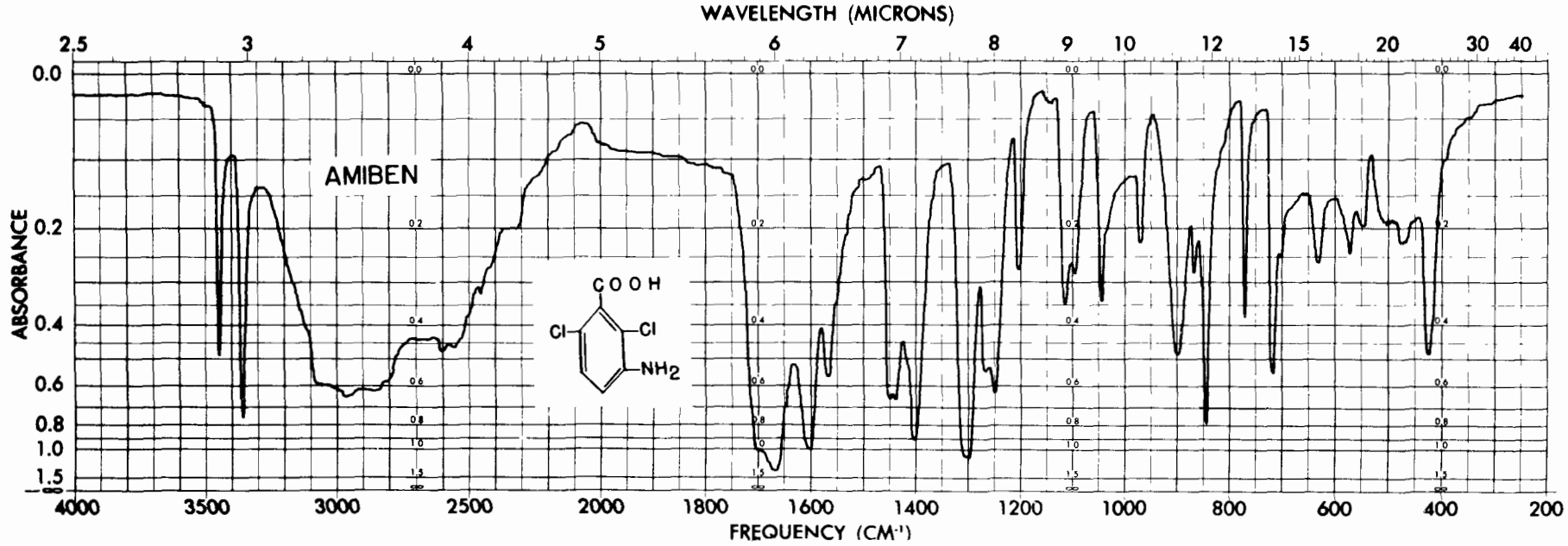
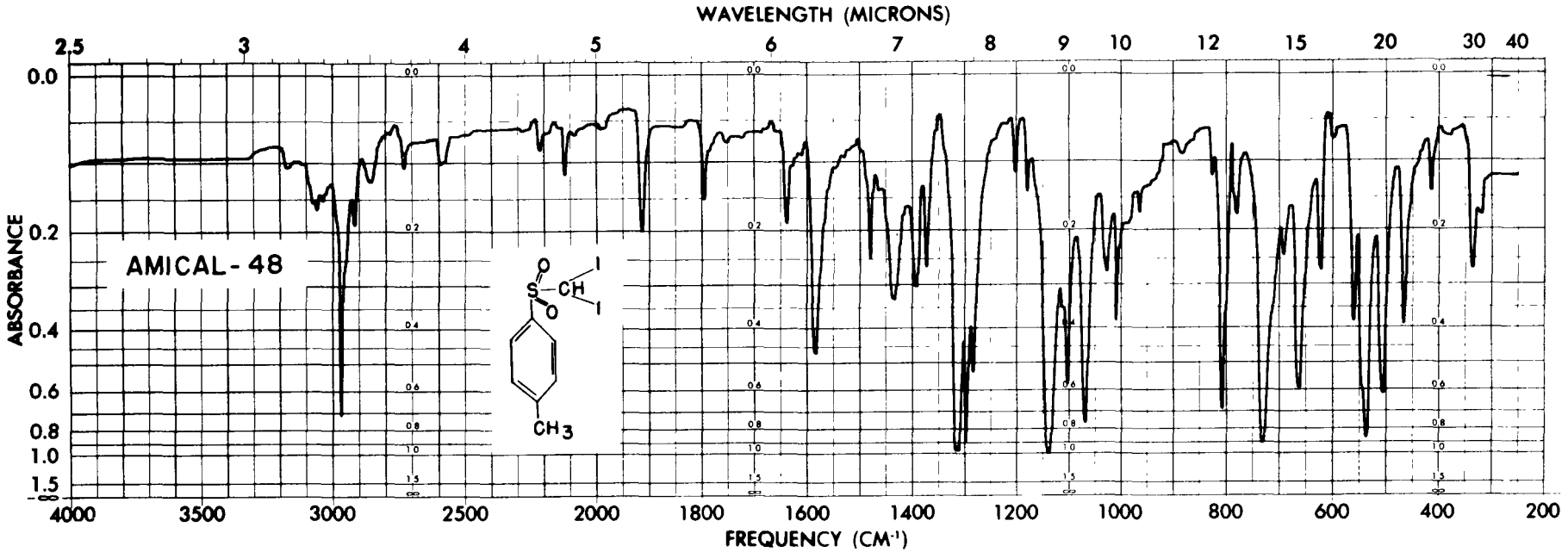
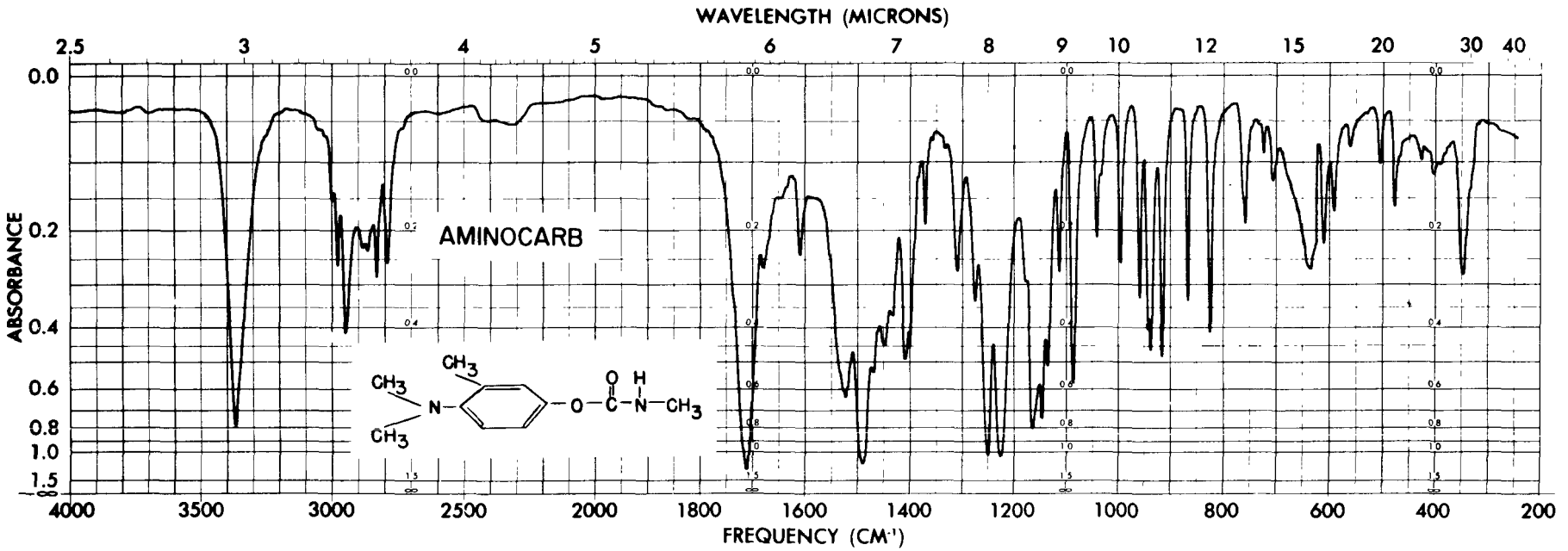
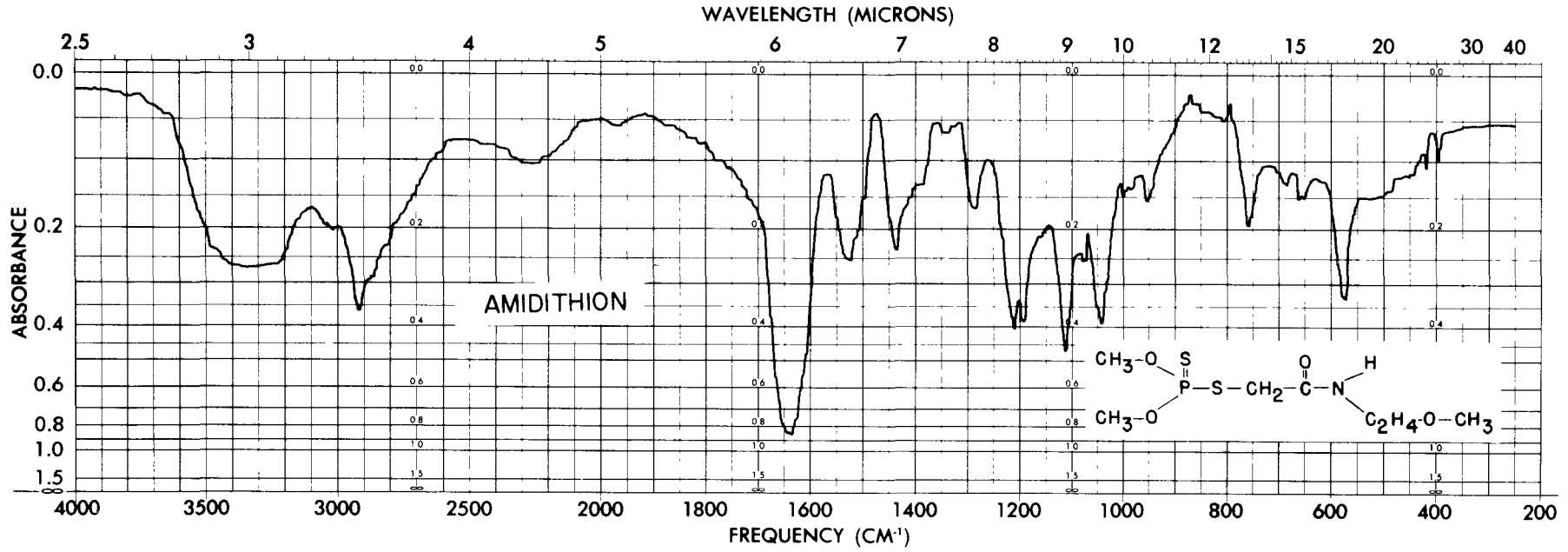
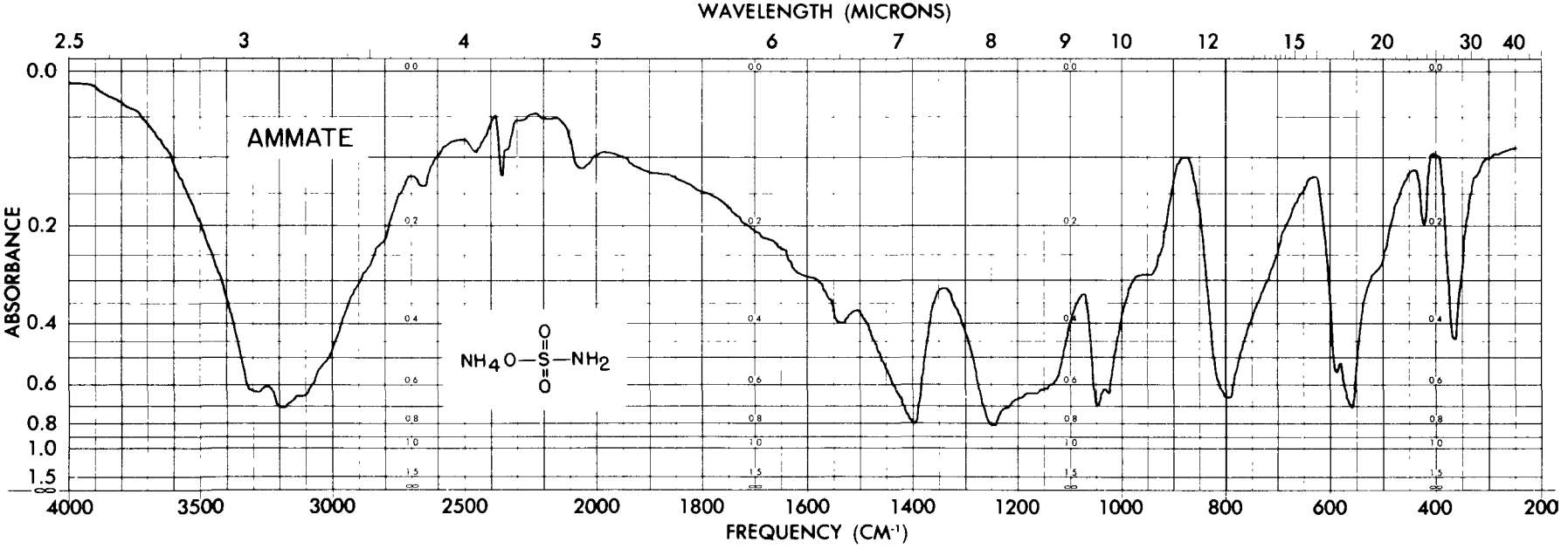
800
600
400
200
FREQUENCY (CM⁻¹)

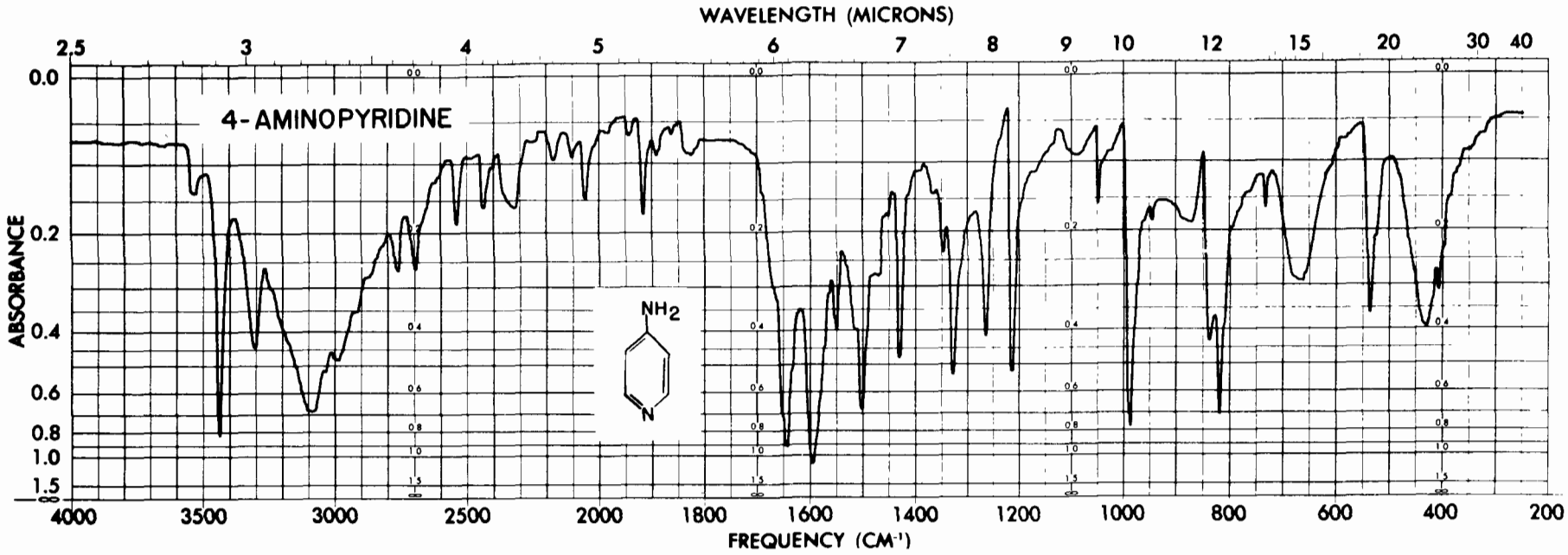

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
AMIBEN
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

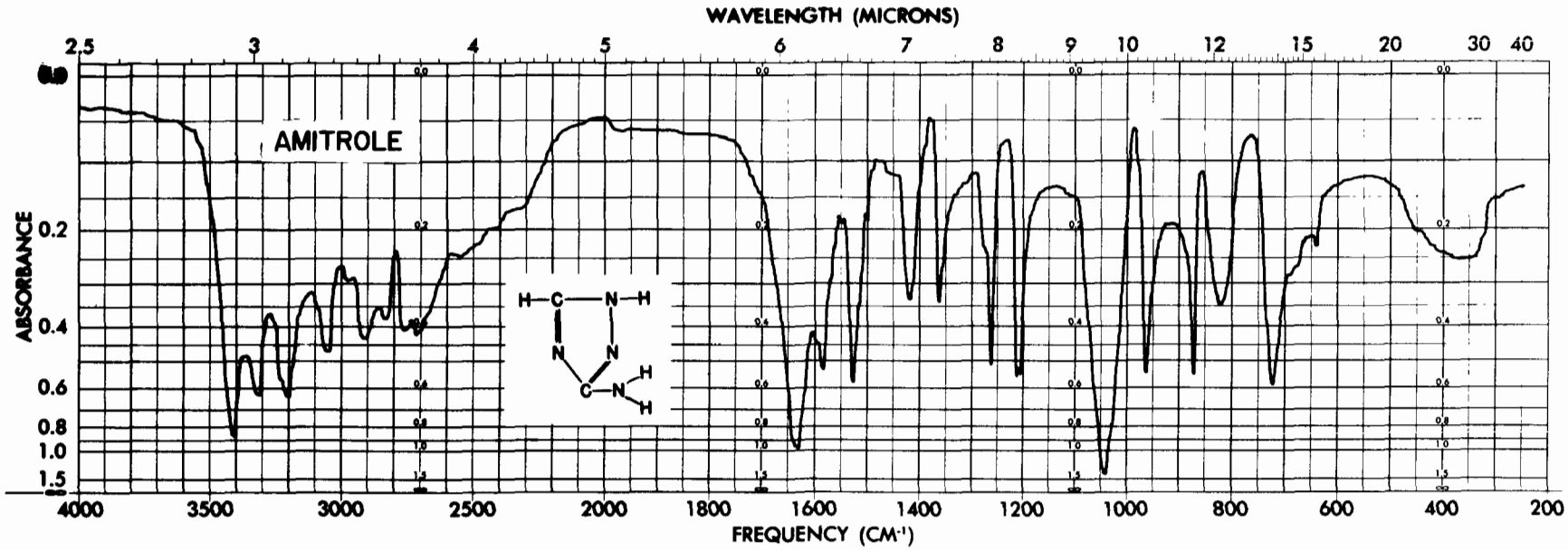

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
AMICAL-48
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

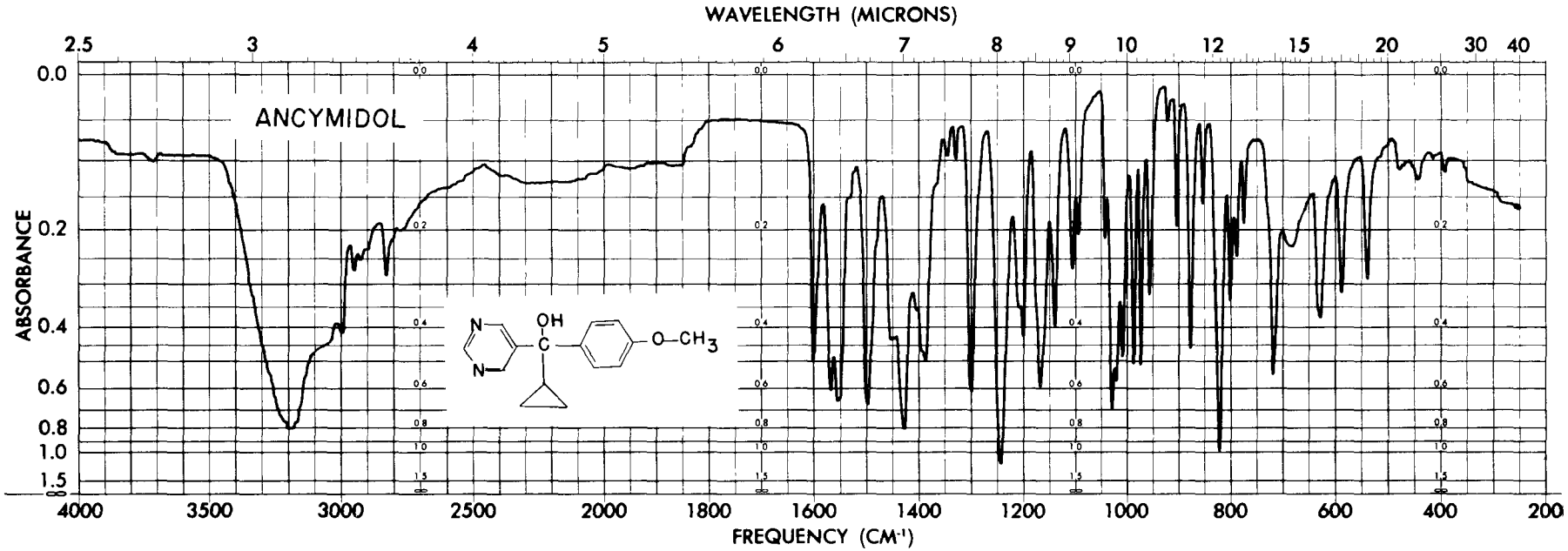

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
AMINOCARB
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

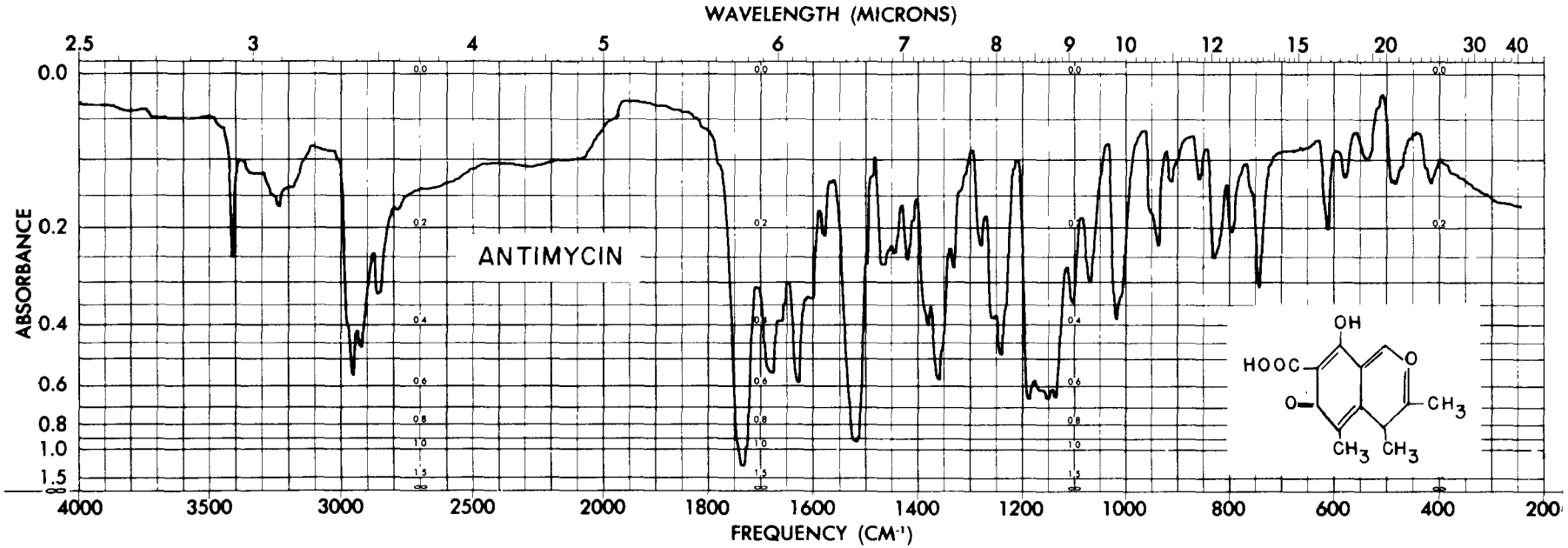

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
AMIDITHION
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

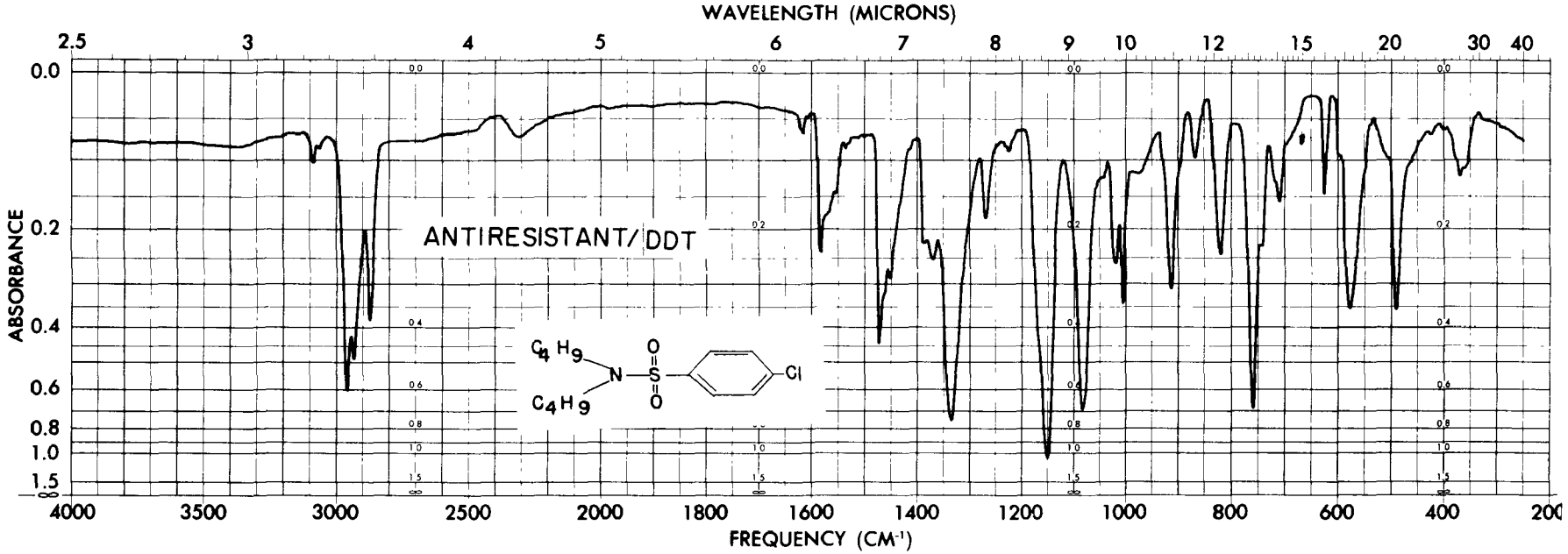

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
AMMATE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

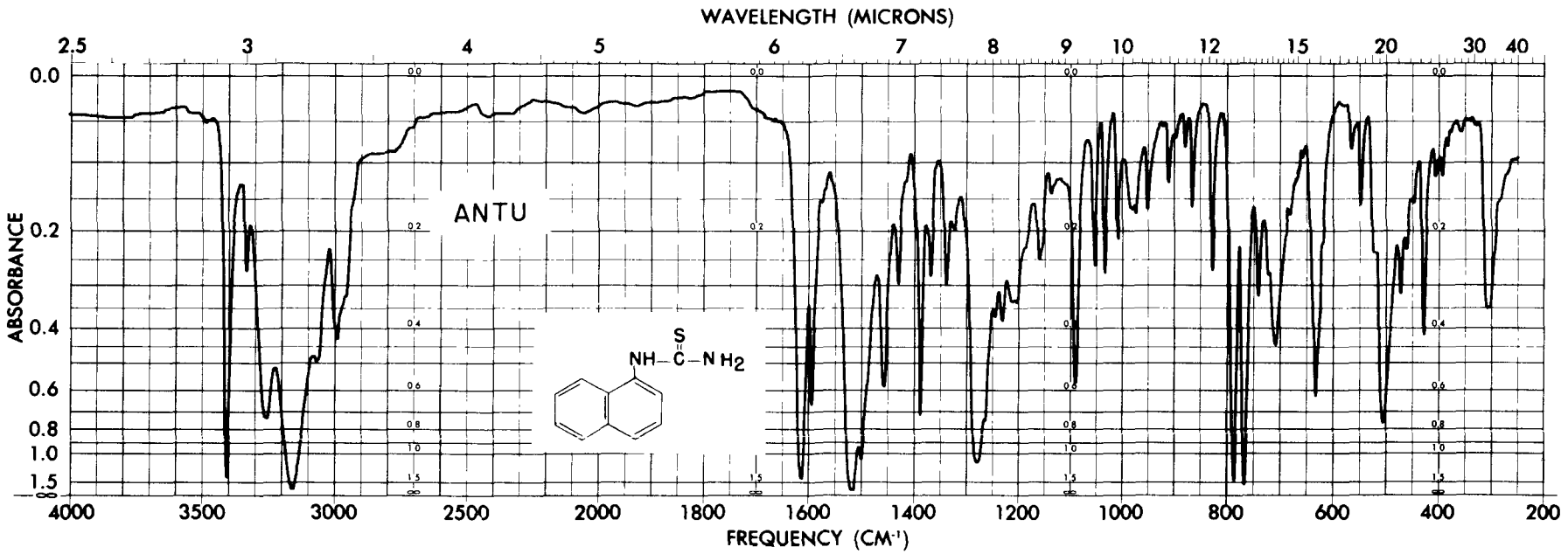

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
4-AMINOPYRIDINE
NH2
N
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

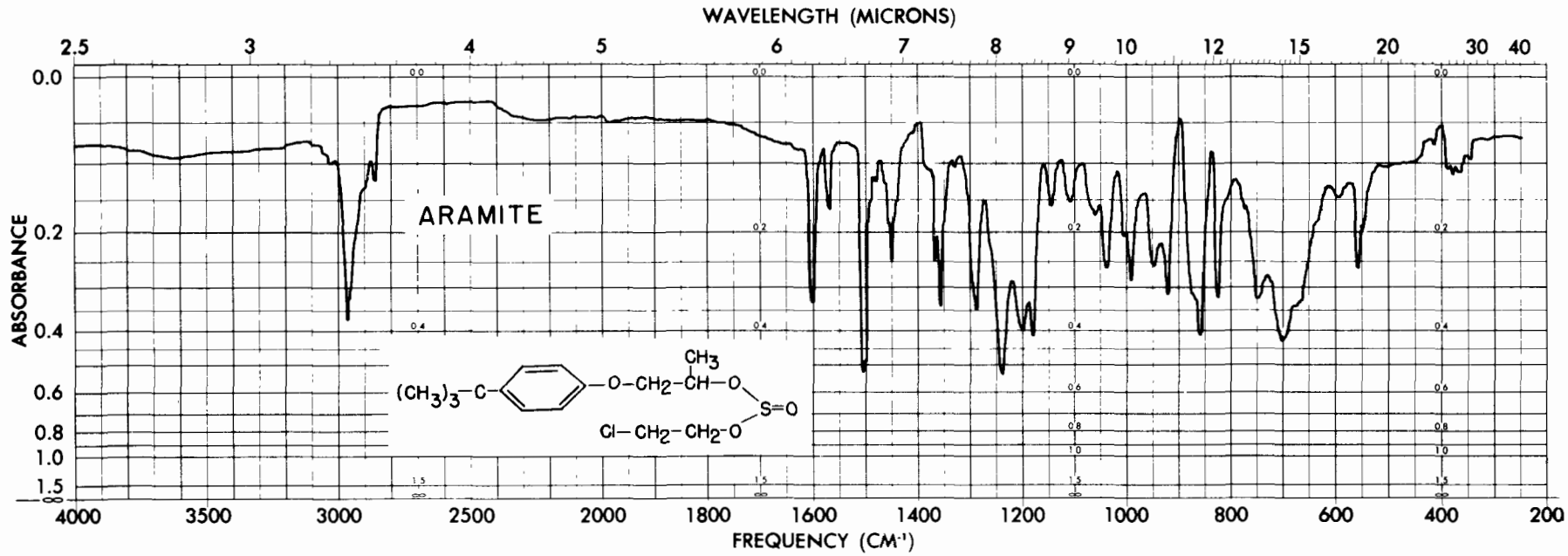

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
AMITROLE
H
C
N
H
N
N
C
N
H
H
ABSORBANCE
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

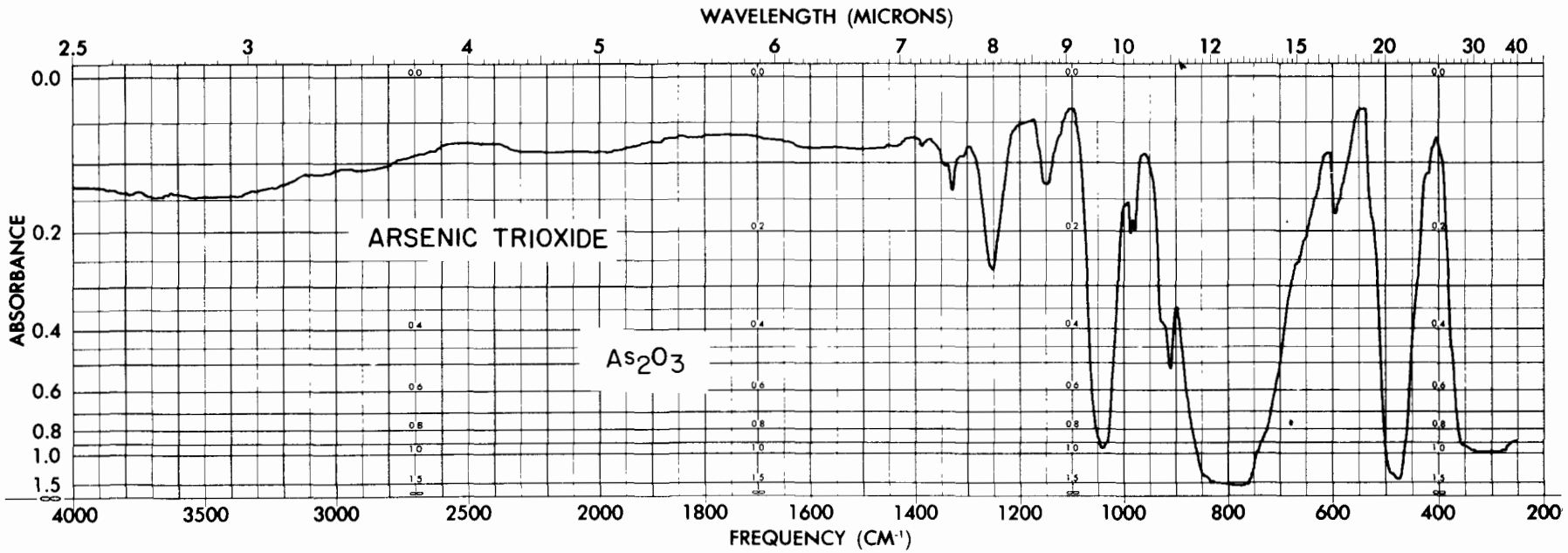

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ANCYMIDOL
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
OH
N
N
O—CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ANTIMYCIN
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
OH
HOOC
O
O
CH3
CH3
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ANTIRESISTANT/DDT
C_4H_9
C_4H_9
N
S
O
O
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ANTU
S
NH—C—NH_2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ARAMITE
(CH3)3-C-
-O-CH2-CH-O
CH3
S=O
Cl-CH2-CH2-O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ARSENIC TRIOXIDE
As2O3
4000
3500
3000
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2000
1800
1600
1400
1200
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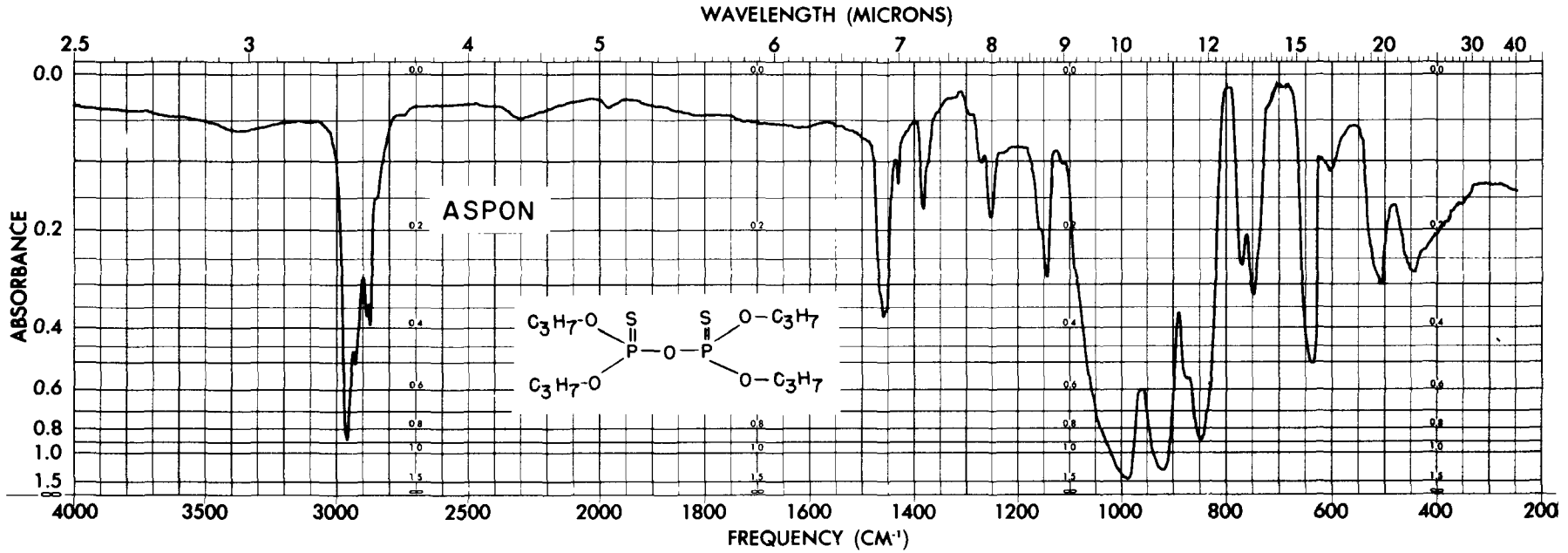
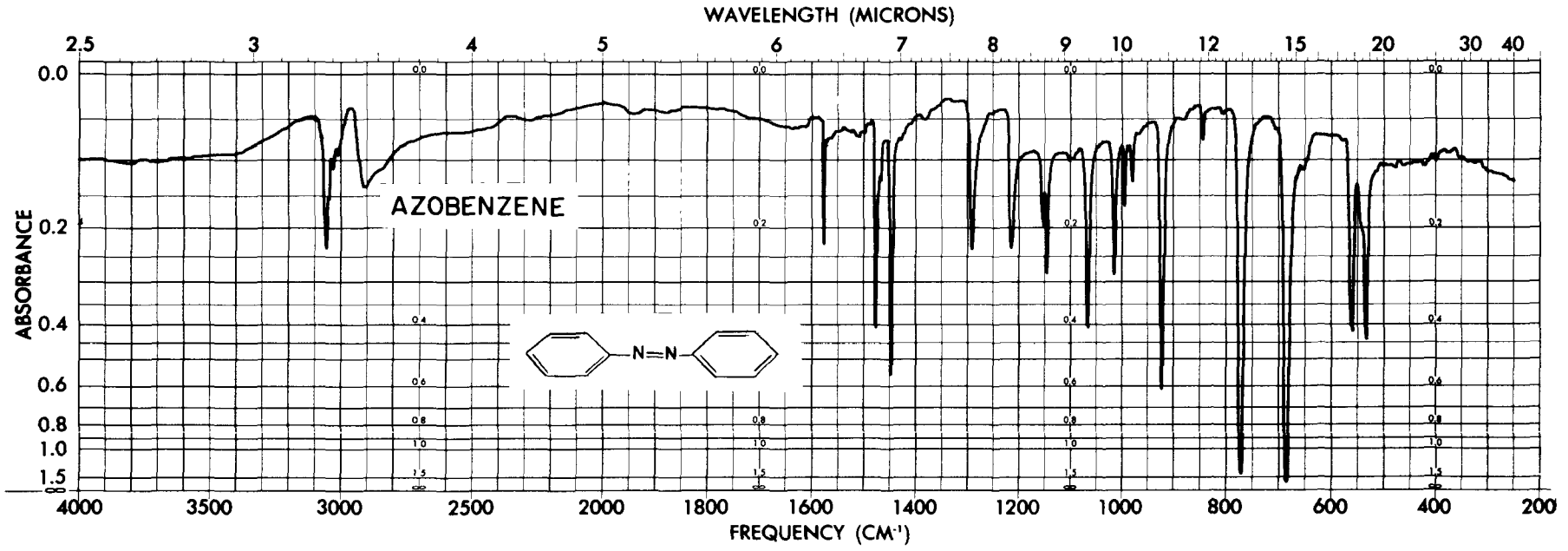
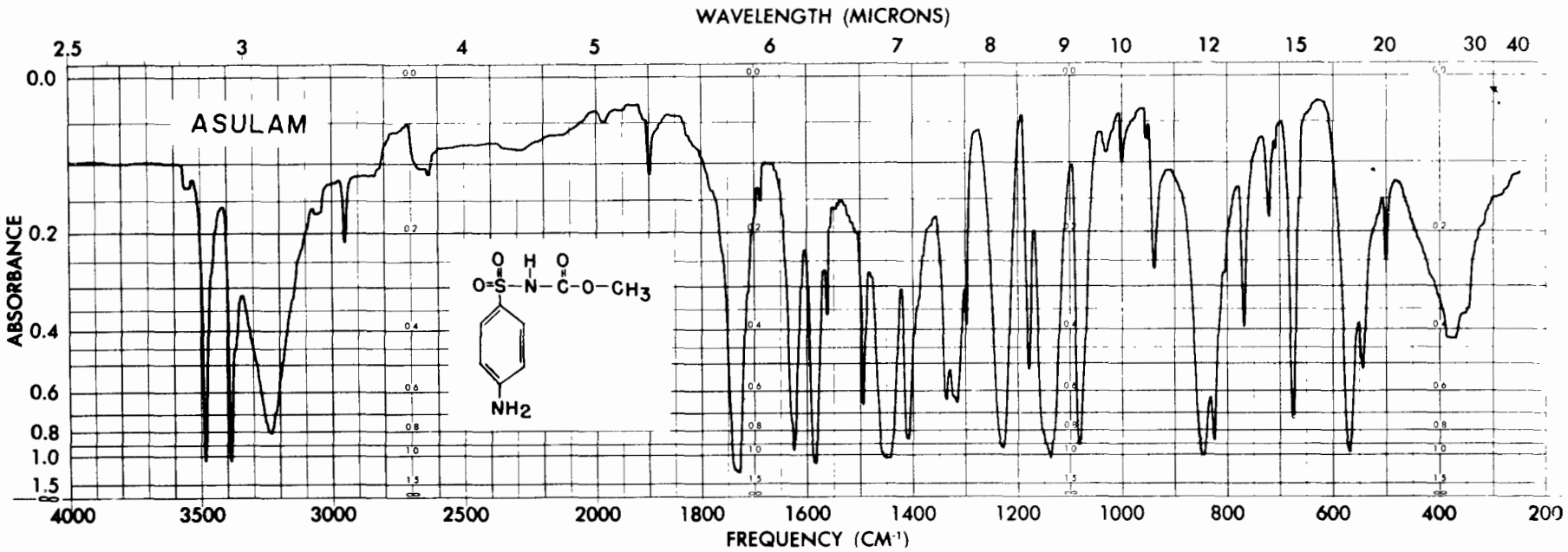
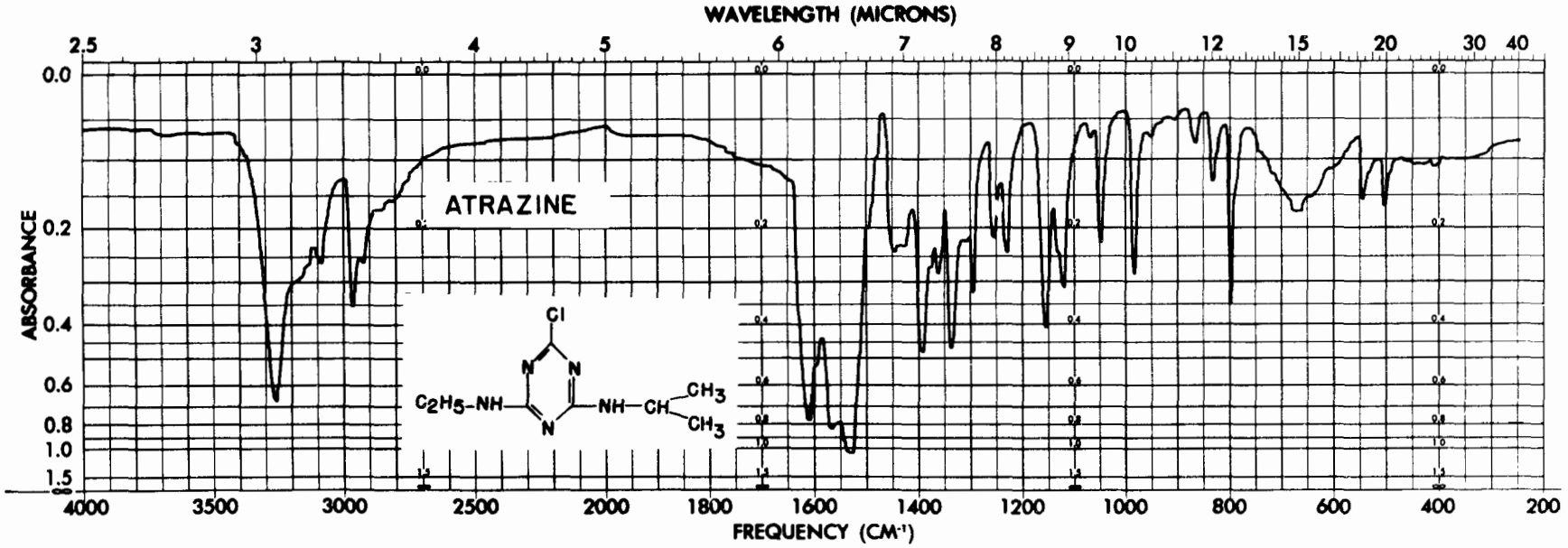
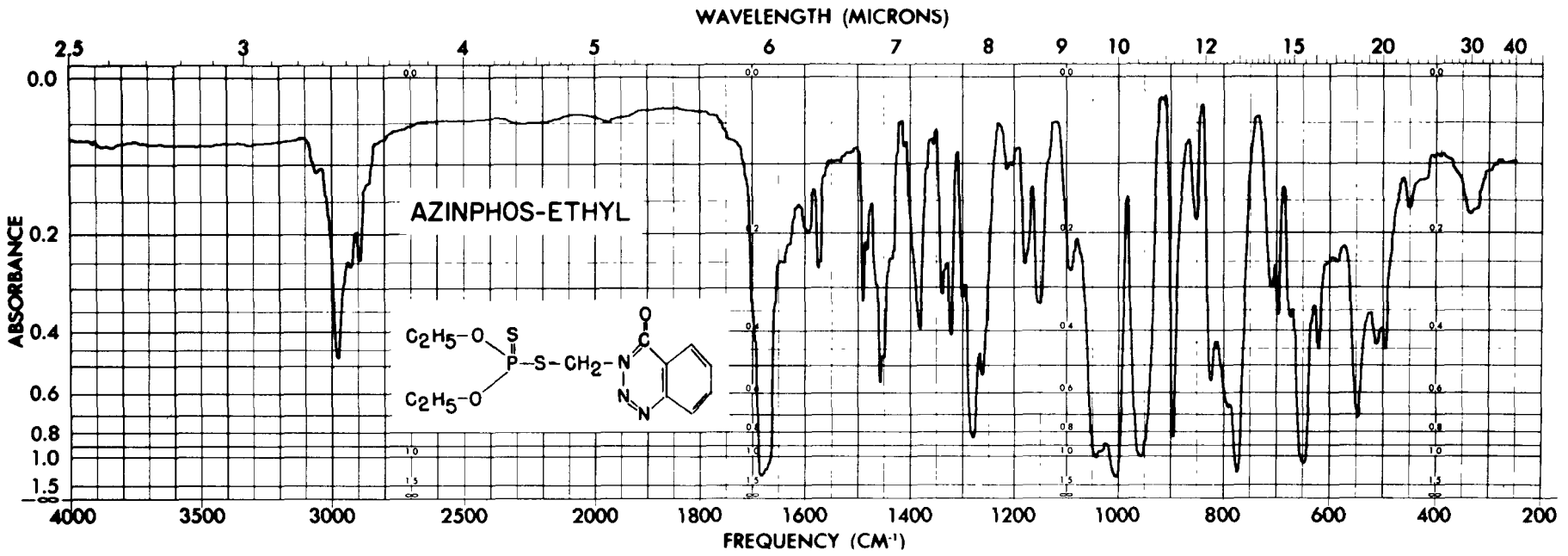
800
600
400
200
FREQUENCY (CM-1)

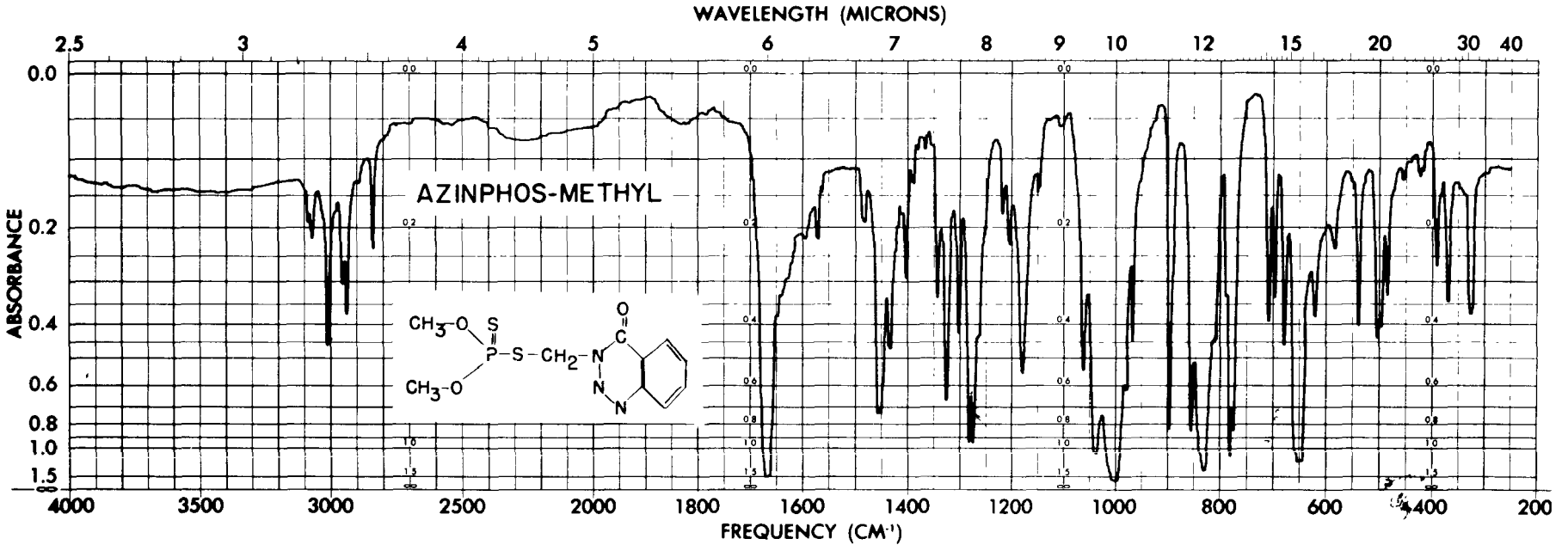

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ASPON
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

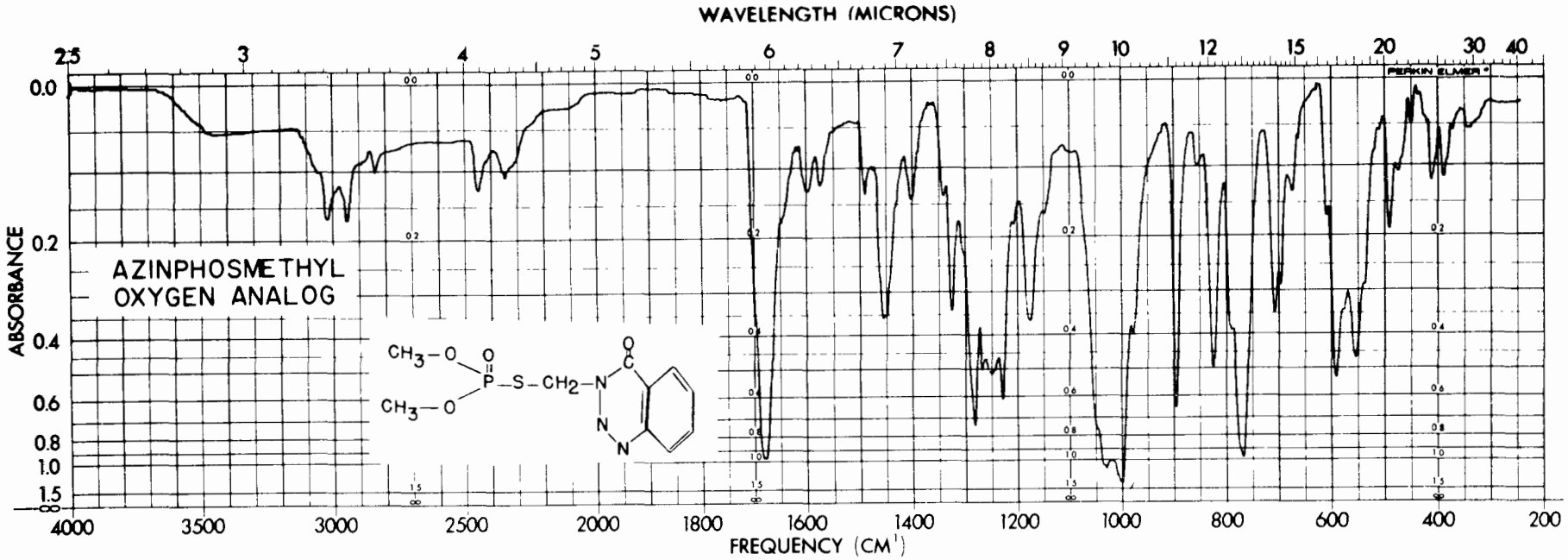

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
AZOBENZENE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

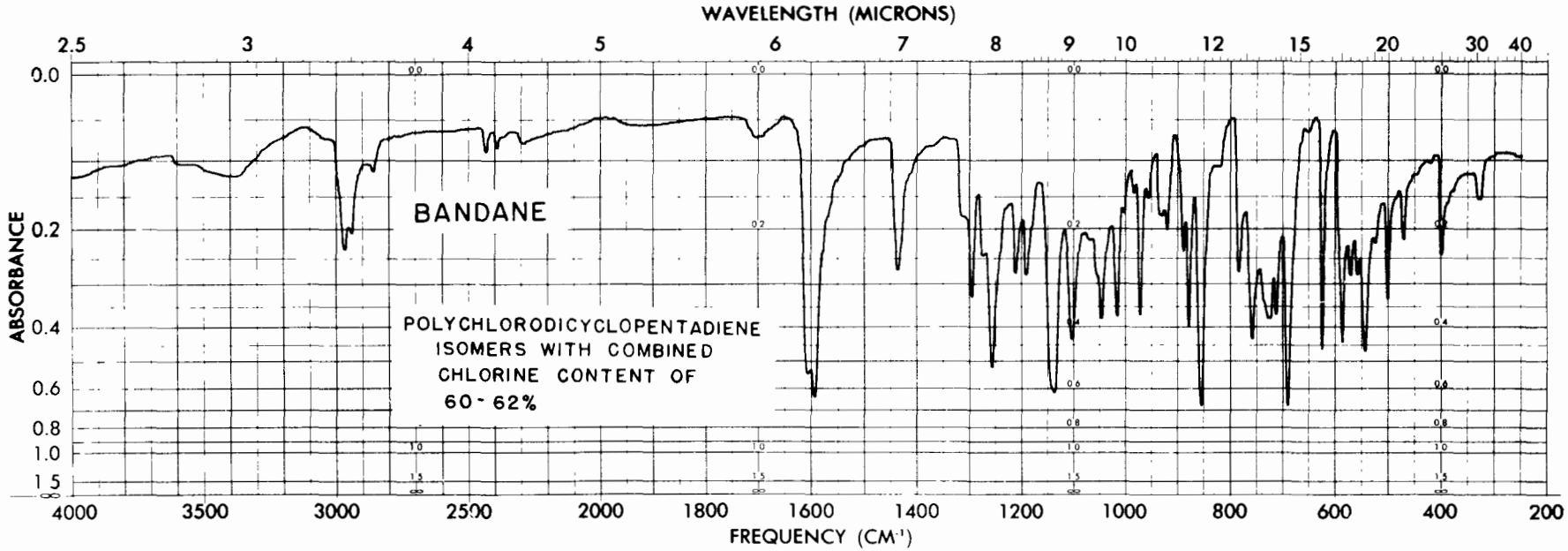

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ASULAM
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)
NH2

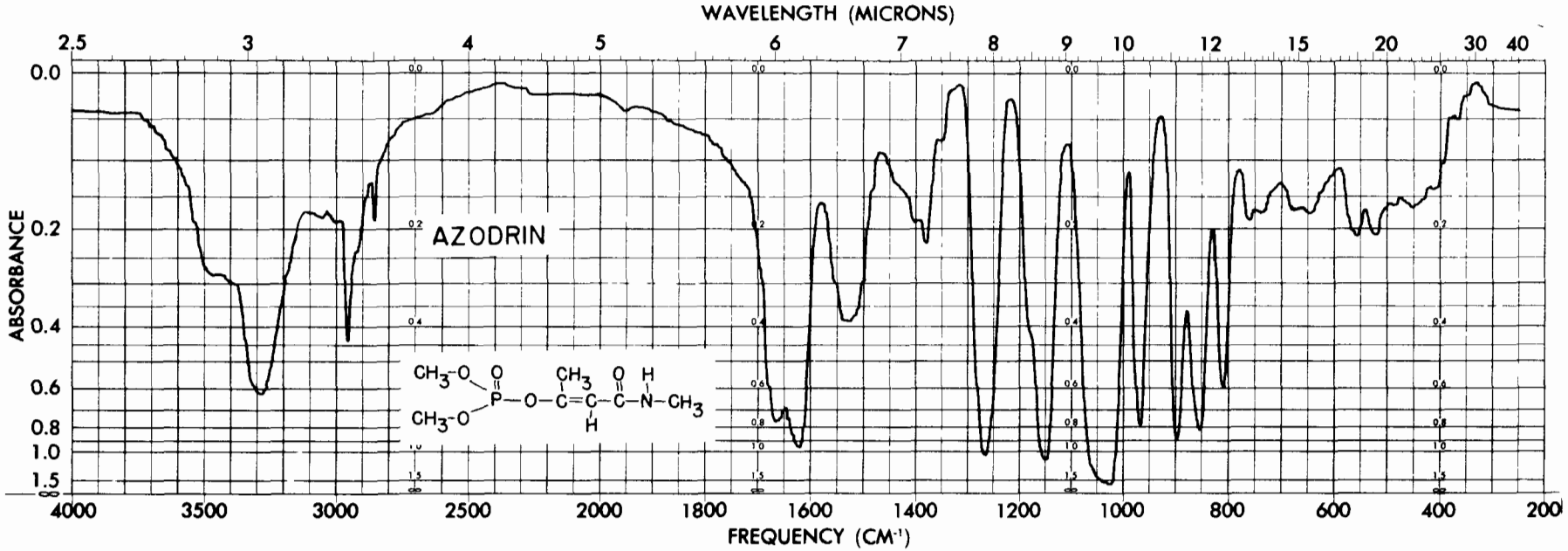

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ATRAZINE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)
Cl
C2H5-NH
NH-CH
CH3
CH3

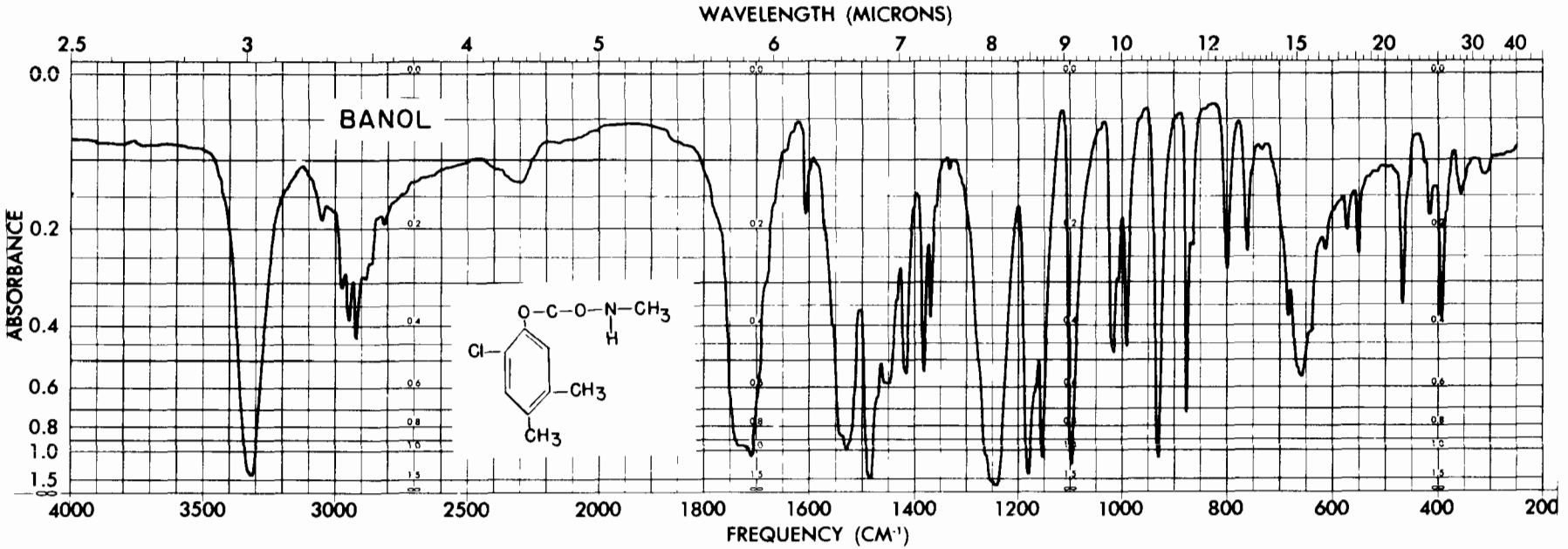

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
AZINPHOS-ETHYL
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

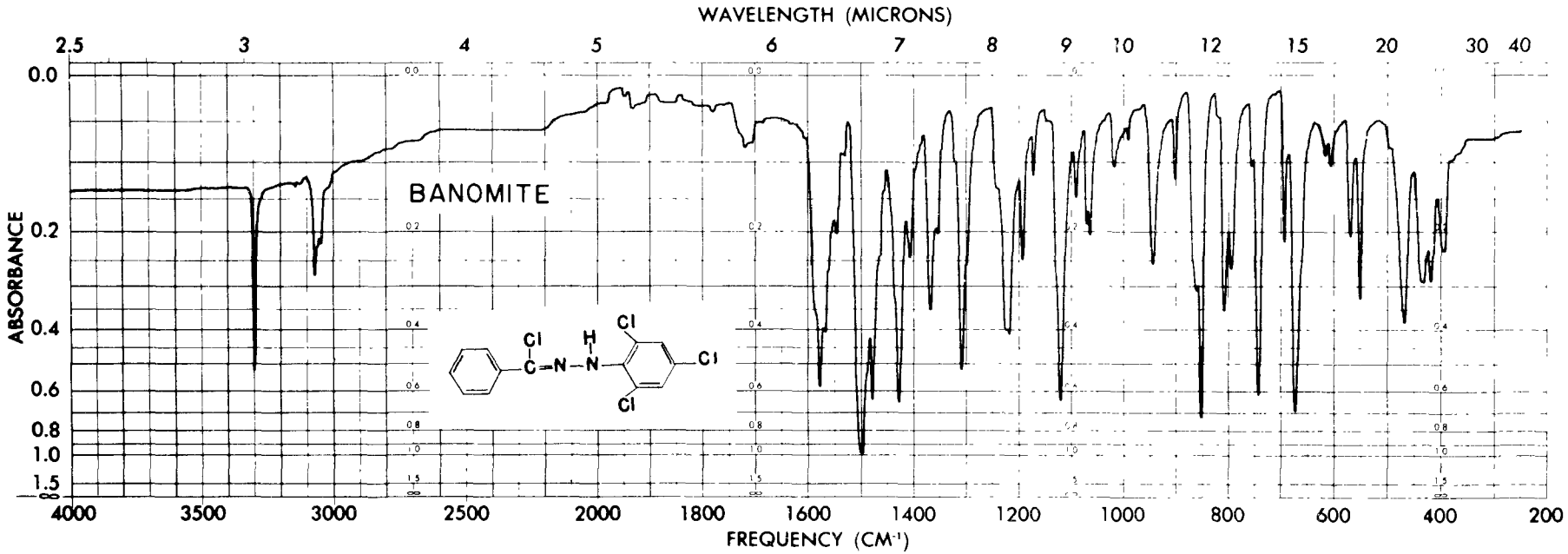

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
AZINPHOS-METHYL
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

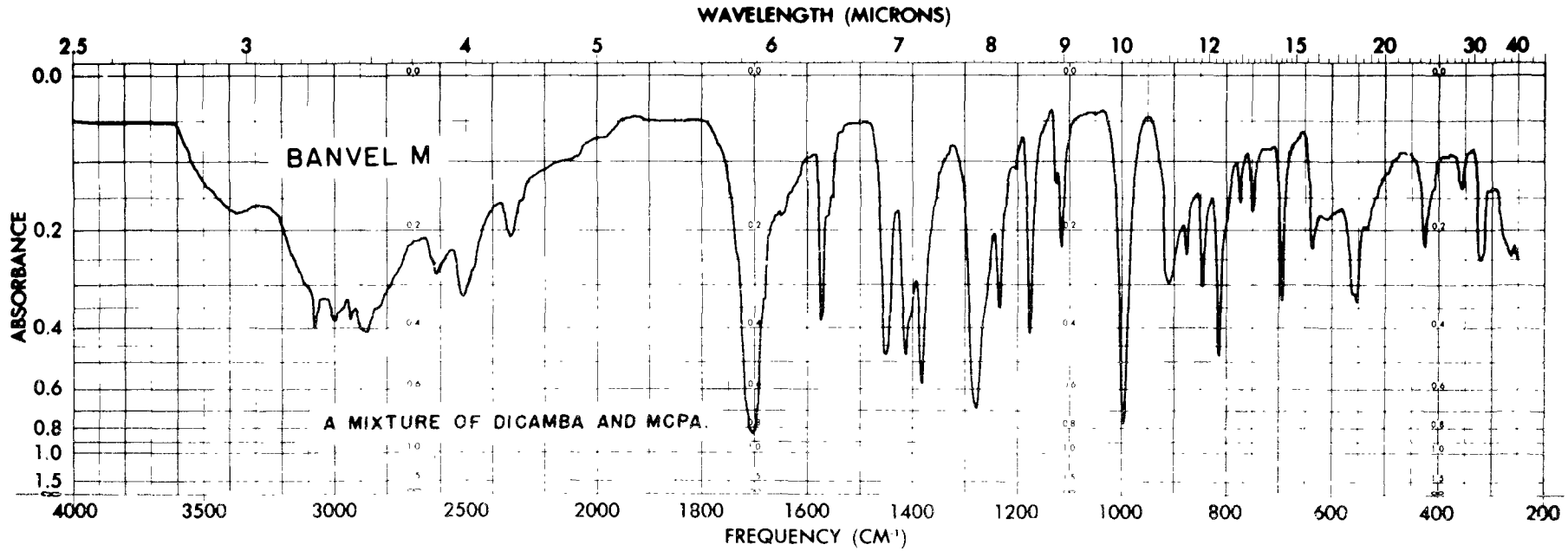

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
AZINPHOSMETHYL
OXYGEN ANALOG
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

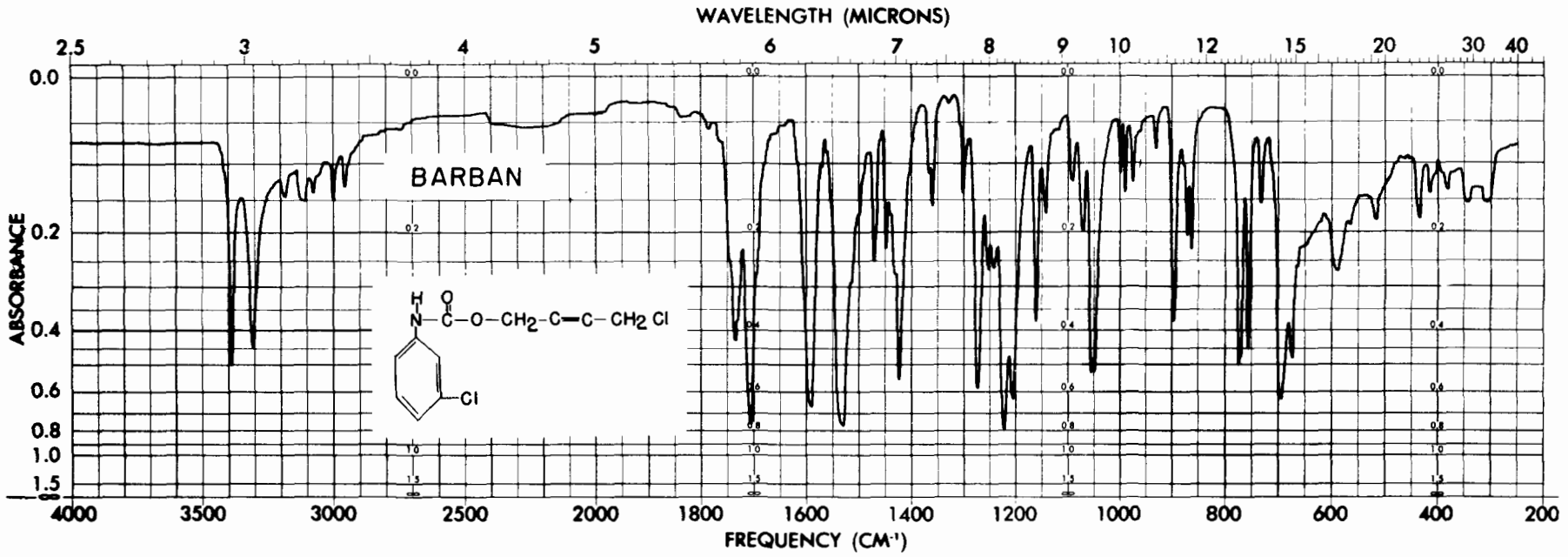

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BANDANE
POLYCHLORODICYCLOPENTADIENE
ISOMERS WITH COMBINED
CHLORINE CONTENT OF
60 - 62%
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

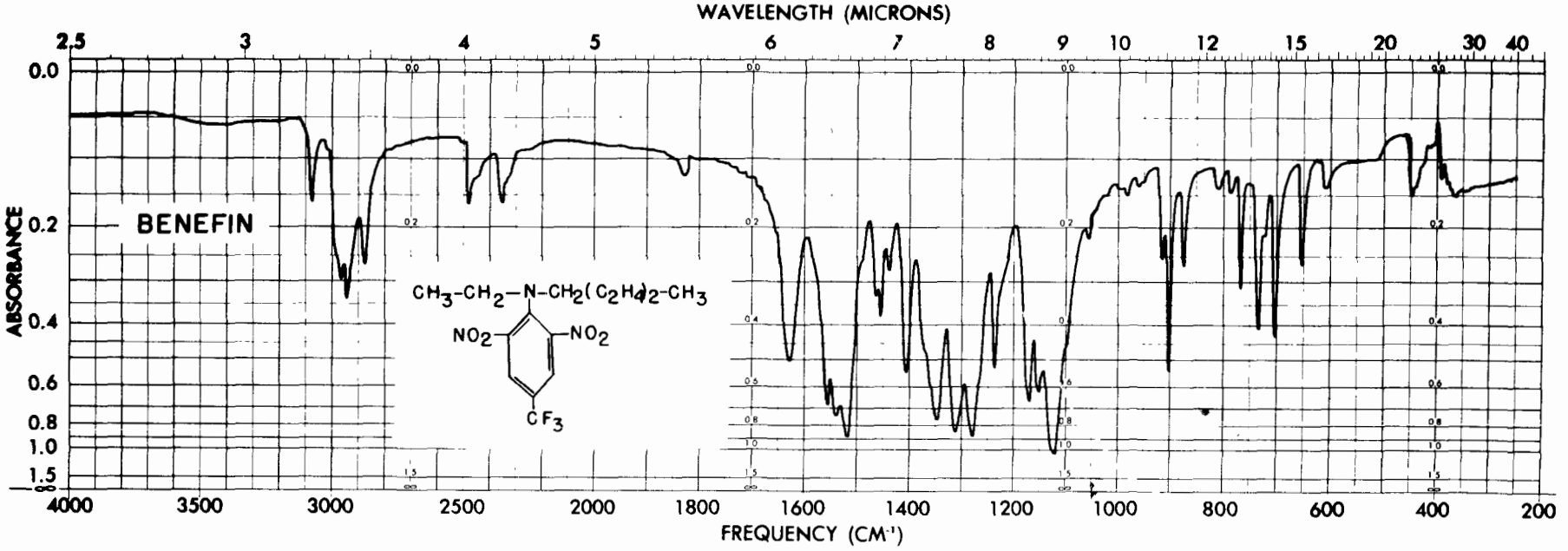

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
AZODRIN
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

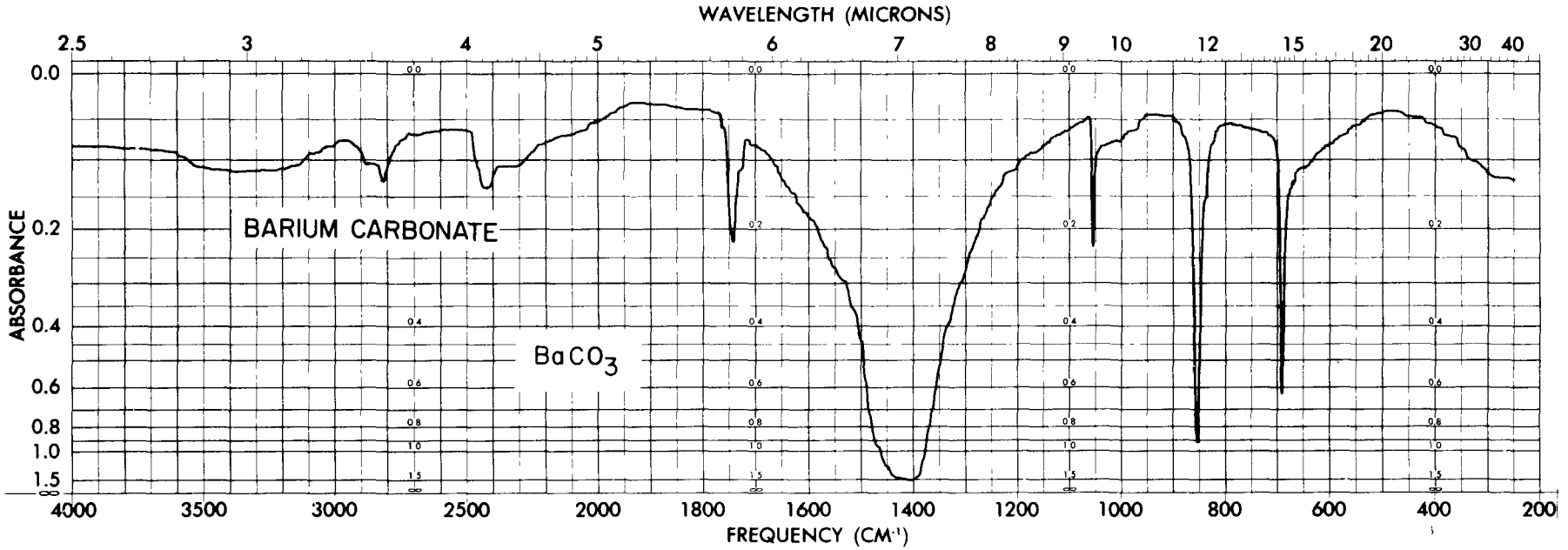

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BANOL
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

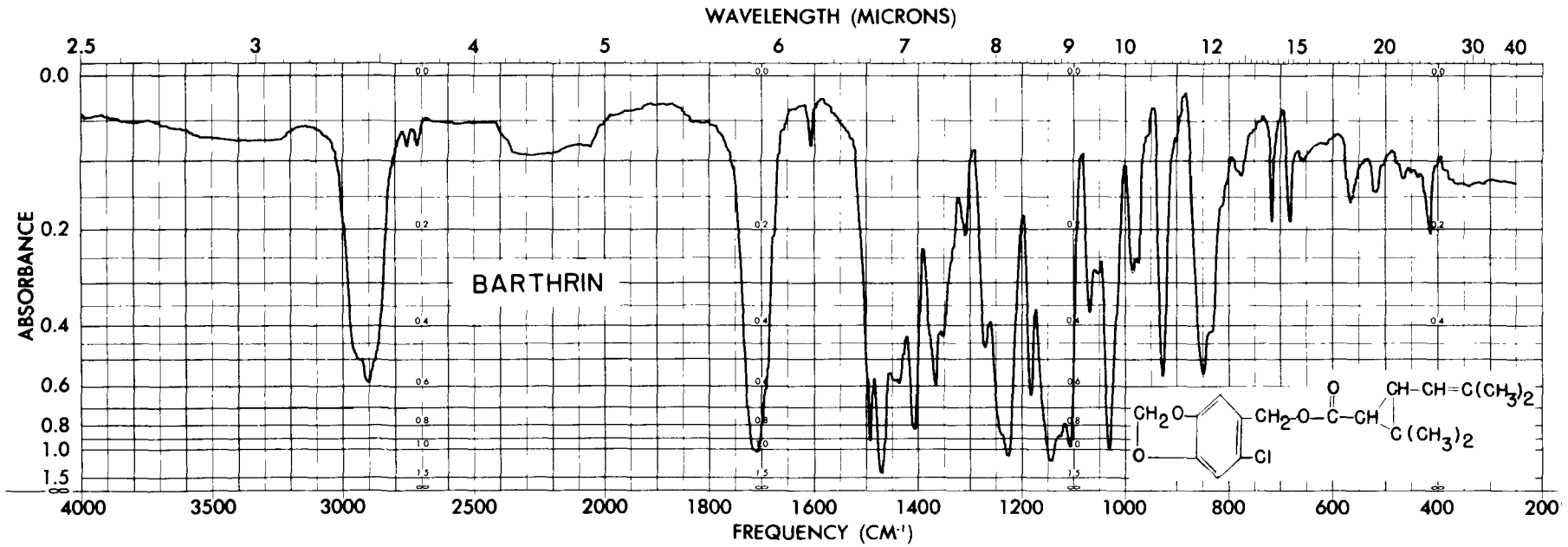

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
BANOMITE
Cl
H
Cl
C=N–N
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

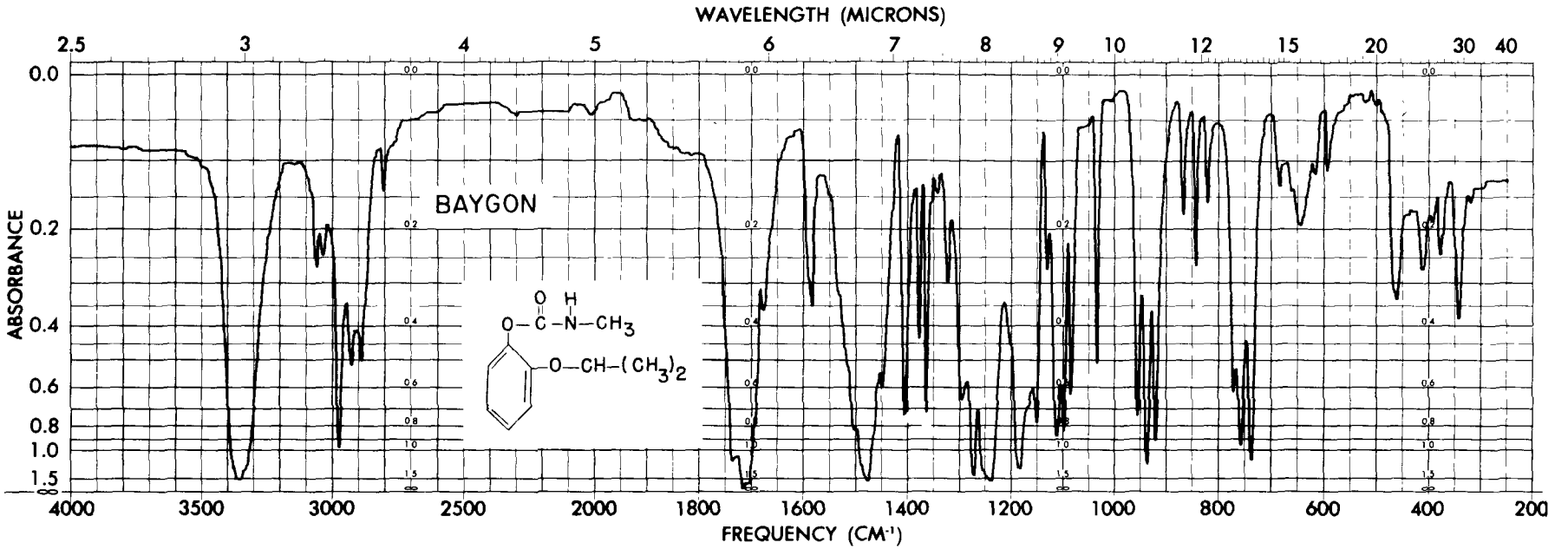

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
BANVEL M
A MIXTURE OF DICAMBA AND MCPA.
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

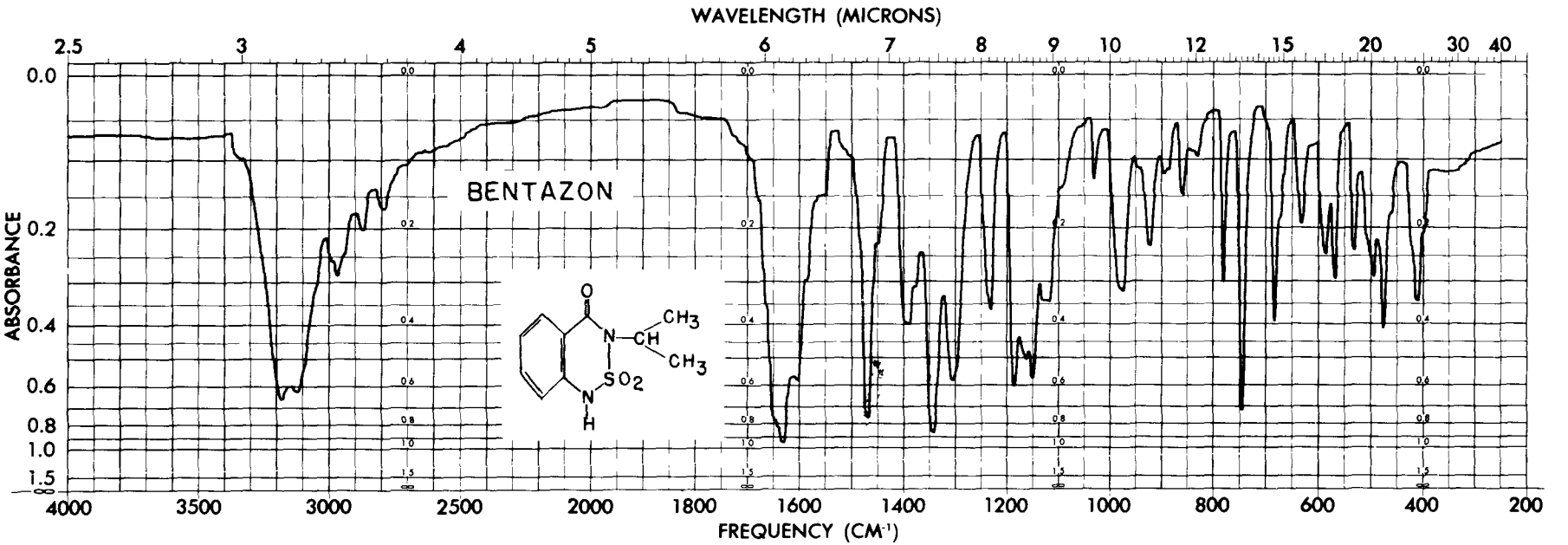

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
BARBAN
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

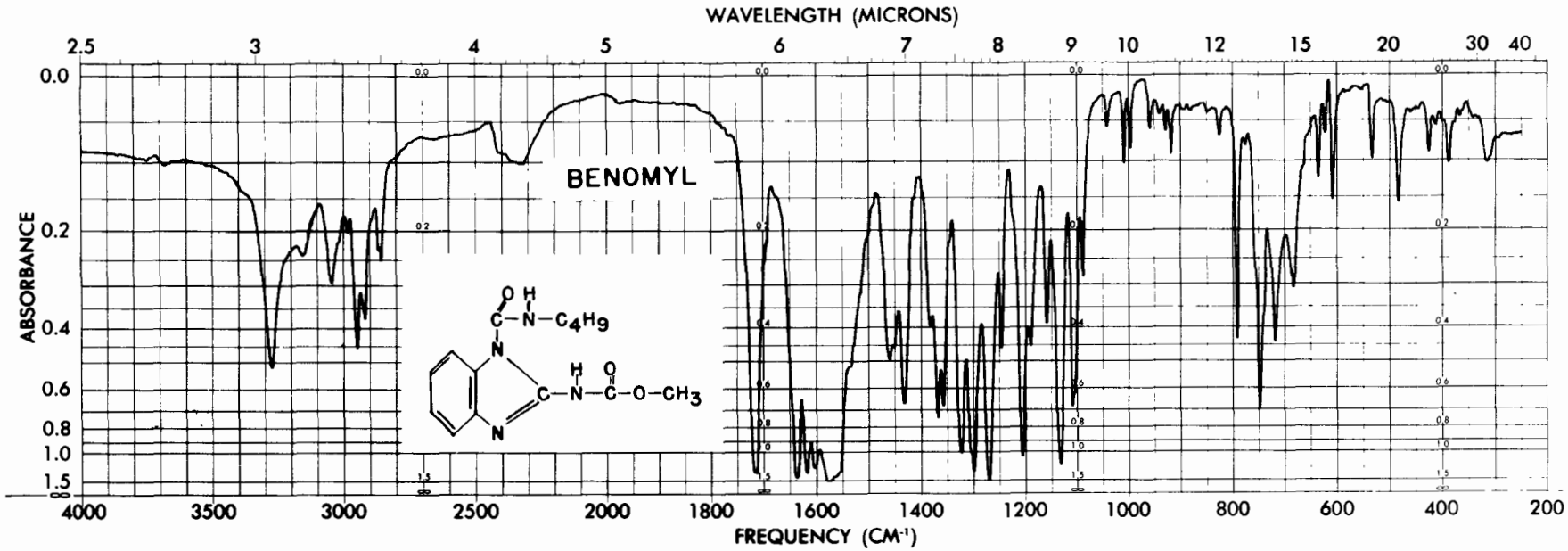

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
BENEFIN
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

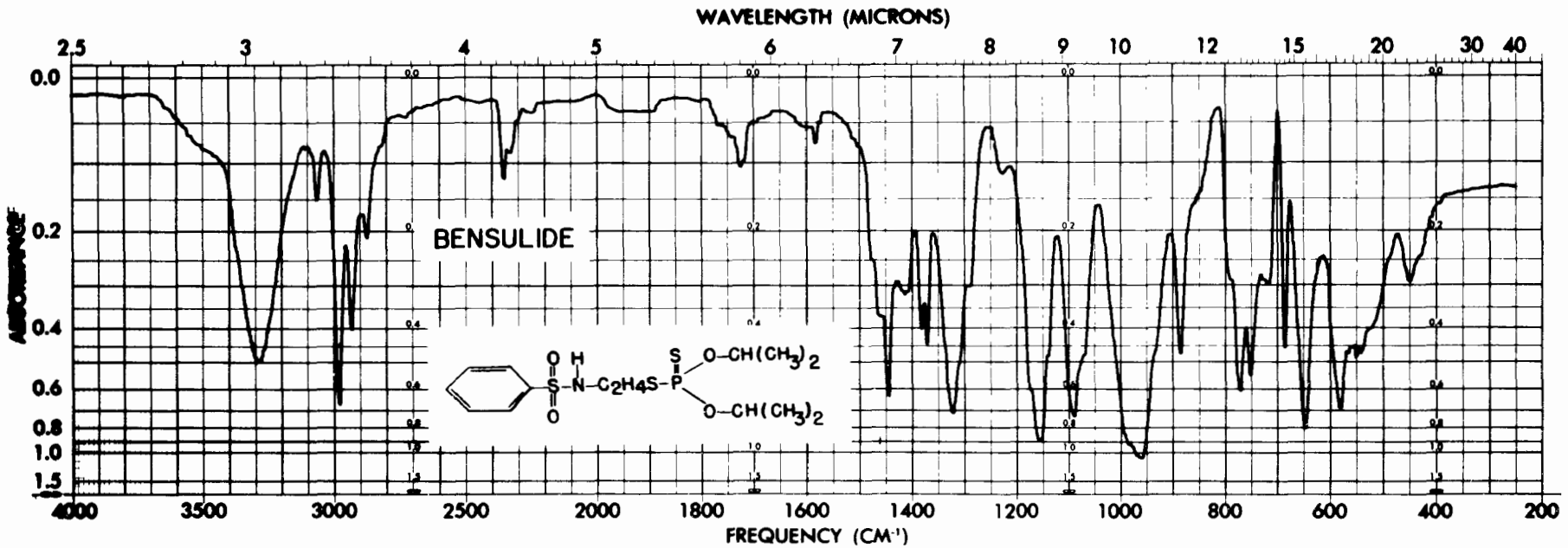

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BARIUM CARBONATE
$BaCO_3$
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

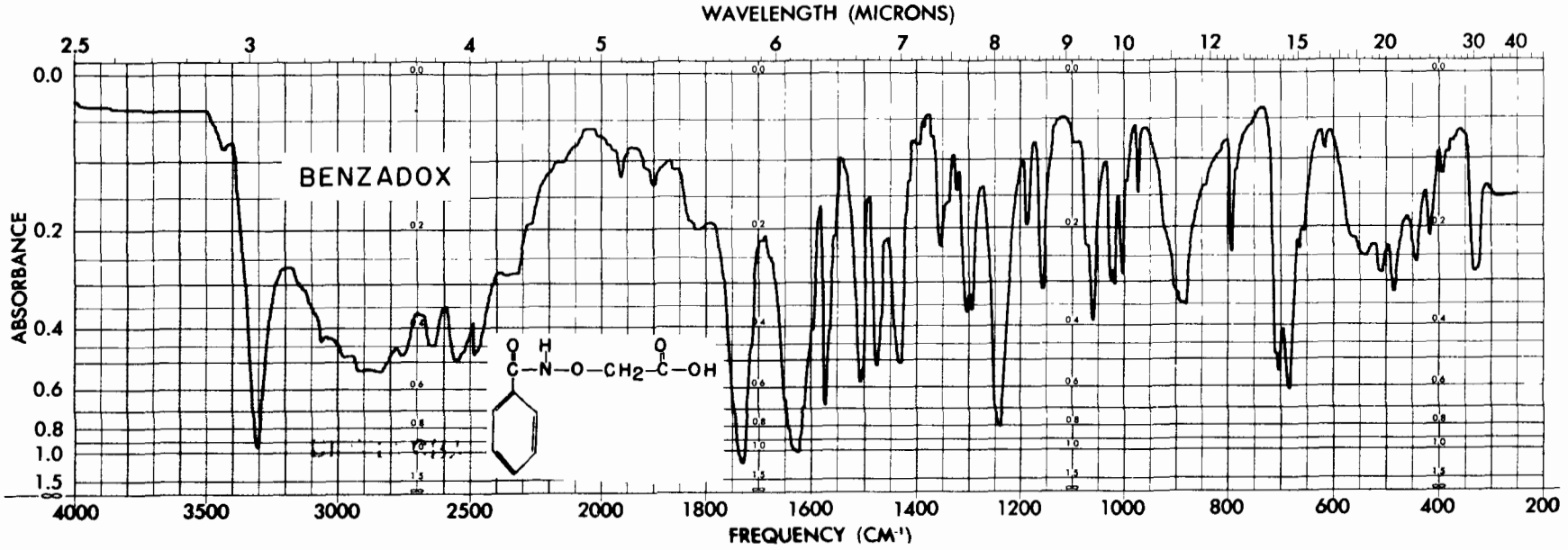

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BARTHRIN
CH_2O
$CH_2-O-C-CH$
O
$CH-CH=C(CH_3)_2$
$C(CH_3)_2$
O
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

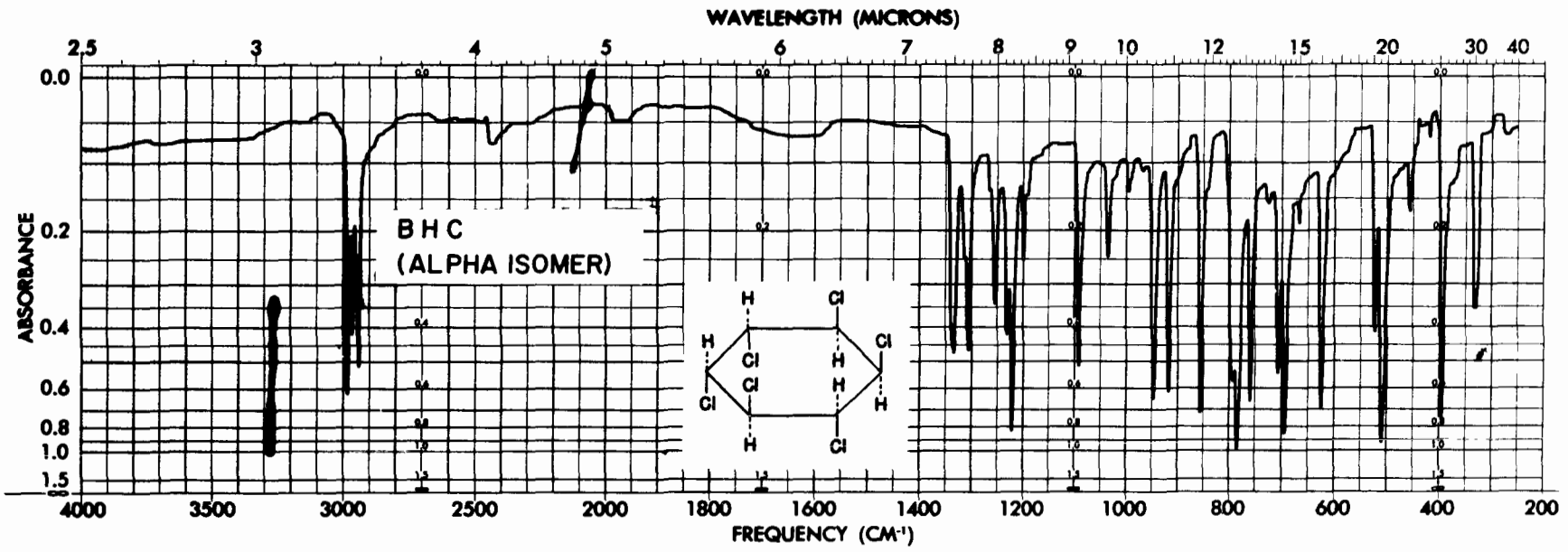

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BAYGON
O H
O–C–N–CH3
O–CH–(CH3)2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

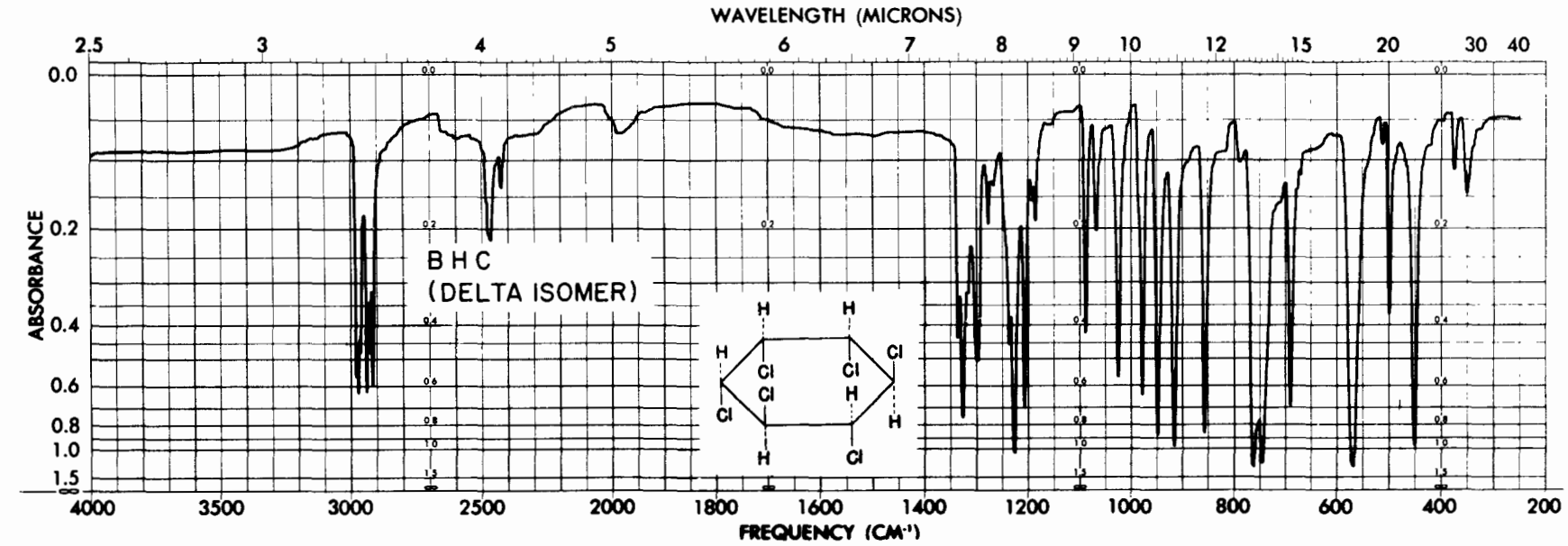

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BENTAZON
O
N–CH
CH3
CH3
SO2
N
H
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

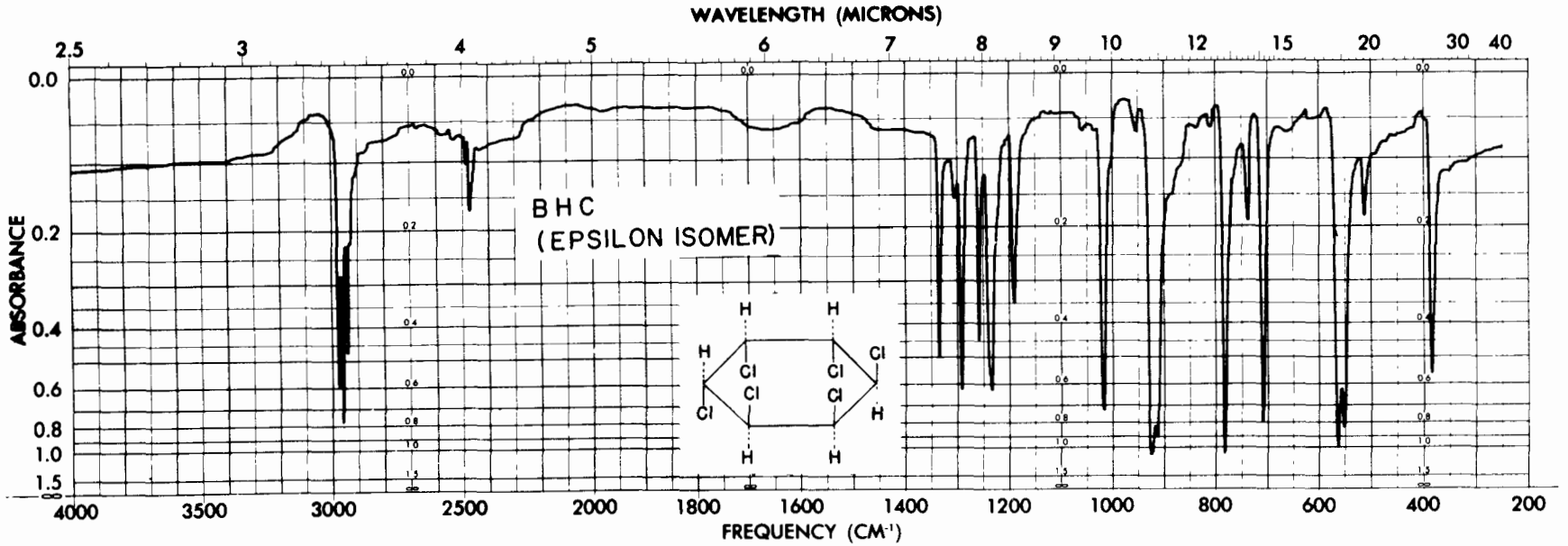

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
BENOMYL
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

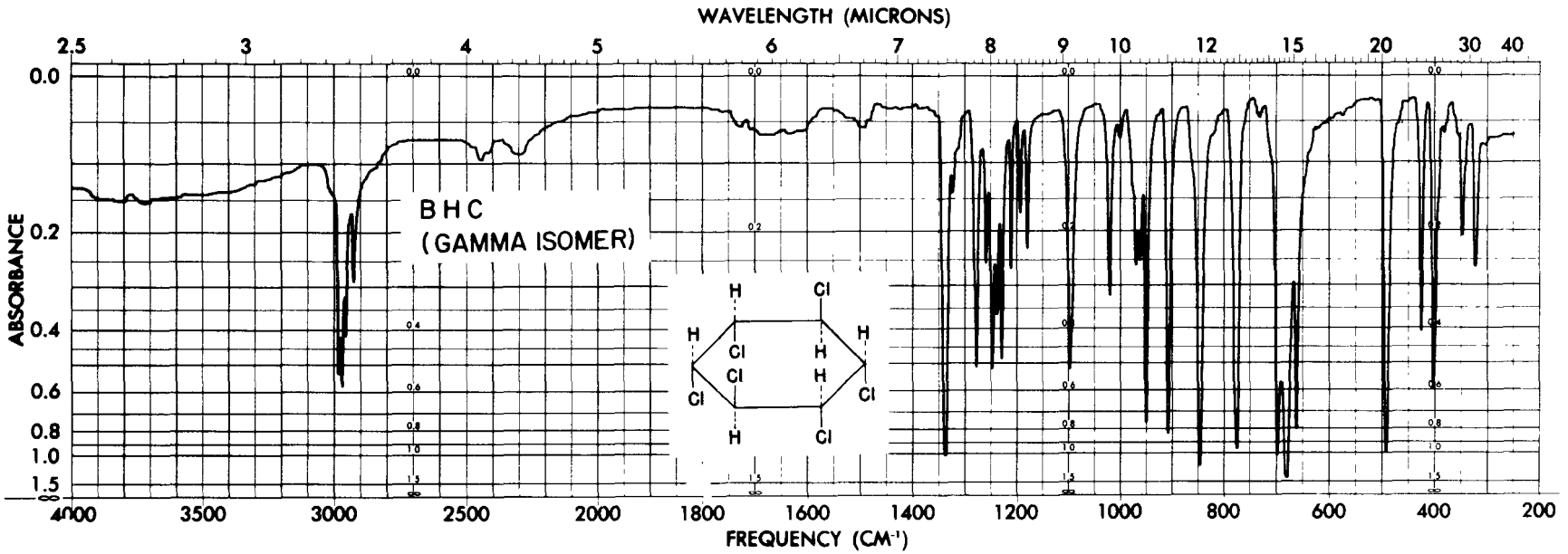

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BENSULIDE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

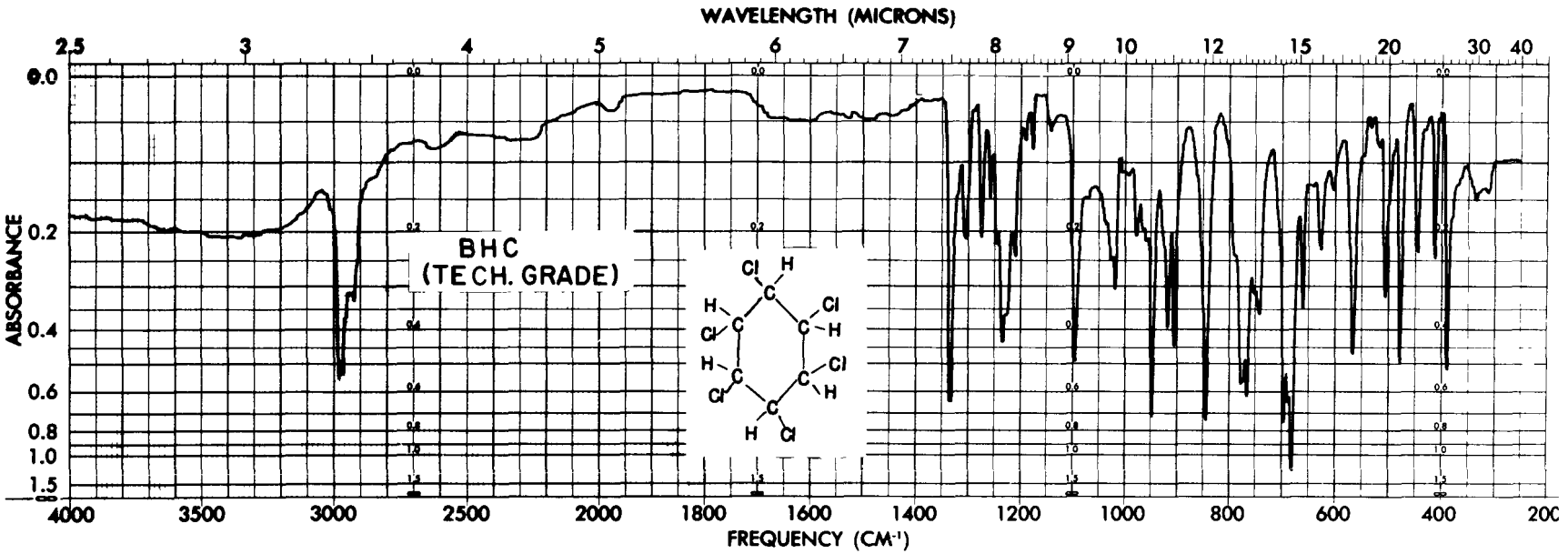

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
BENZADOX
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

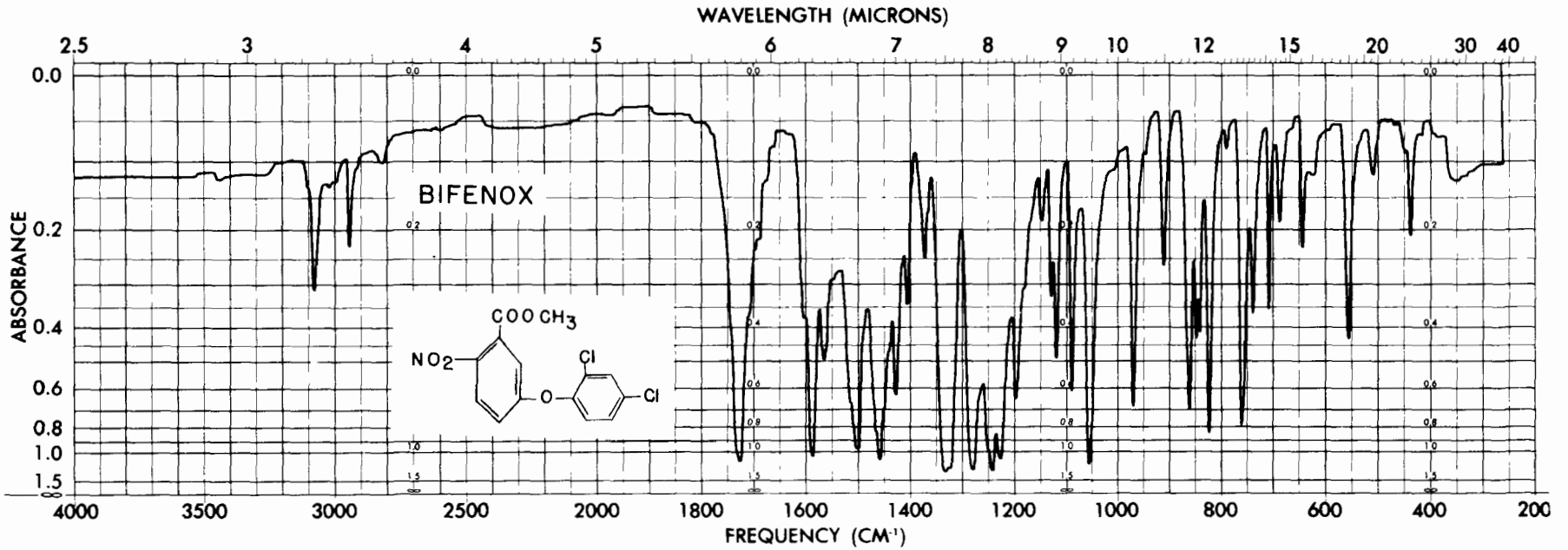

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
BHC
(ALPHA ISOMER)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

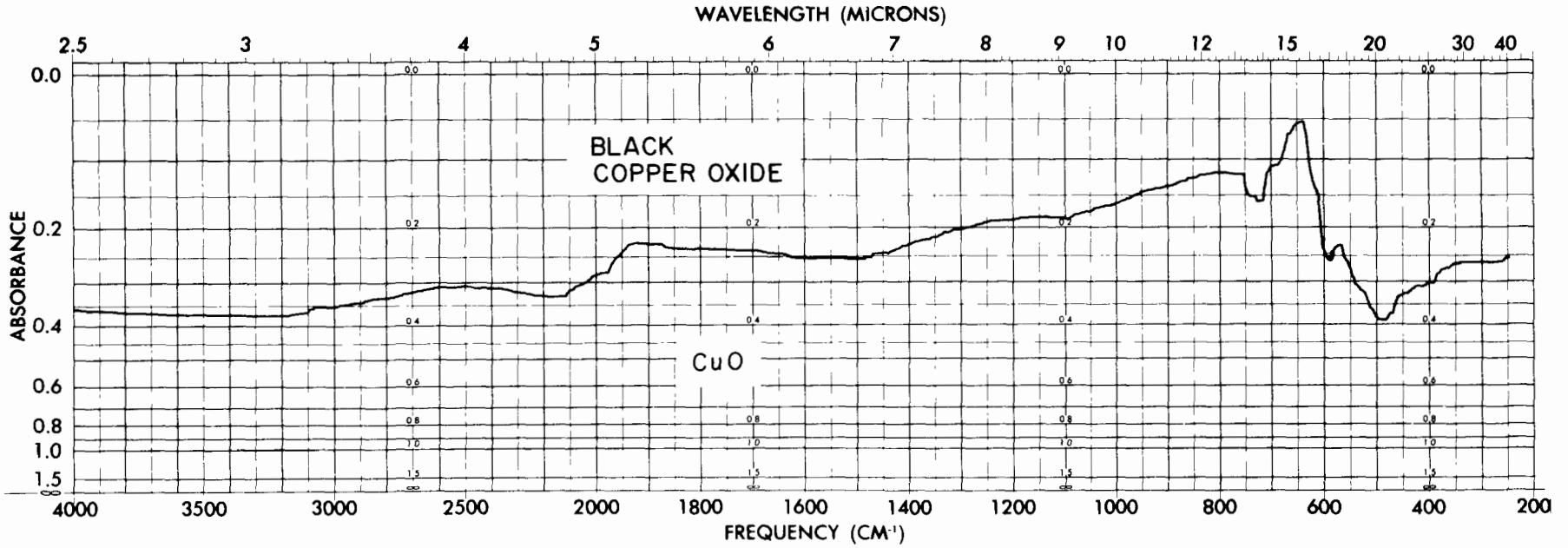

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
BHC
(DELTA ISOMER)
H
H
H
Cl
Cl
Cl
Cl
Cl
H
H
H
H
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

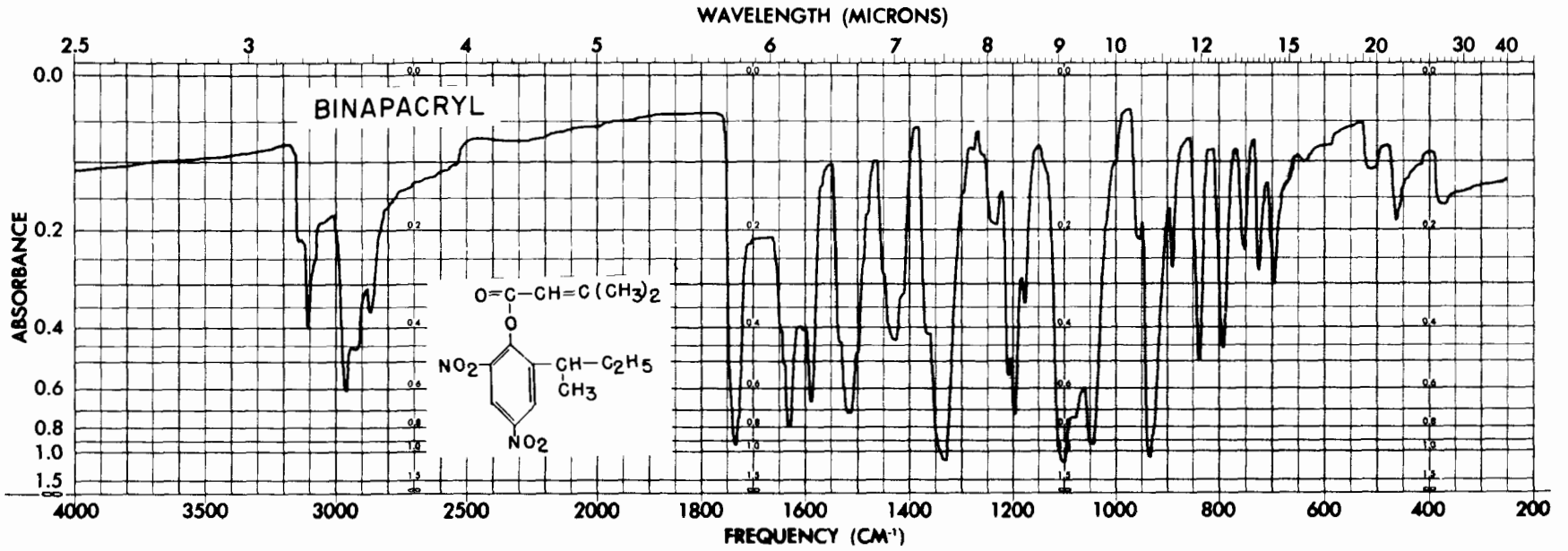

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
BHC
(EPSILON ISOMER)
H
H
H
Cl
Cl
Cl
Cl
Cl
H
H
H
H
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

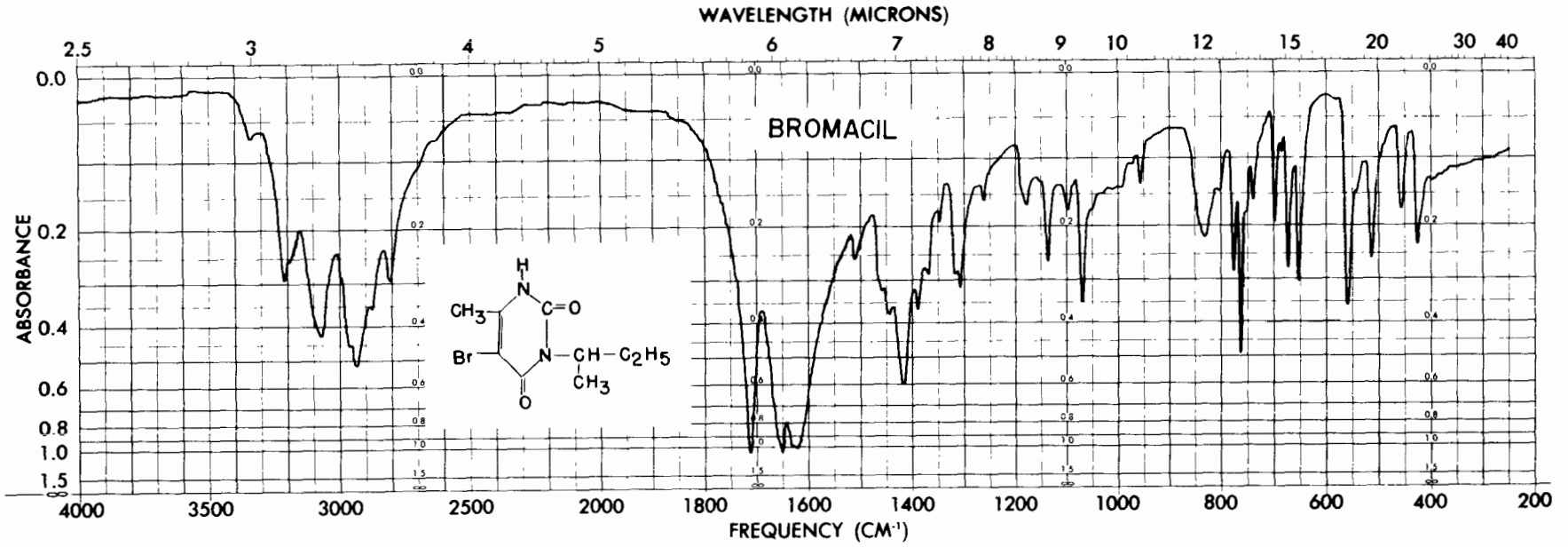

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BHC
(GAMMA ISOMER)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

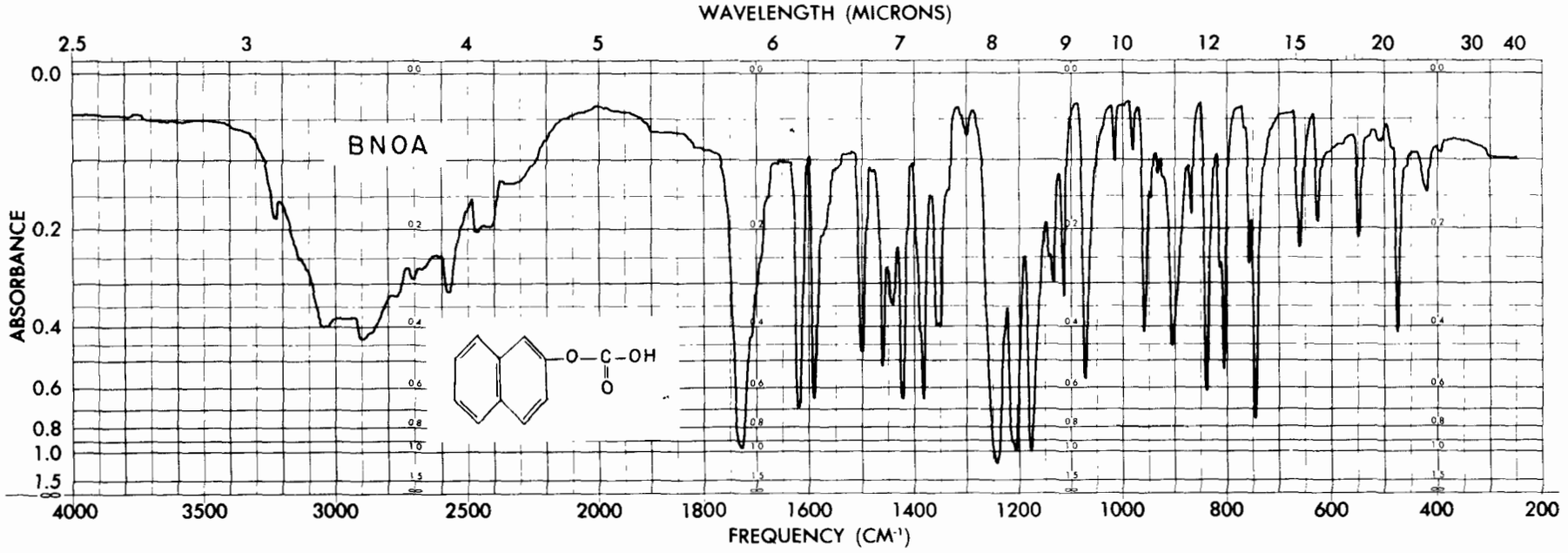

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BHC
(TECH. GRADE)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

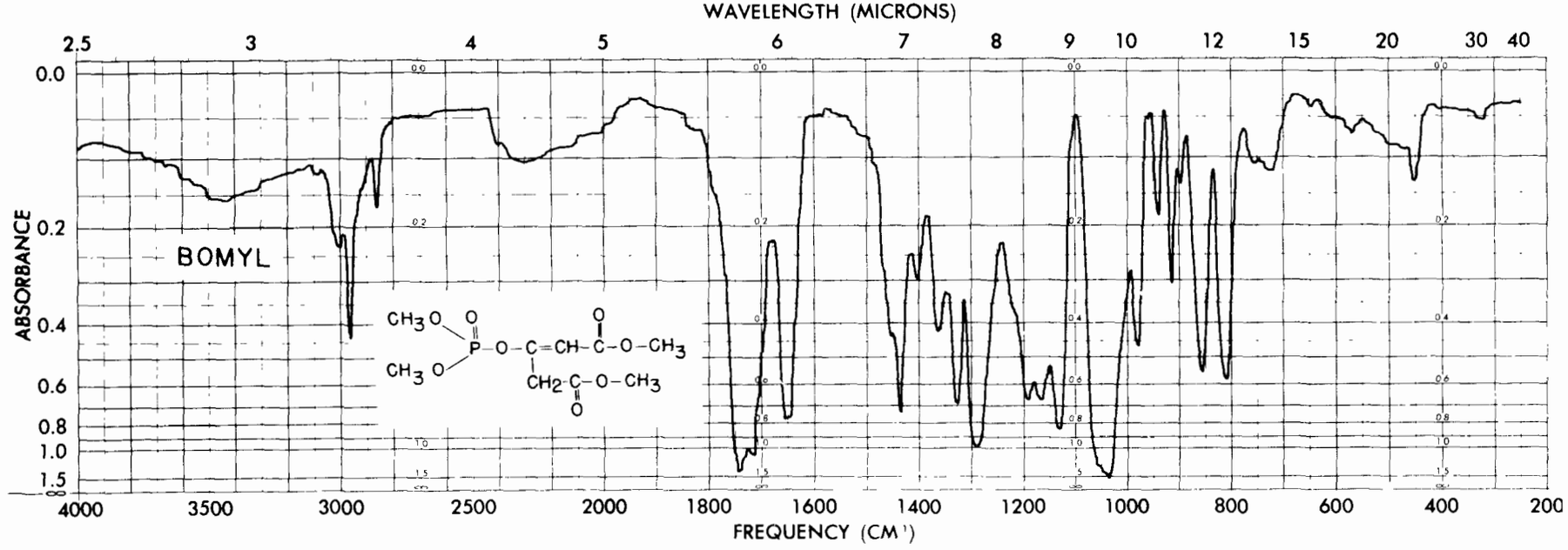

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BIFENOX
COOCH3
NO2
Cl
O
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

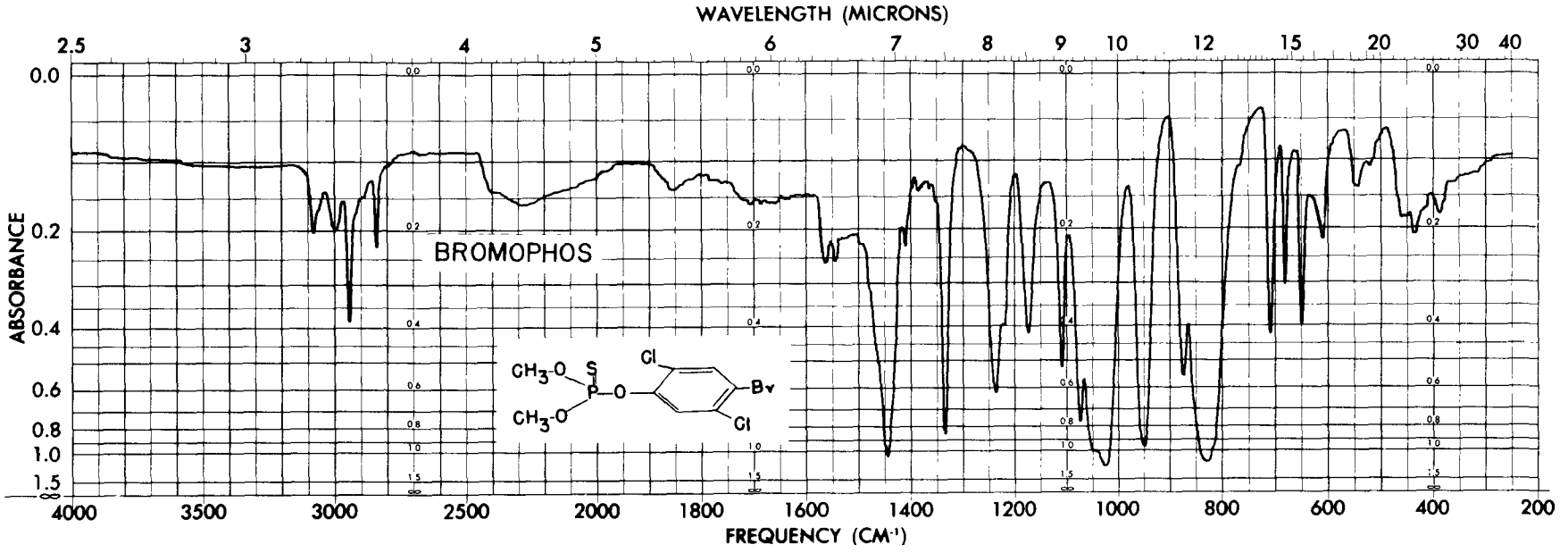

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BLACK
COPPER OXIDE
CuO
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

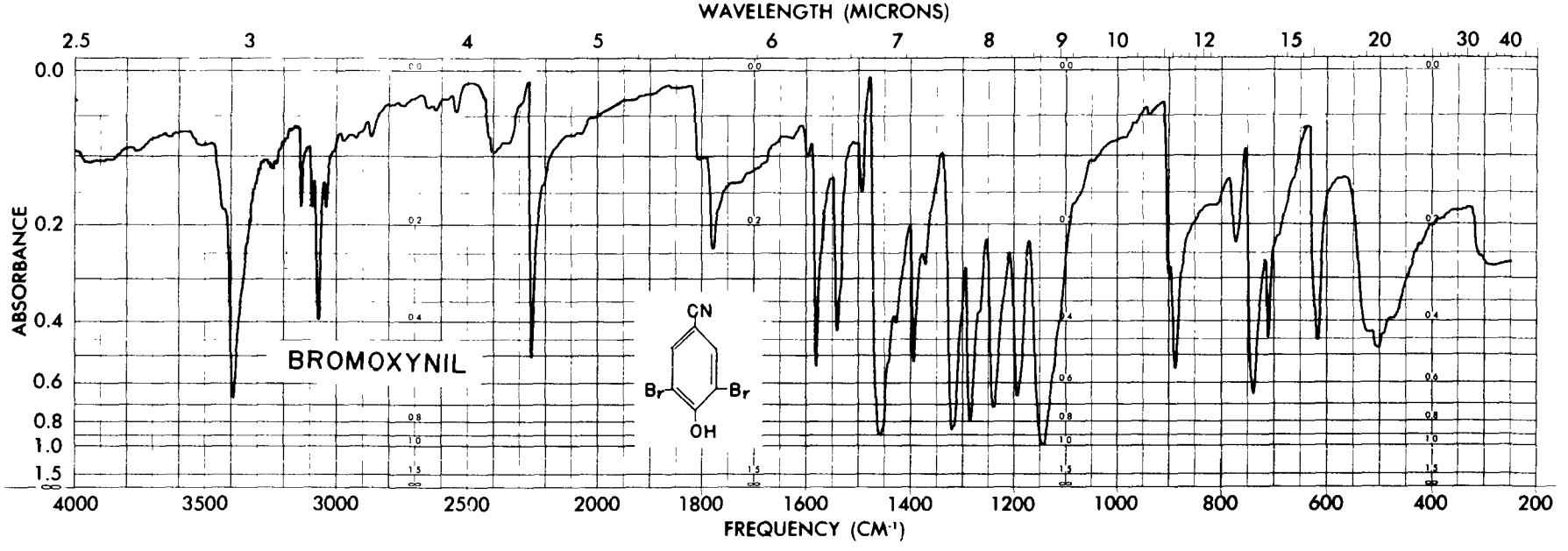

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
BINAPACRYL
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
O=C—CH=C(CH3)2
O
NO2
CH—C2H5
CH3
NO2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

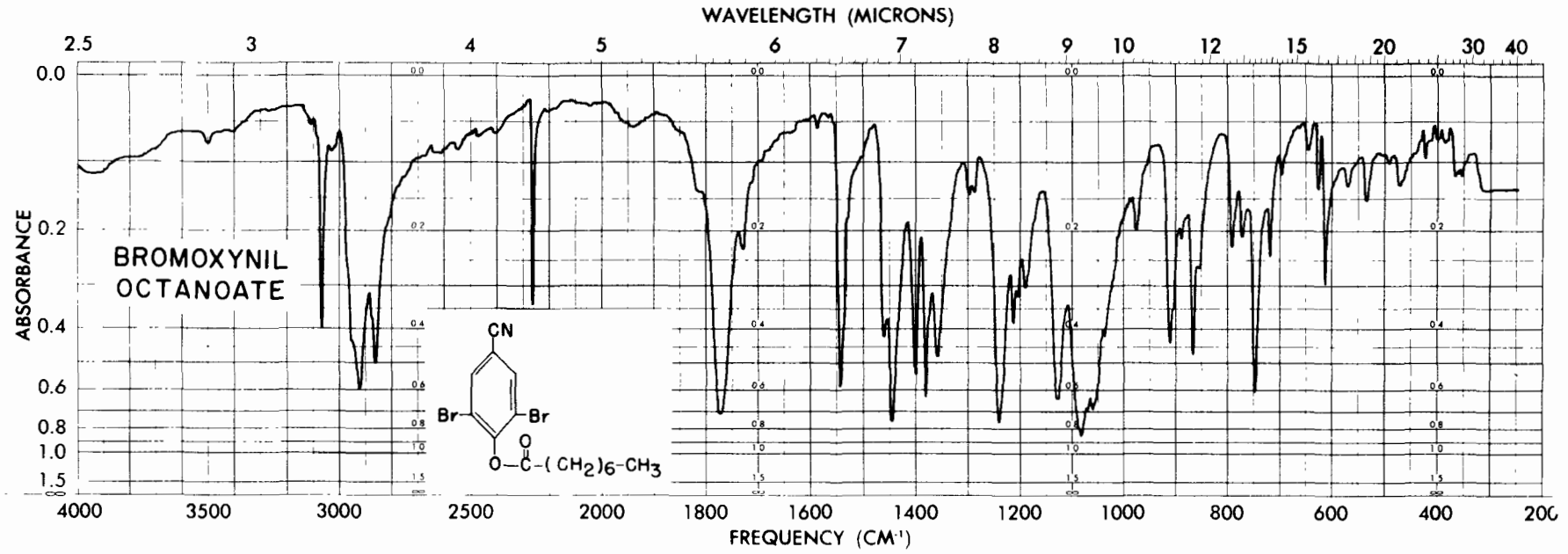

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
BROMACIL
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
H
N
CH3
C=O
Br
N—CH—C2H5
CH3
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

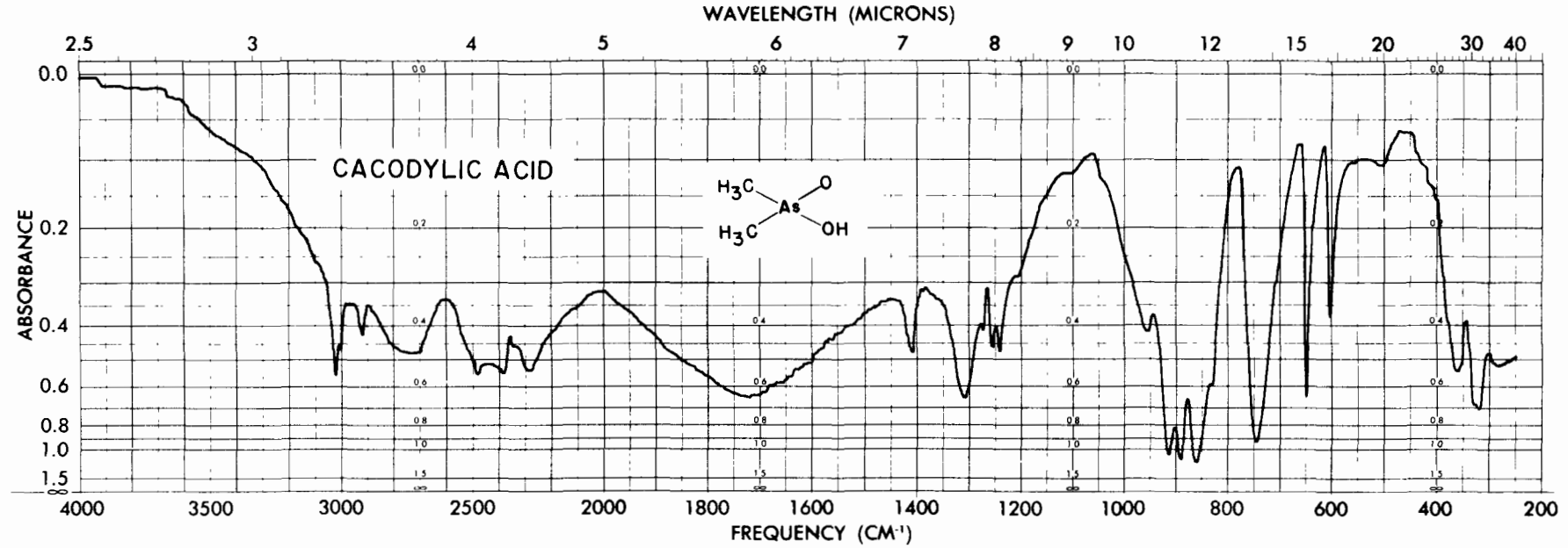

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
BNOA
O—C—OH
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

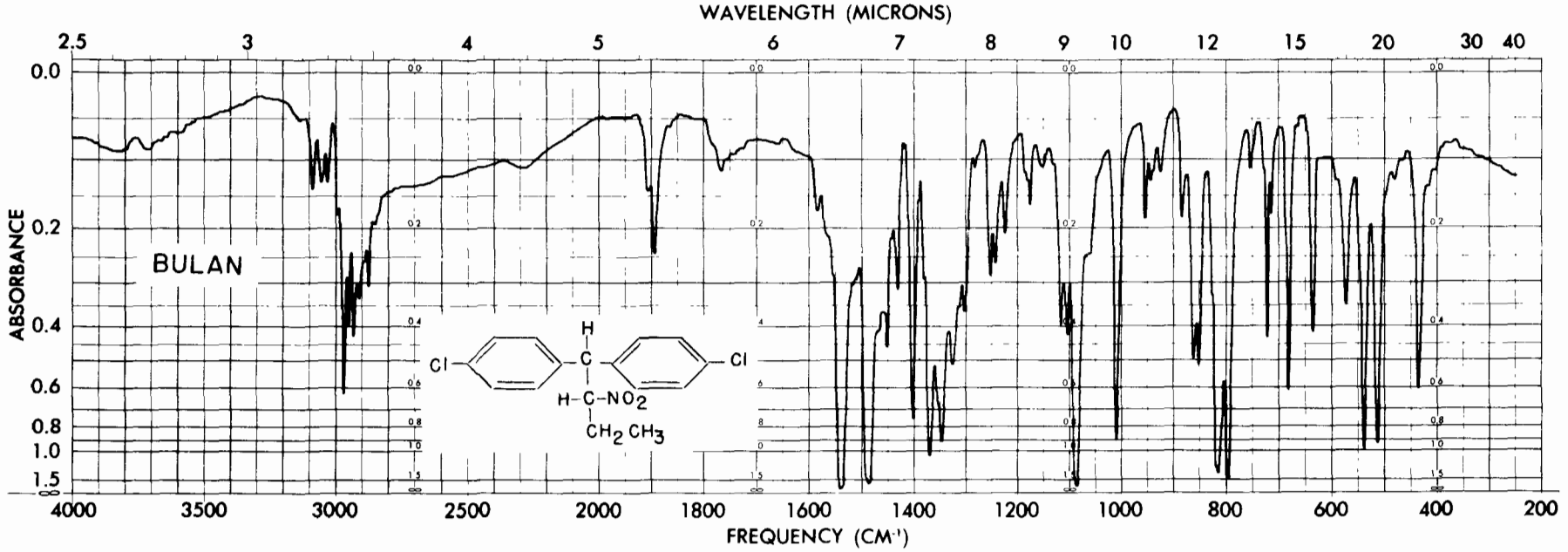

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
BOMYL
CH3O
O
P
O
C=CH
C
O
CH3
CH3O
O
CH2
C
O
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

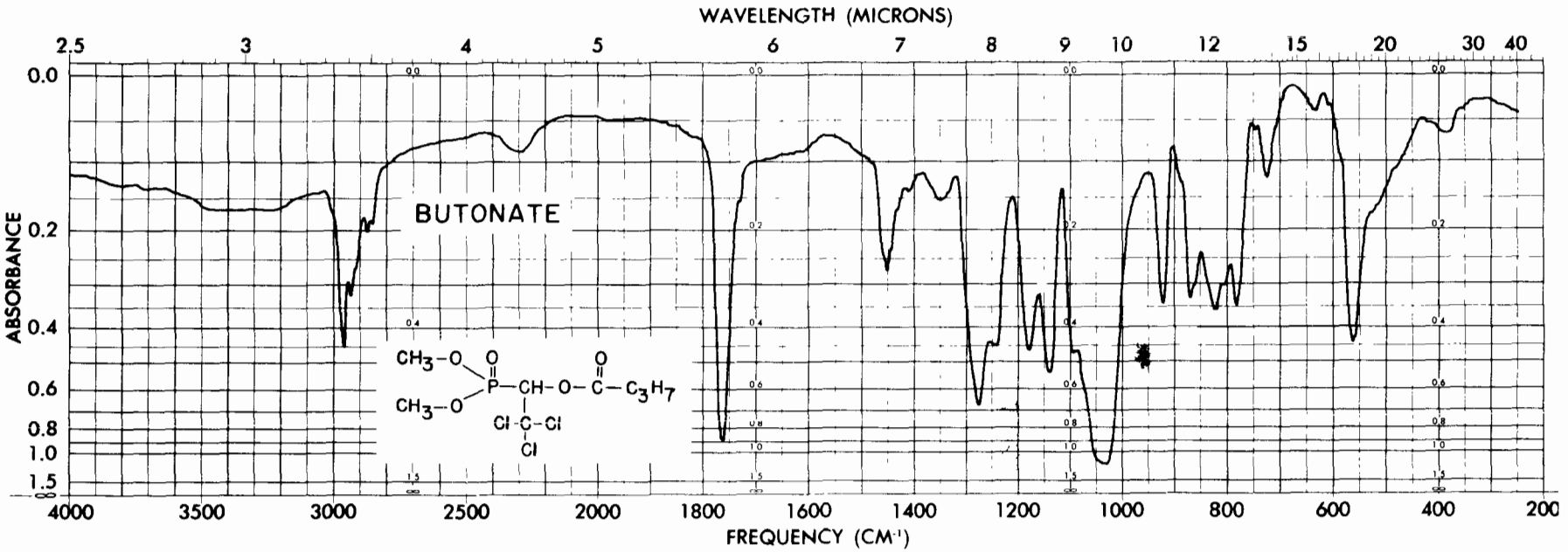

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BROMOPHOS
CH3-O
S
P
O
CH3-O
Cl
Br
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

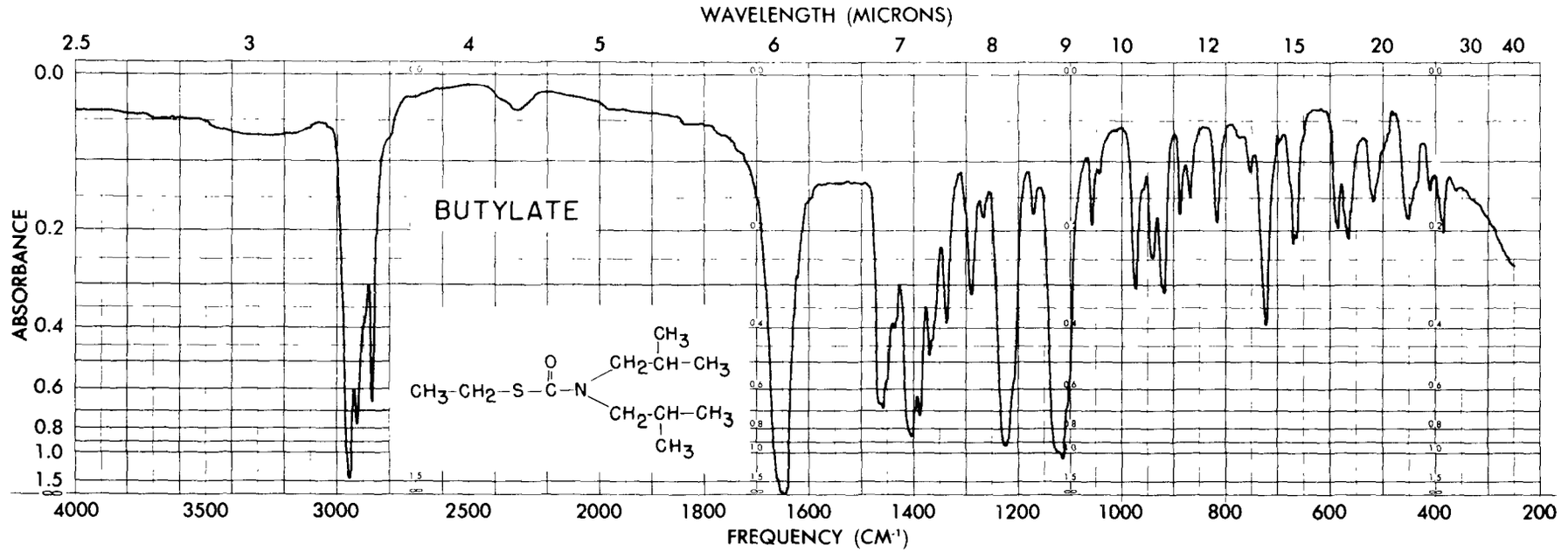

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BROMOXYNIL
CN
Br
Br
OH
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

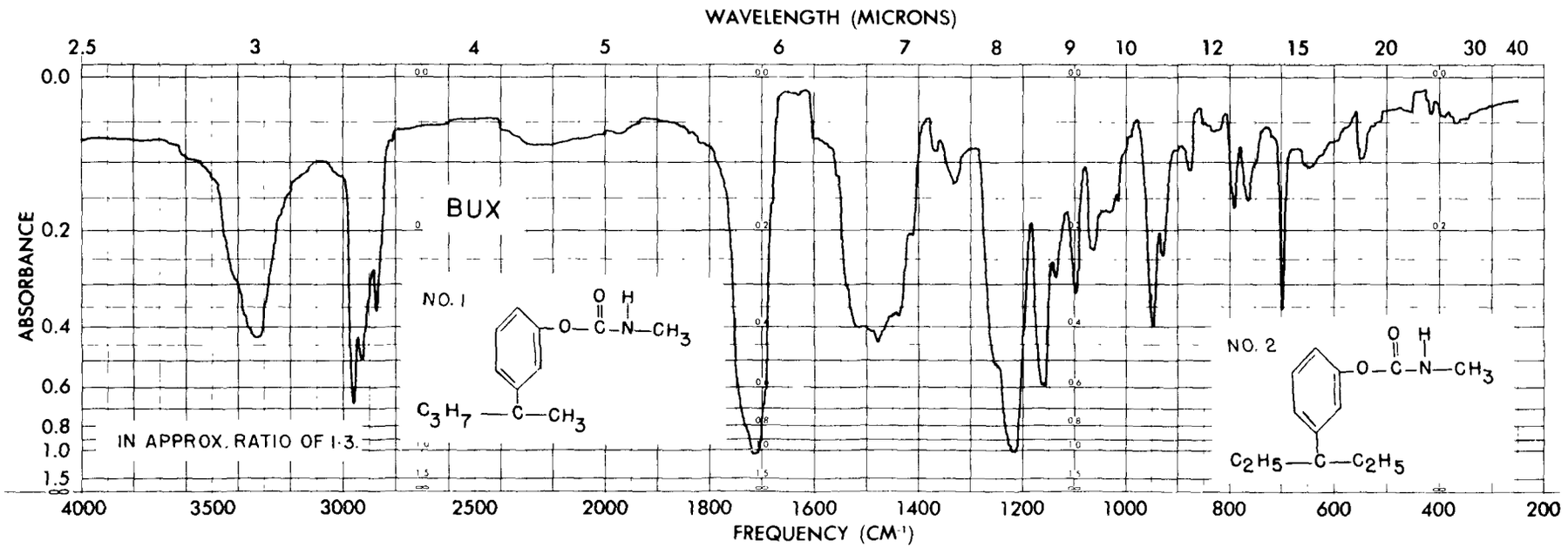

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BROMOXYNIL
OCTANOATE
CN
Br
Br
O
O—C-(CH2)6-CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

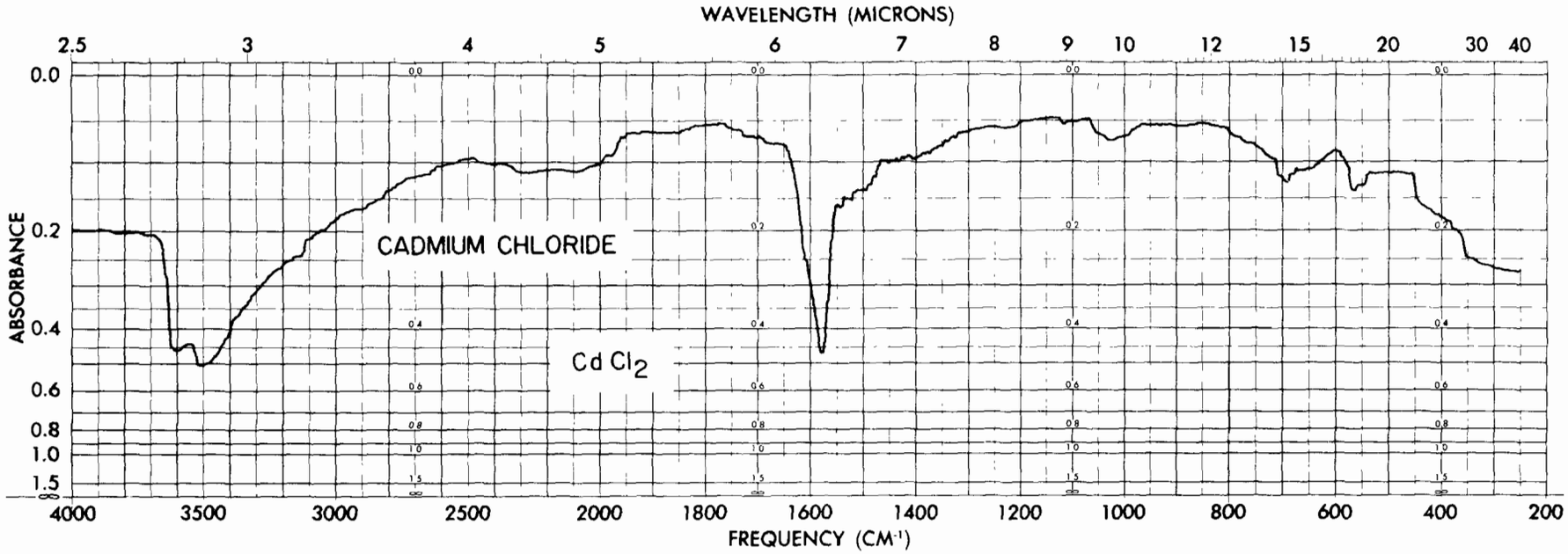

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CACODYLIC ACID
H3C
As
O
H3C
OH
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

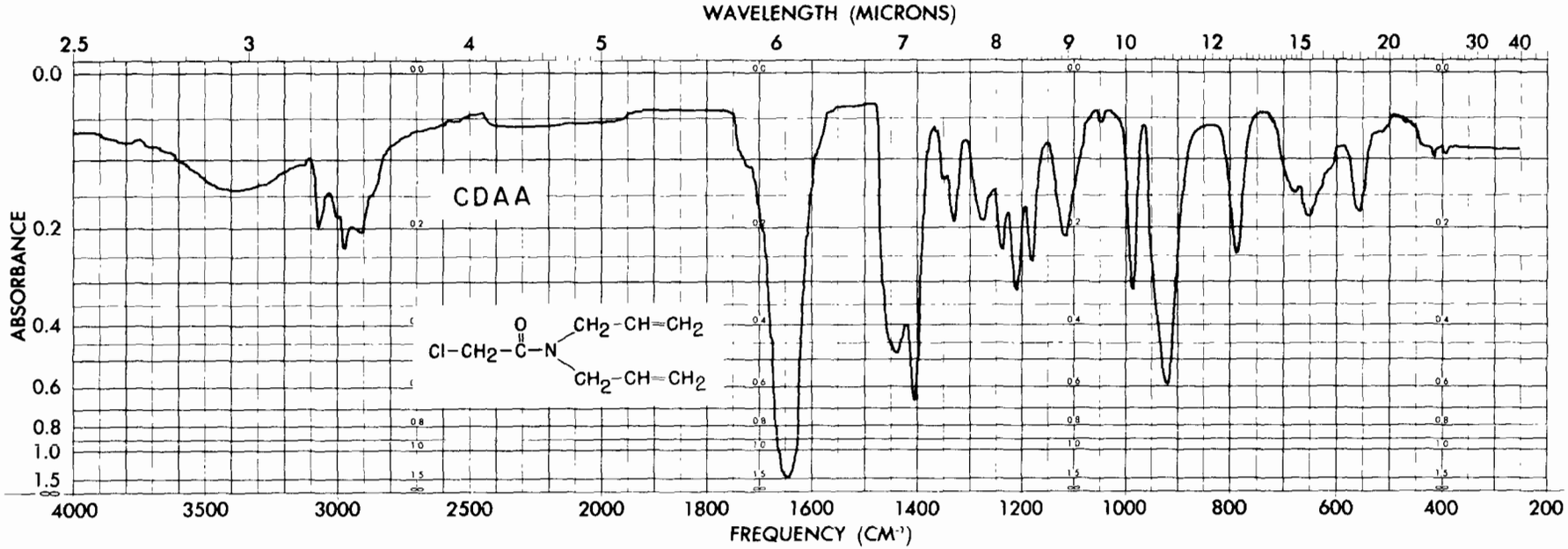

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BULAN
Cl
H
C
Cl
H-C-NO2
CH2 CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

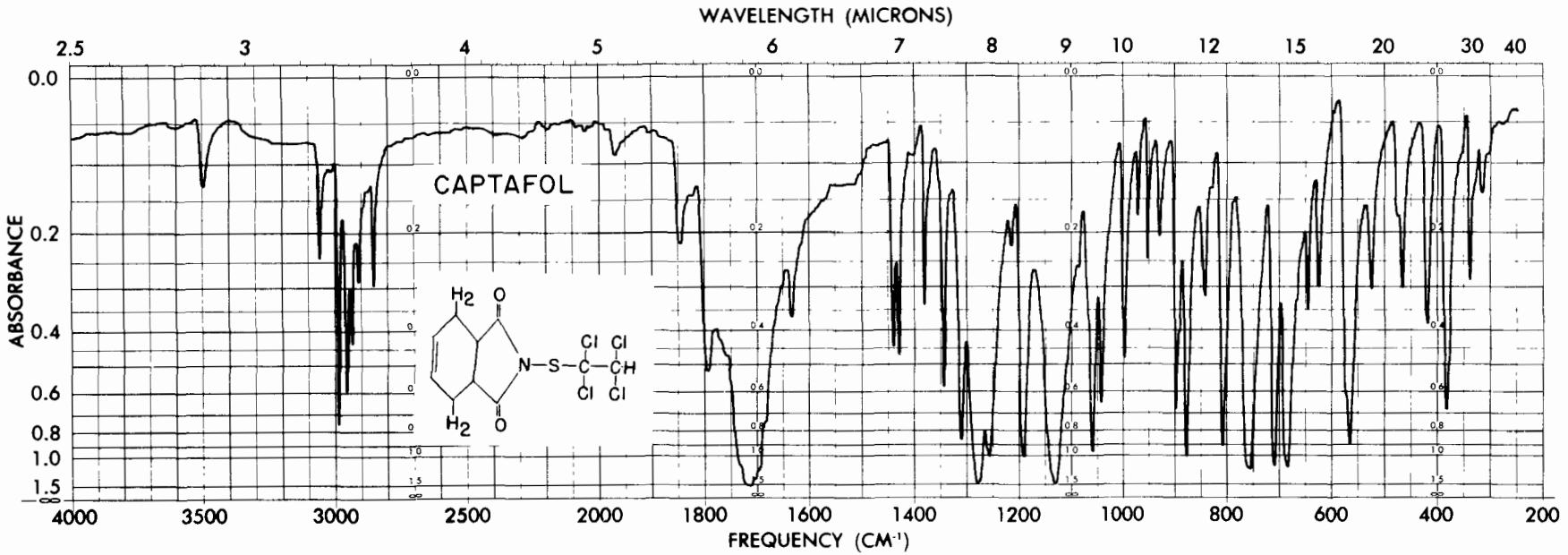

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BUTONATE
CH3-O
O
P
CH-O-C-C3H7
CH3-O
Cl-C-Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

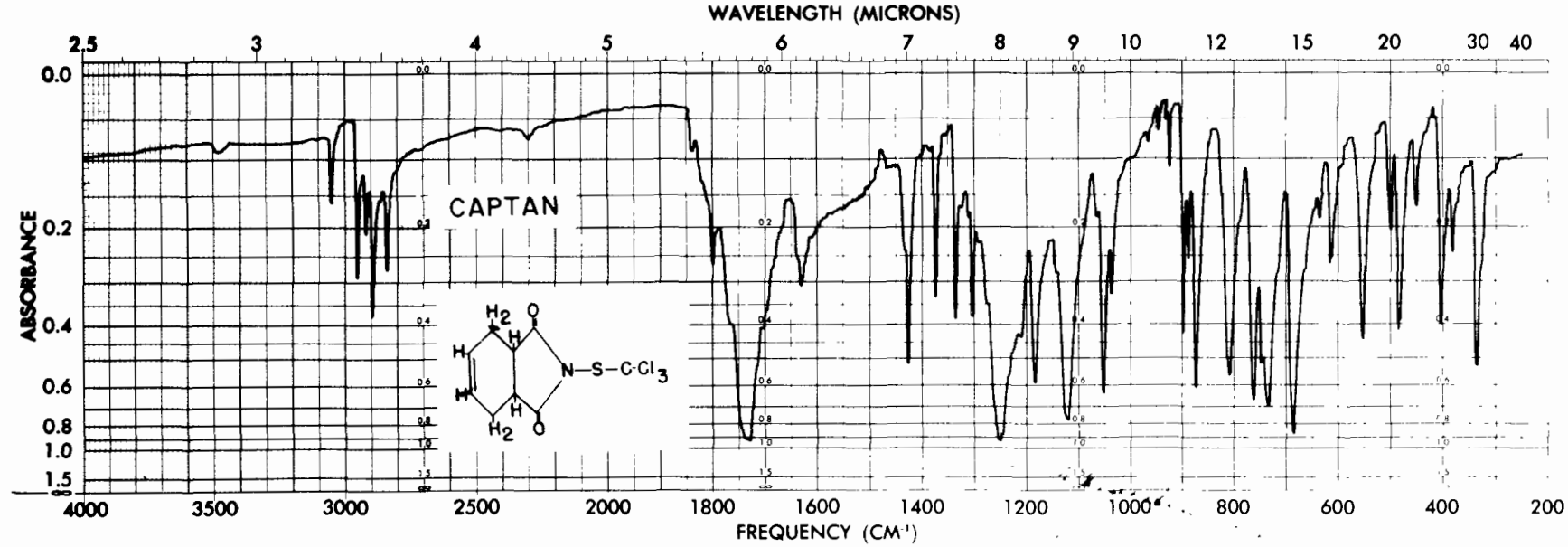

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BUTYLATE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

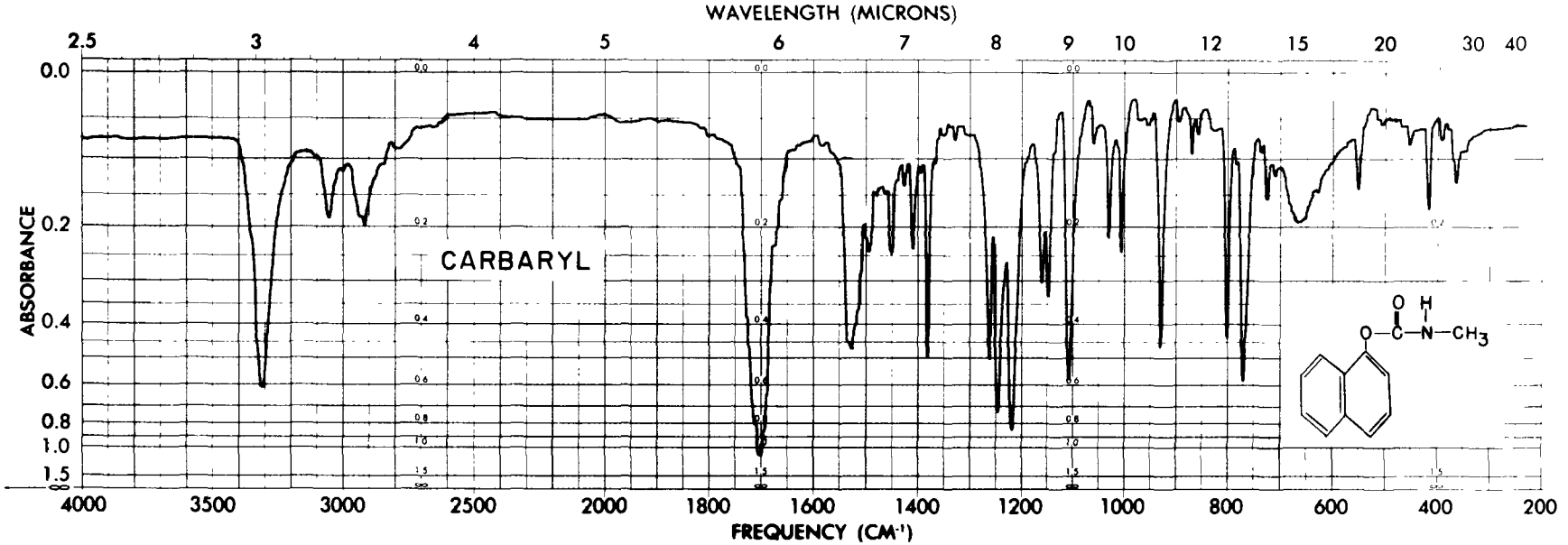

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
BUX
NO. 1
NO. 2
IN APPROX. RATIO OF 1:3.
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

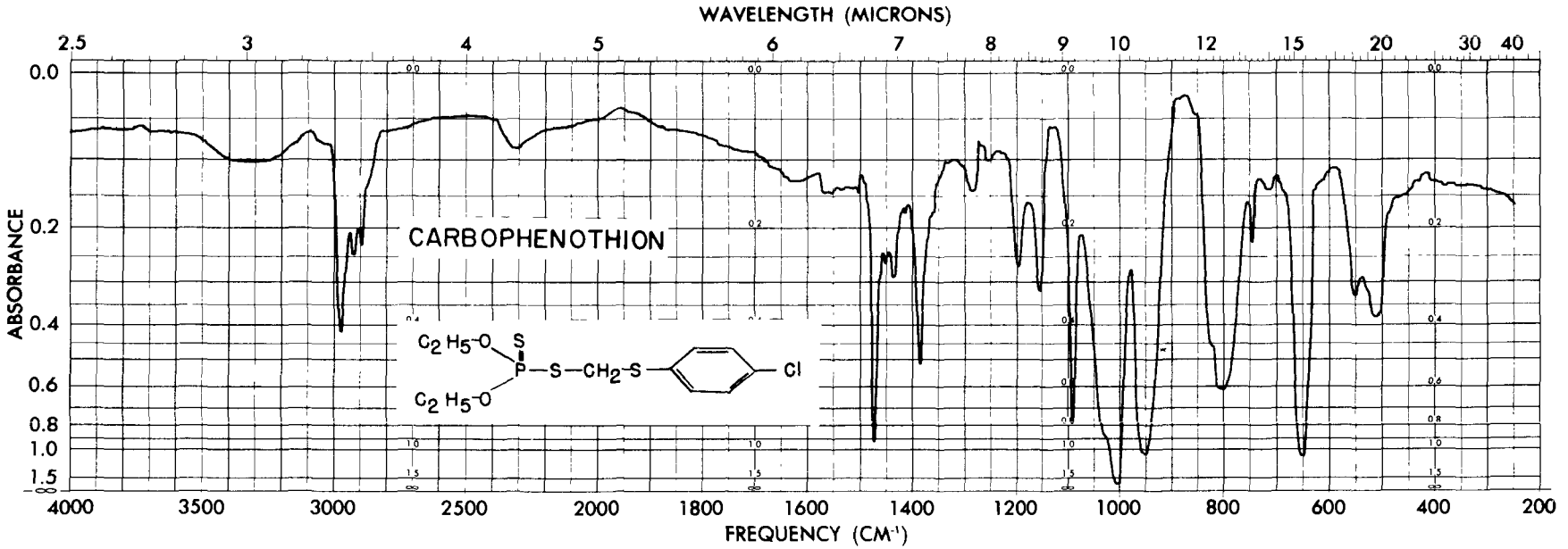

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CADMIUM CHLORIDE
Cd Cl2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

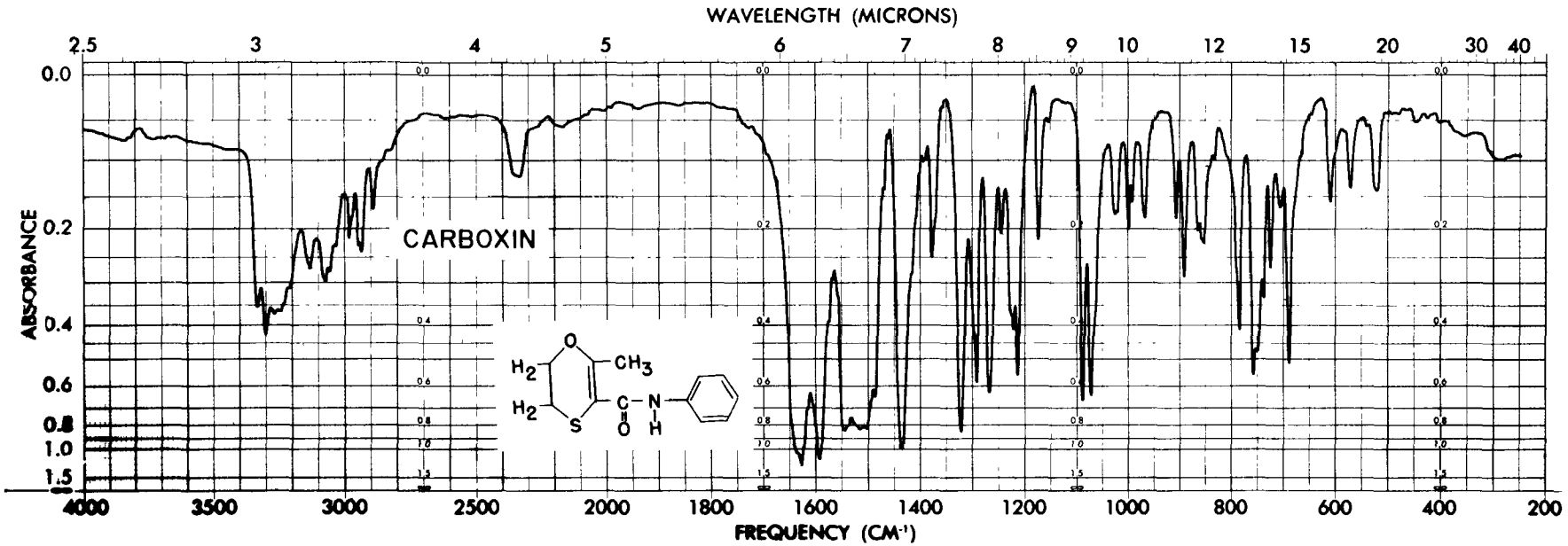

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CDAA
Cl-CH2-C(=O)-N(CH2-CH=CH2)(CH2-CH=CH2)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

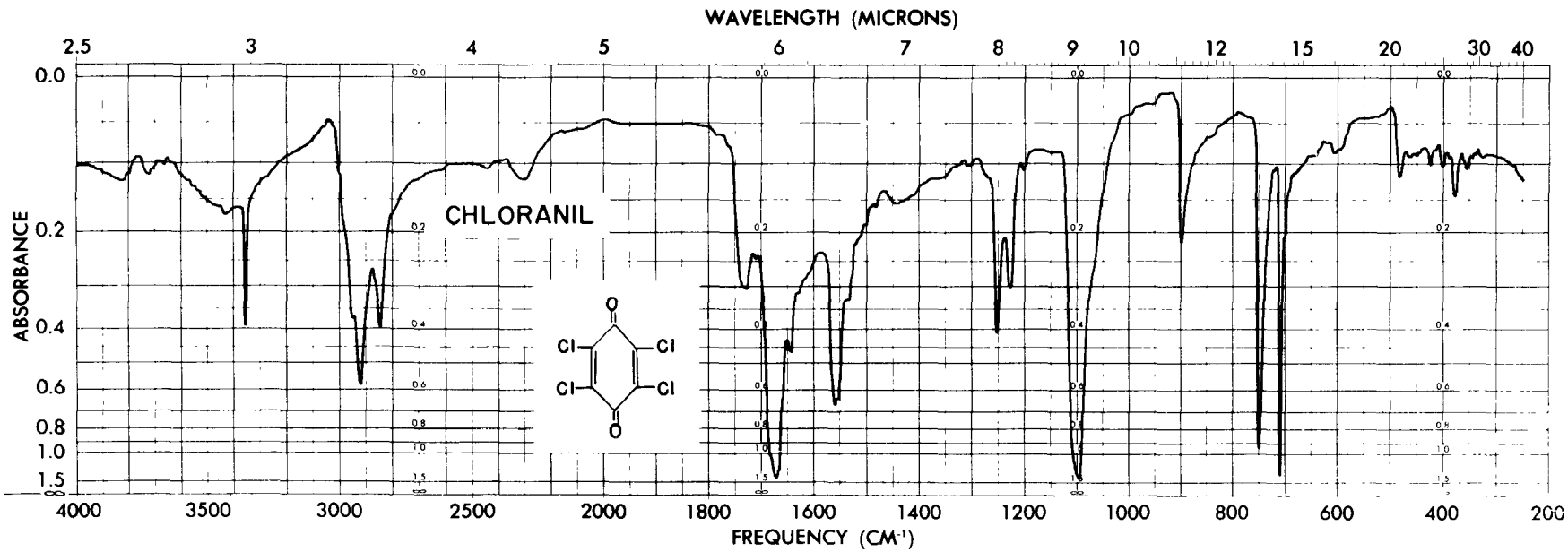

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
CAPTAFOL
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

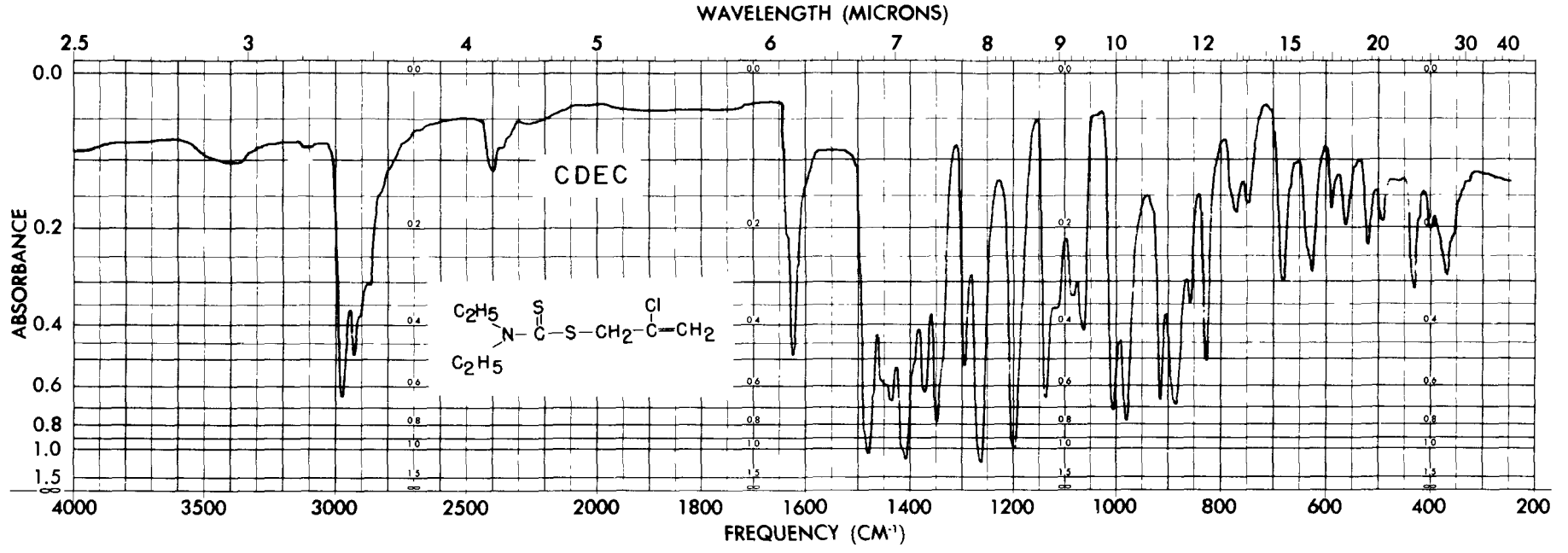

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
CAPTAN
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

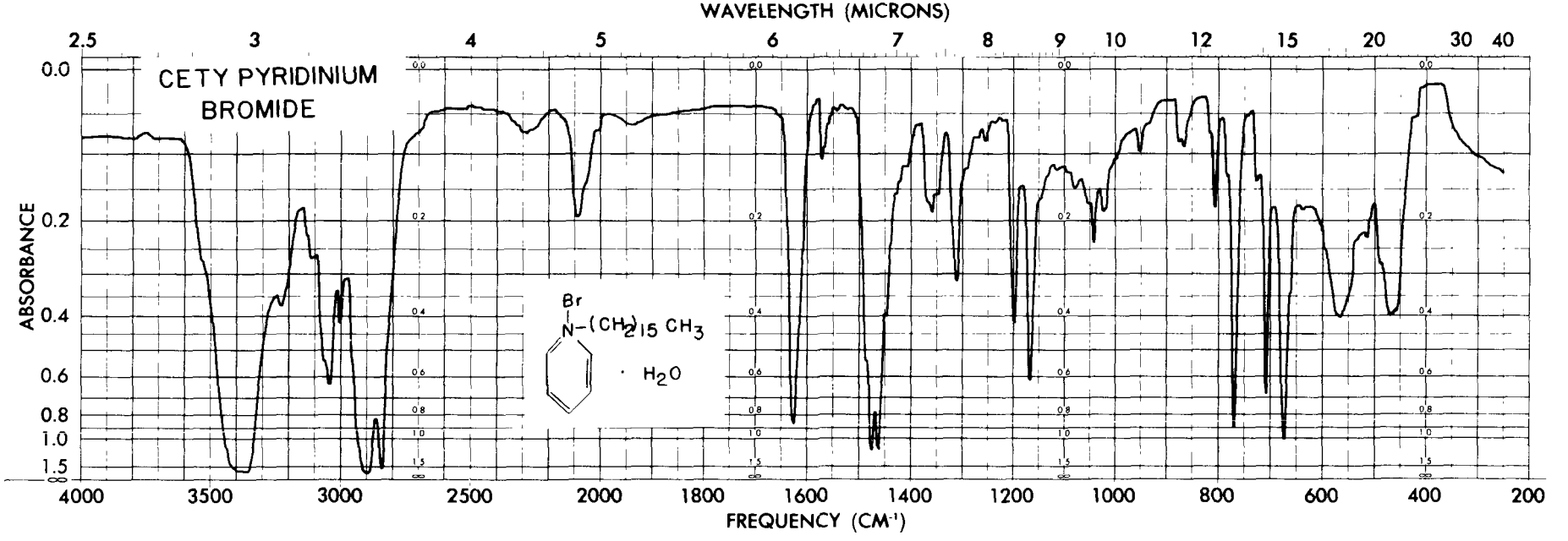

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
CARBARYL
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

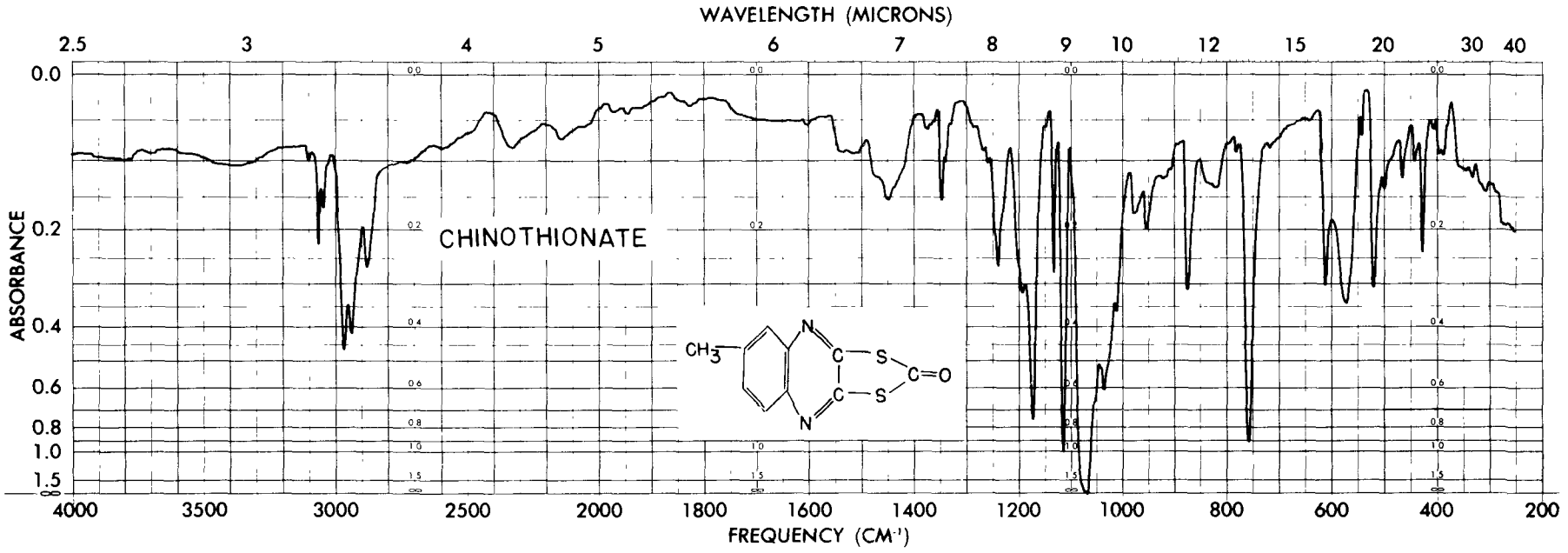

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
CARBOPHENOTHION
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

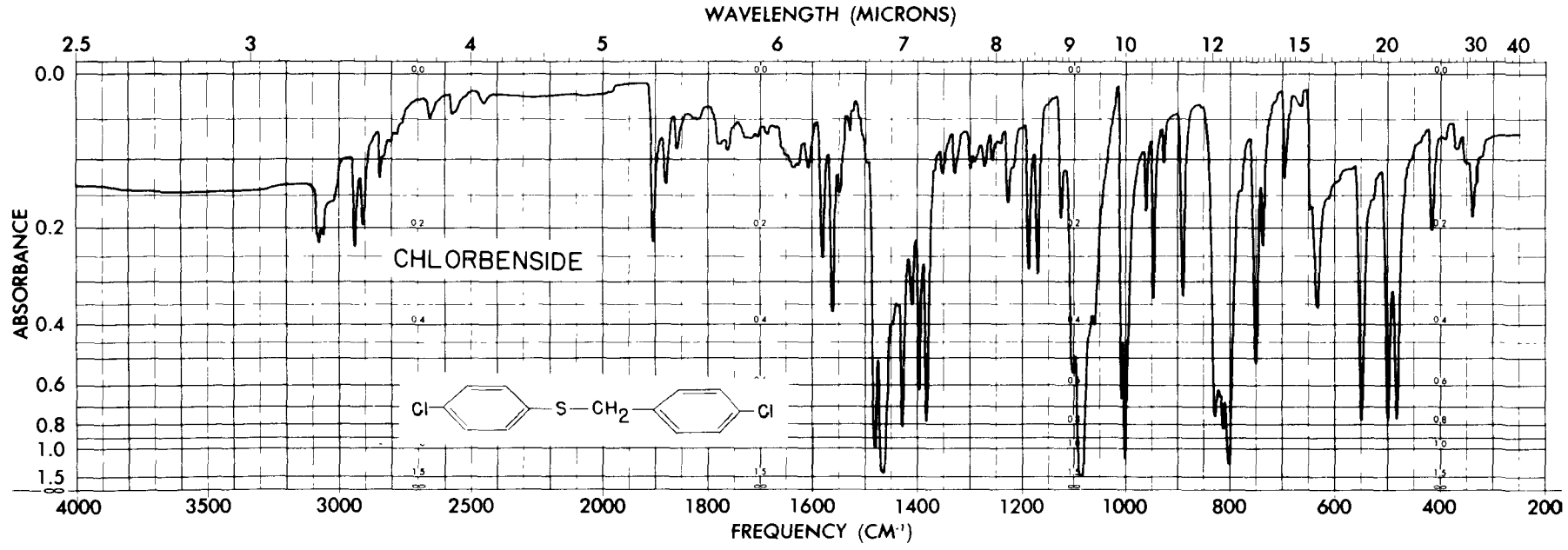

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CARBOXIN
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

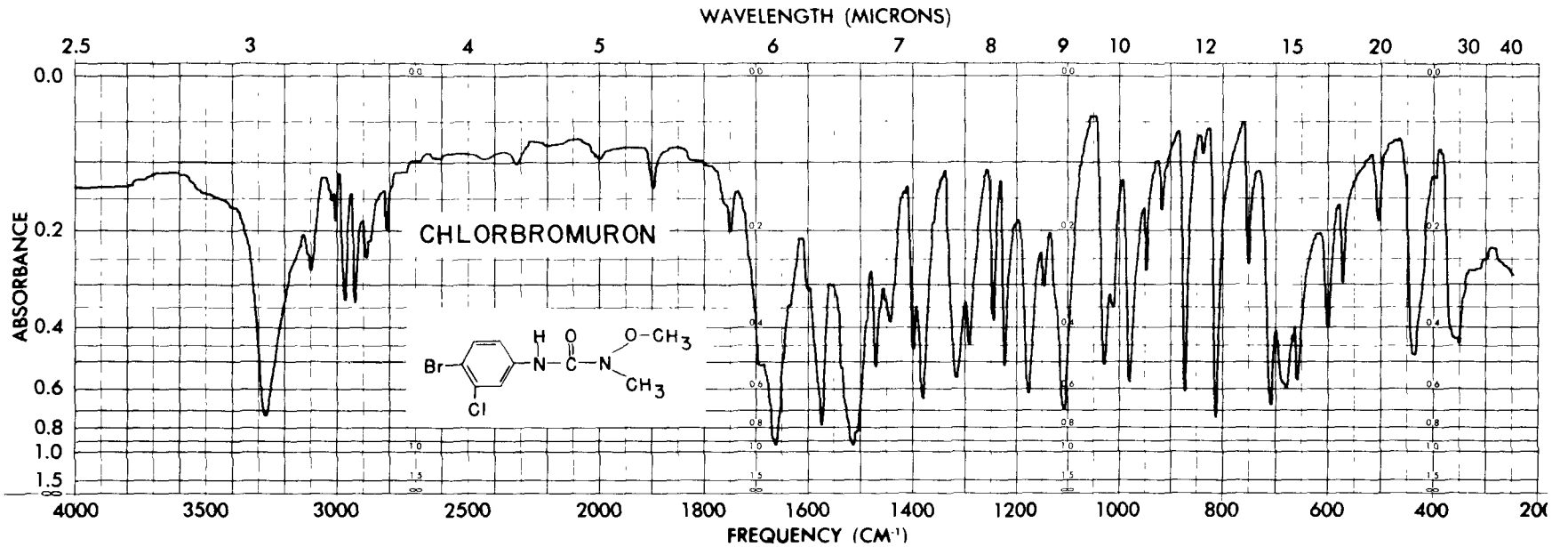

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CHLORANIL
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

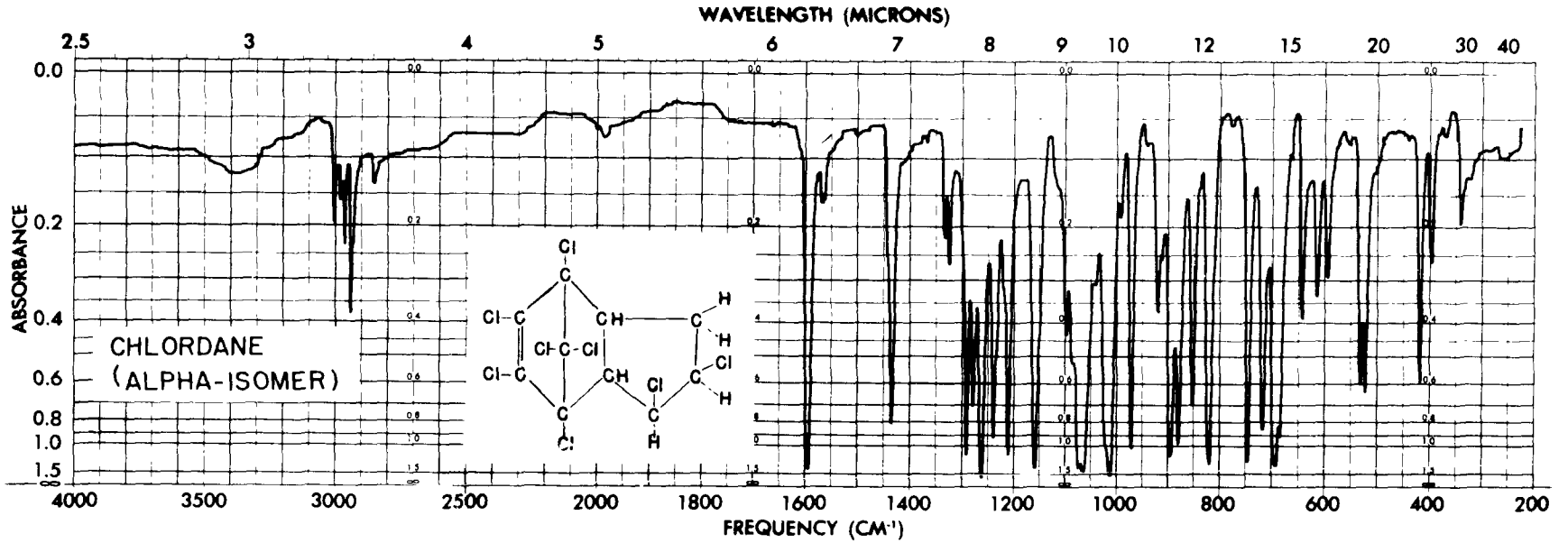

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CDEC
C_2H_5
S
Cl
N– C–S–CH_2–C=CH_2
C_2H_5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

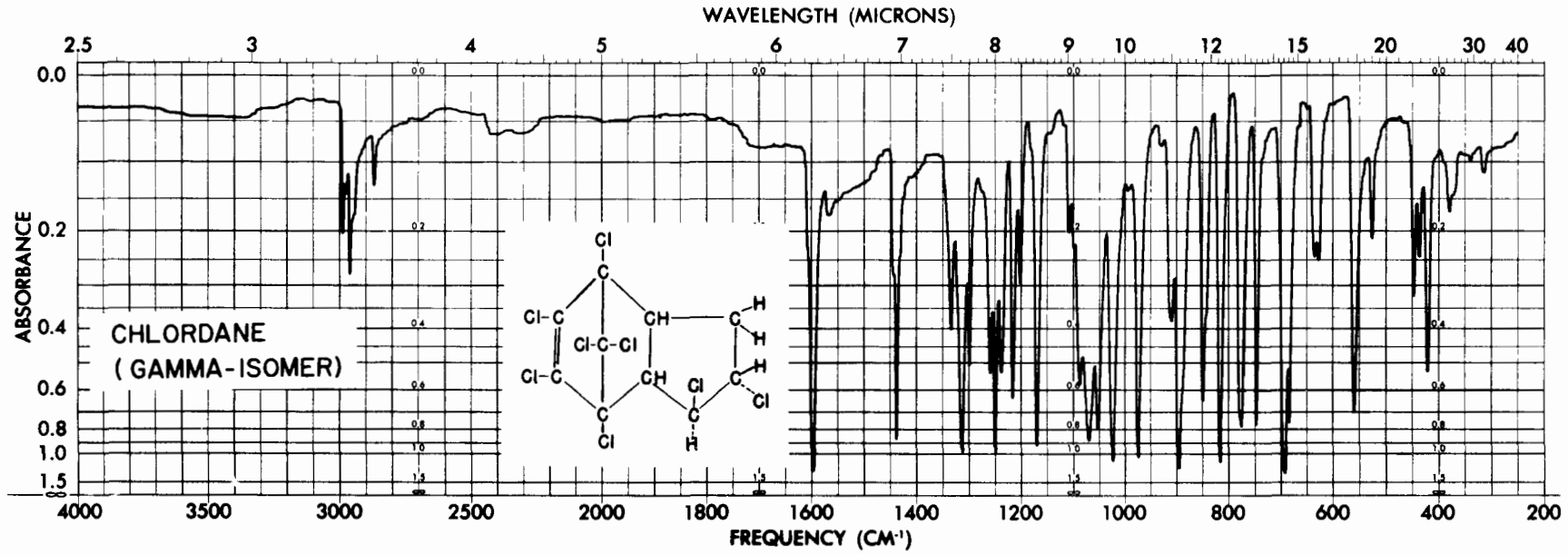

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CETY PYRIDINIUM
BROMIDE
Br
N–$(CH_2)_{15}$ CH_3
· H_2O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

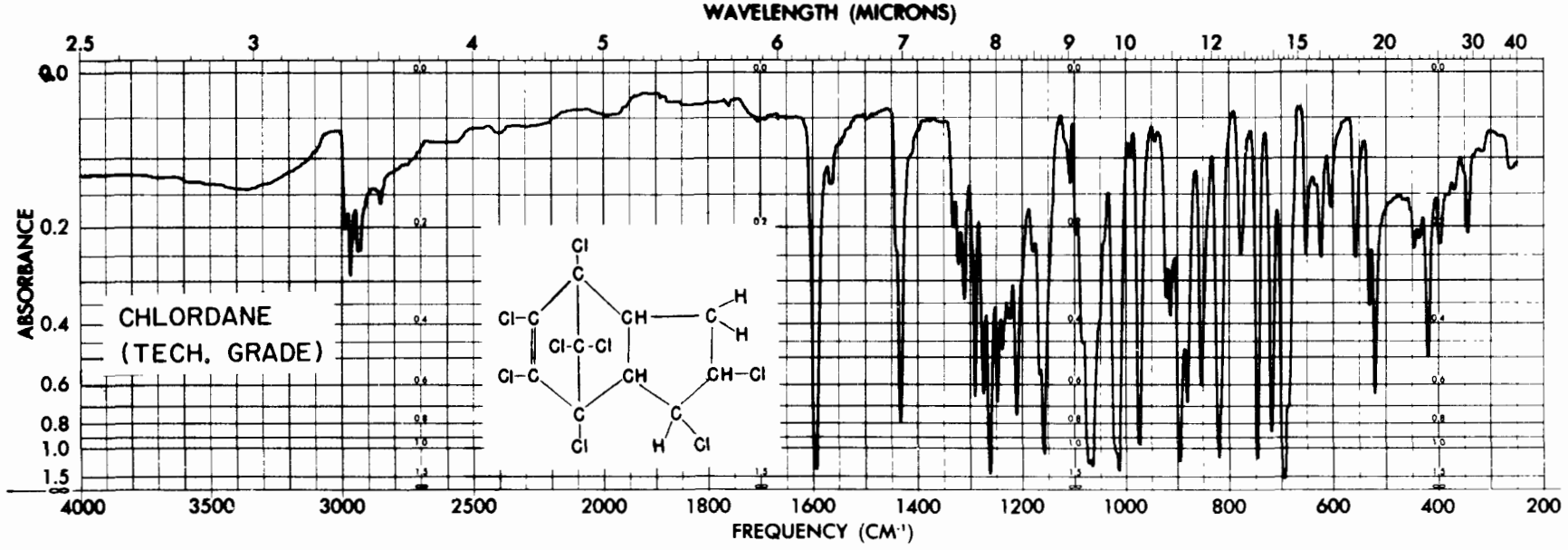

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
CHINOTHIONATE
CH3
N
C
S
C=O
C
S
N
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

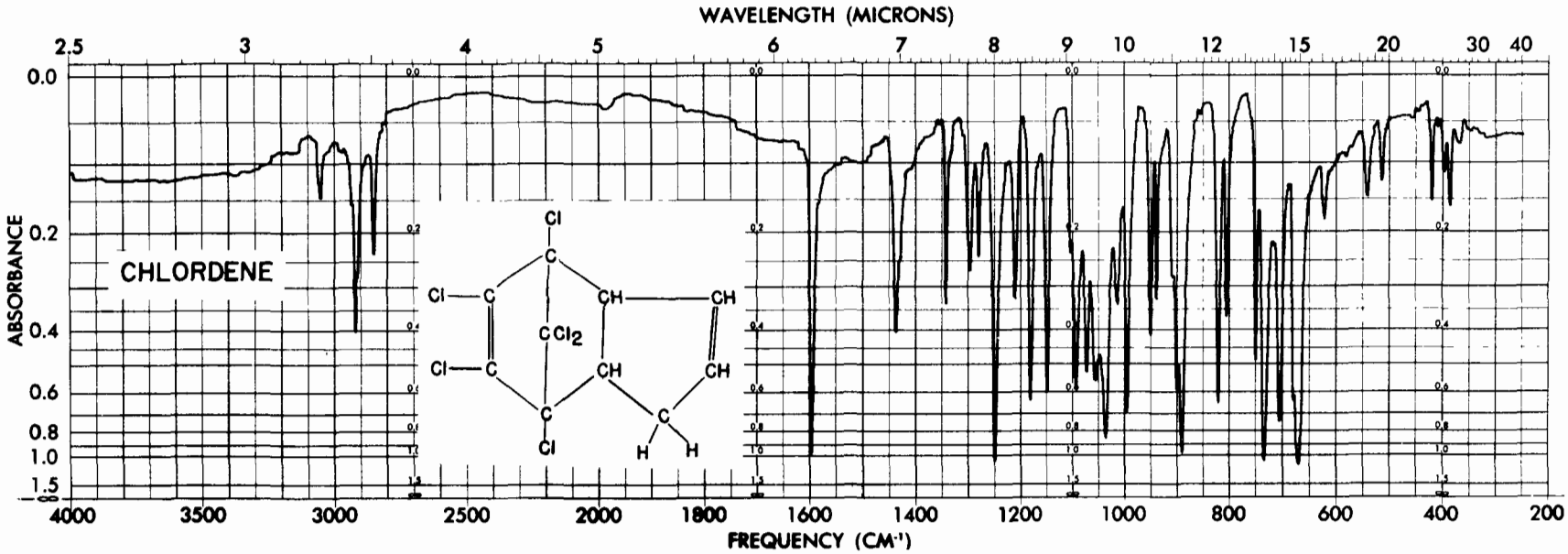

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
CHLORBENSIDE
Cl
S
CH2
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

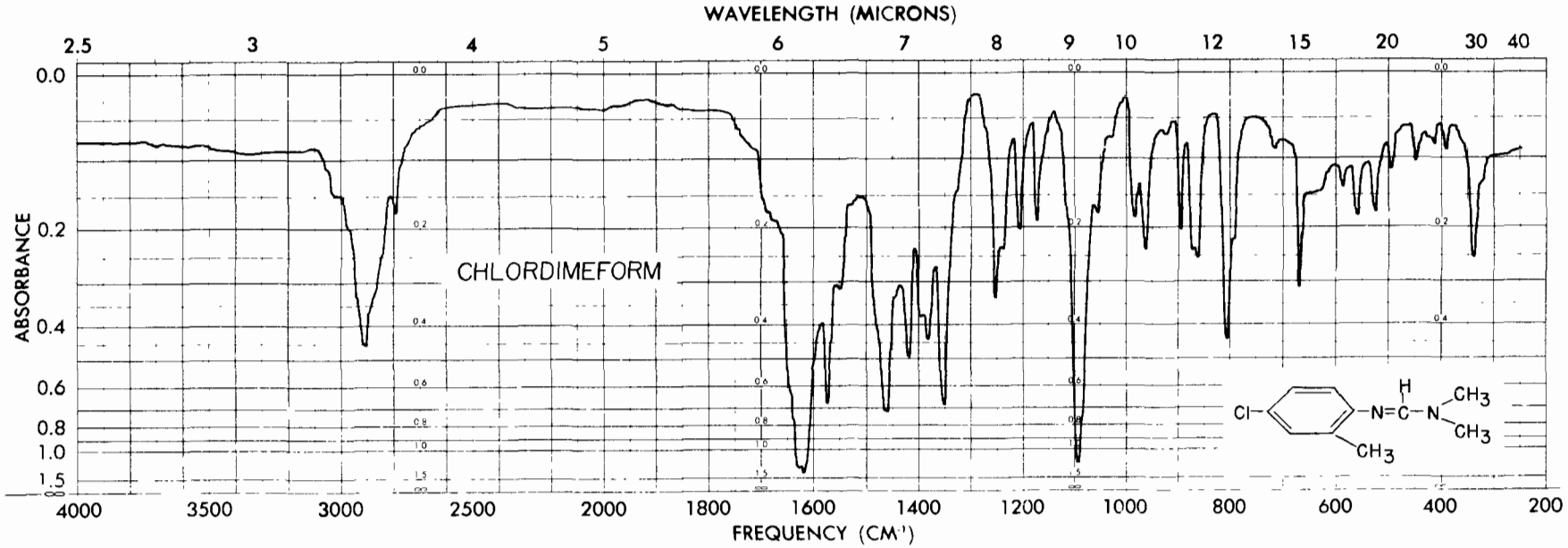

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CHLORBROMURON
Br
Cl
H
O
N
C
O-CH3
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
FREQUENCY (CM-1)

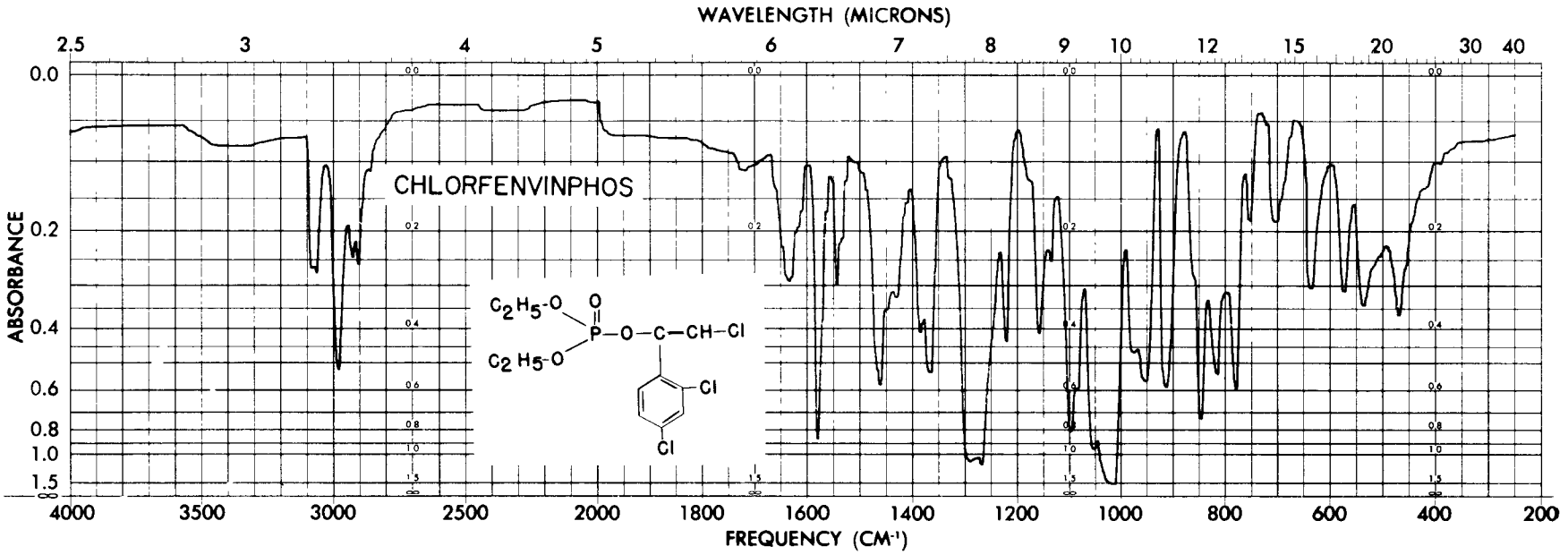

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CHLORDANE
(ALPHA-ISOMER)
Cl
H
CH
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

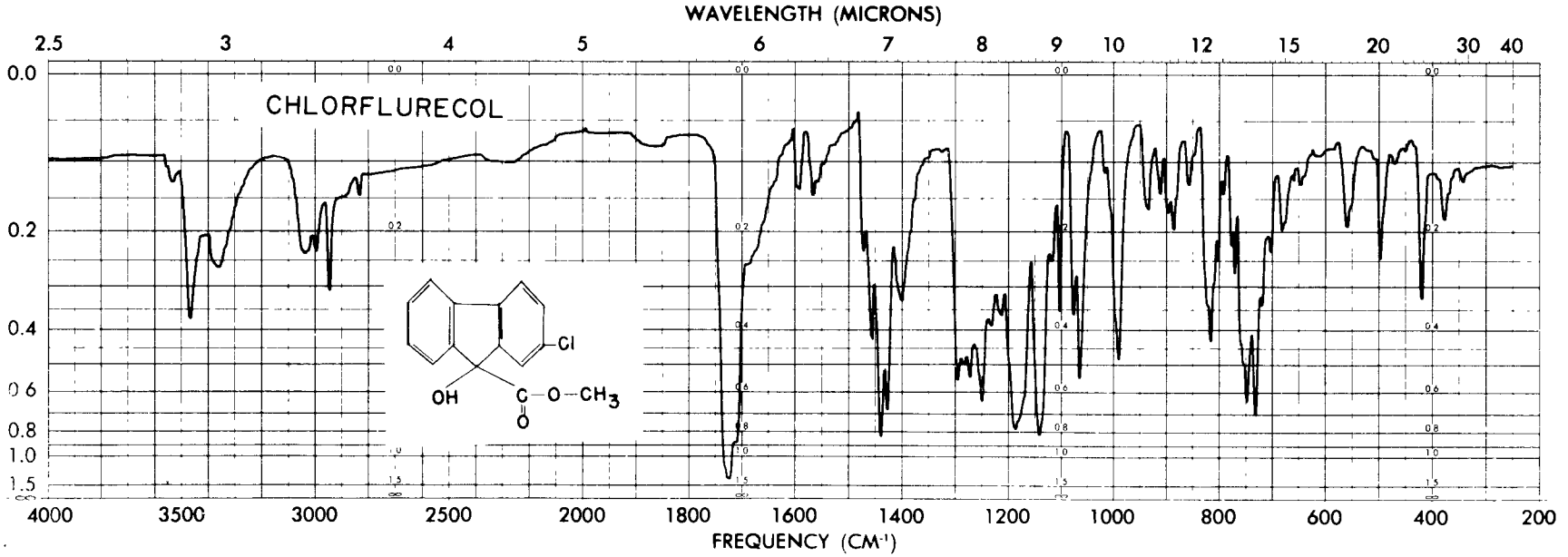

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CHLORDANE
(GAMMA-ISOMER)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

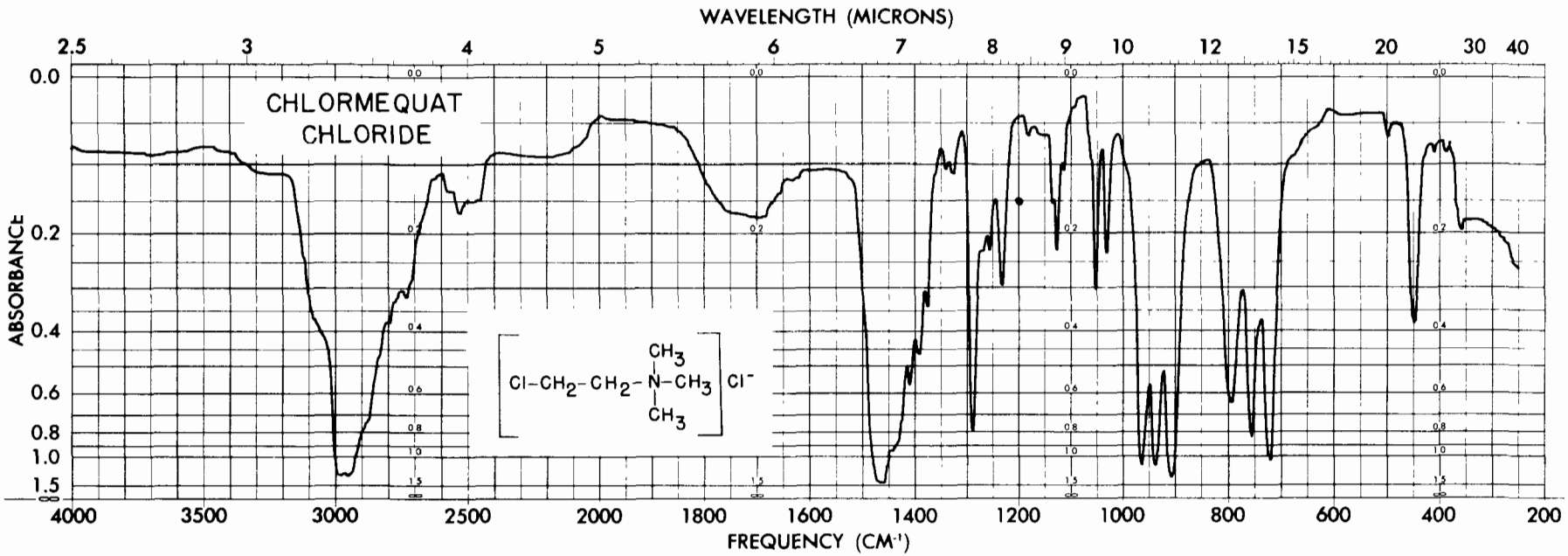

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CHLORDANE
(TECH. GRADE)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

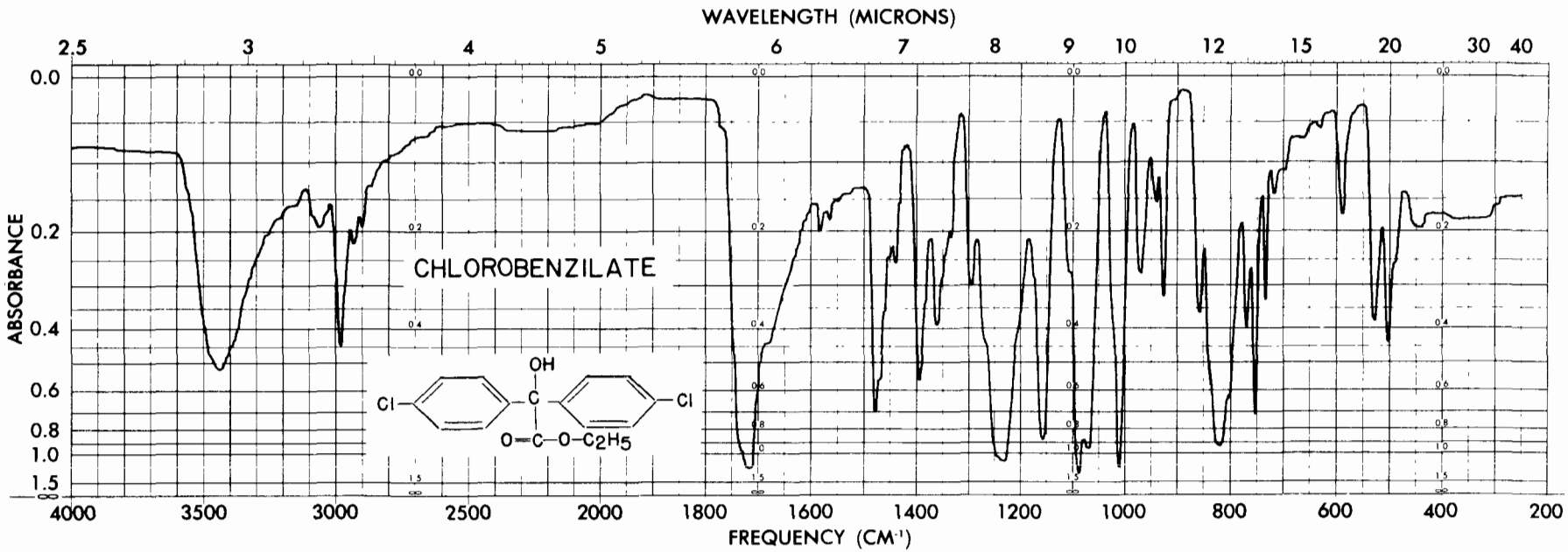

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
CHLORDENE
Cl
C
CH
CCl2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

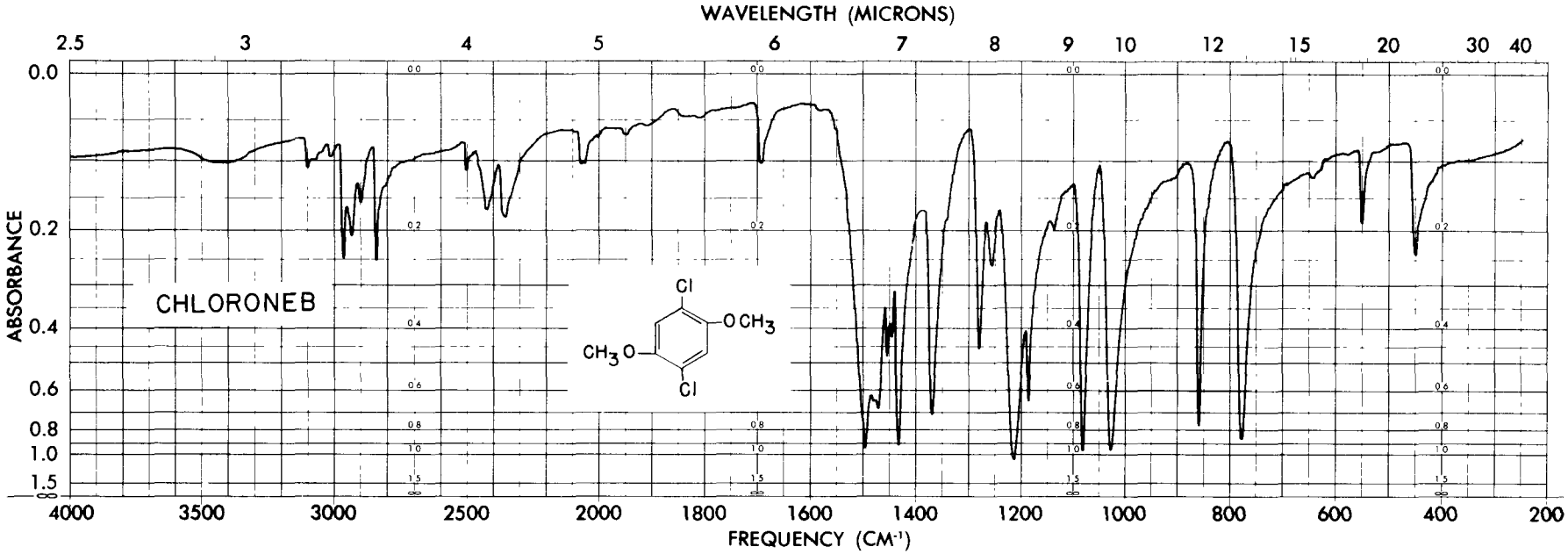

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
CHLORDIMEFORM
Cl
N=C-N
H
CH3
CH3
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

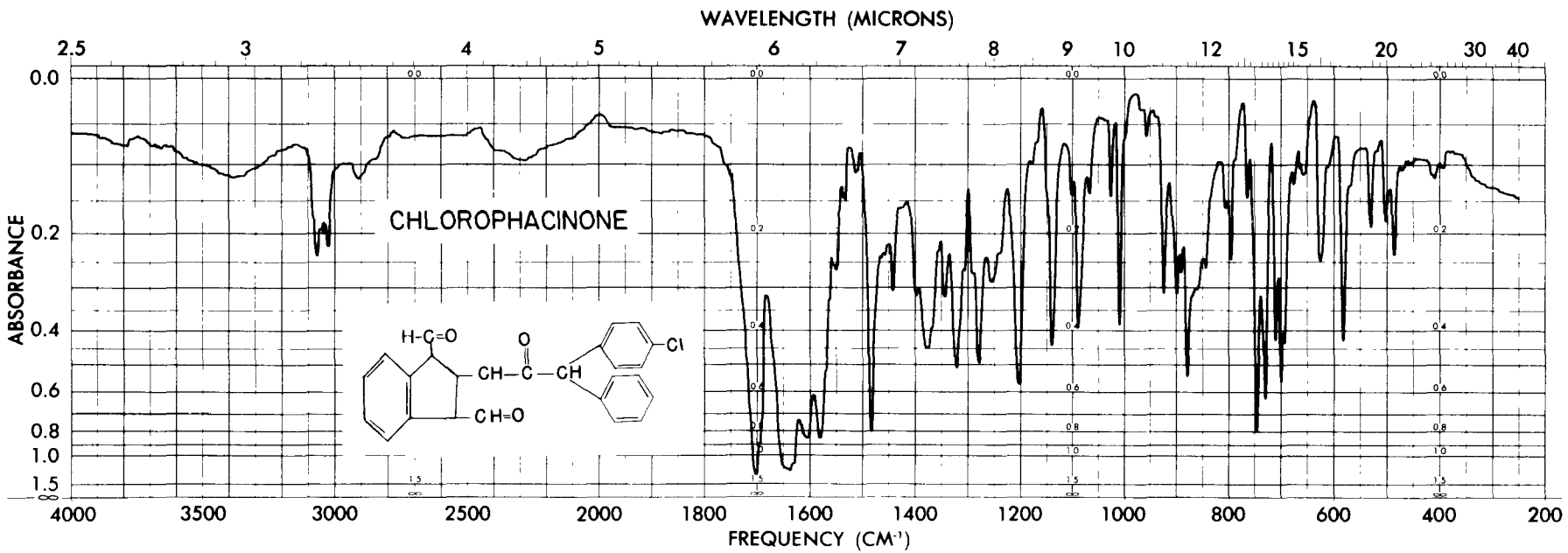

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CHLORFENVINPHOS
C_2H_5-O
O
P-O-C-CH-Cl
C_2H_5-O
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

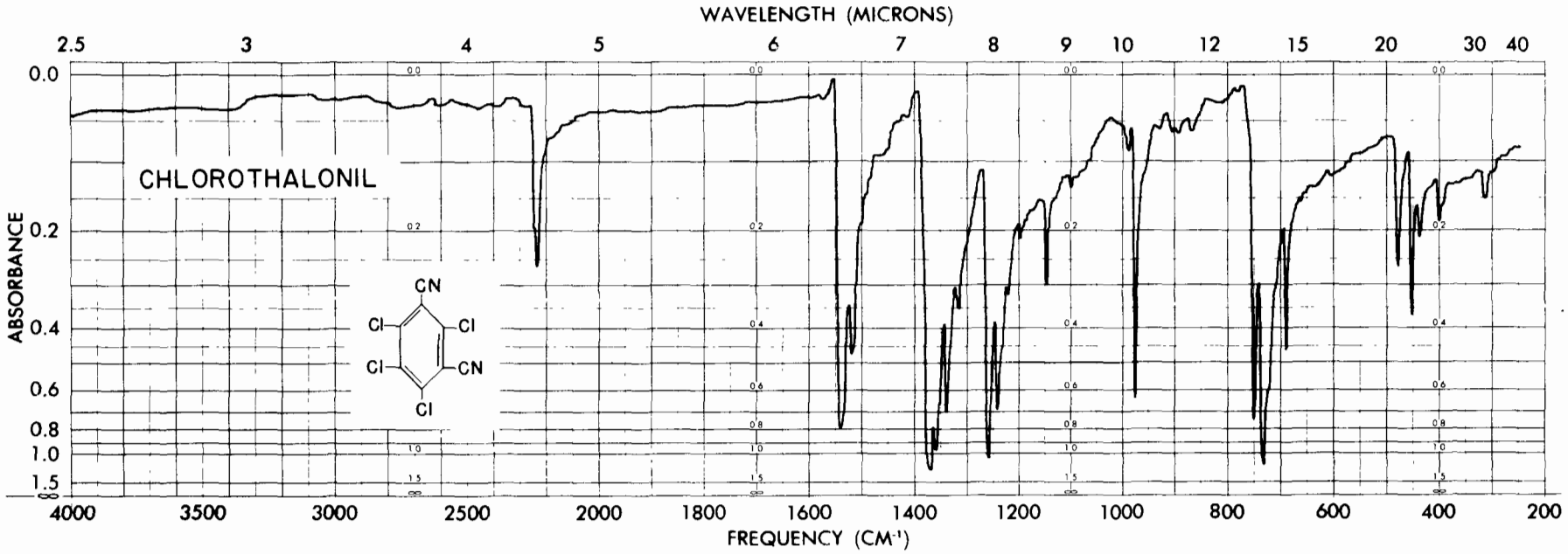

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CHLORFLURECOL
Cl
OH
C-O-CH_3
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

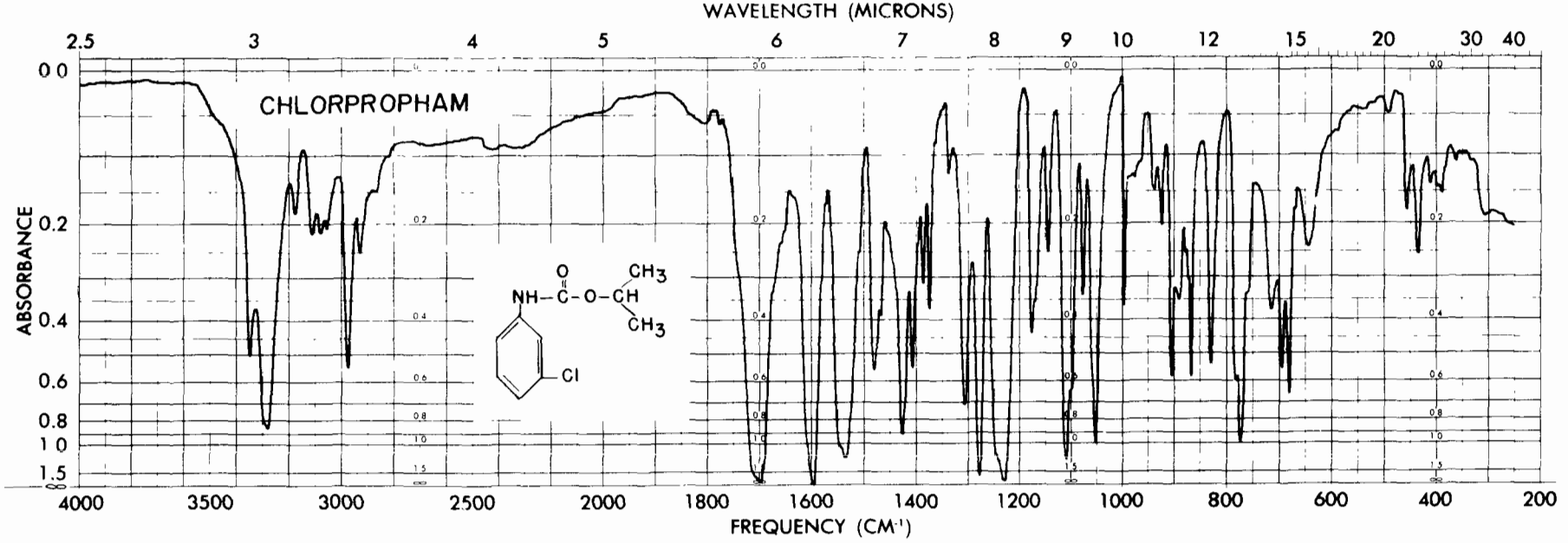

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
CHLORMEQUAT
CHLORIDE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
Cl-CH2-CH2-N(CH3)3 Cl⁻
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

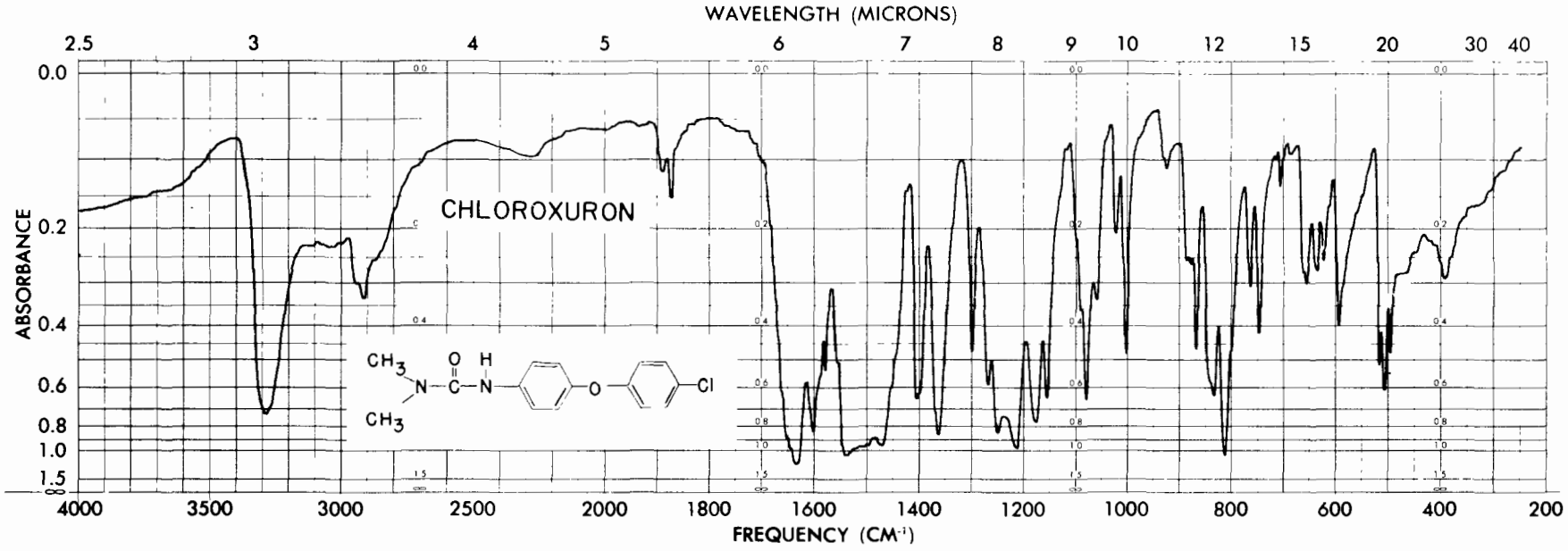

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
CHLOROBENZILATE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
OH
Cl
C
Cl
O=C-O-C2H5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

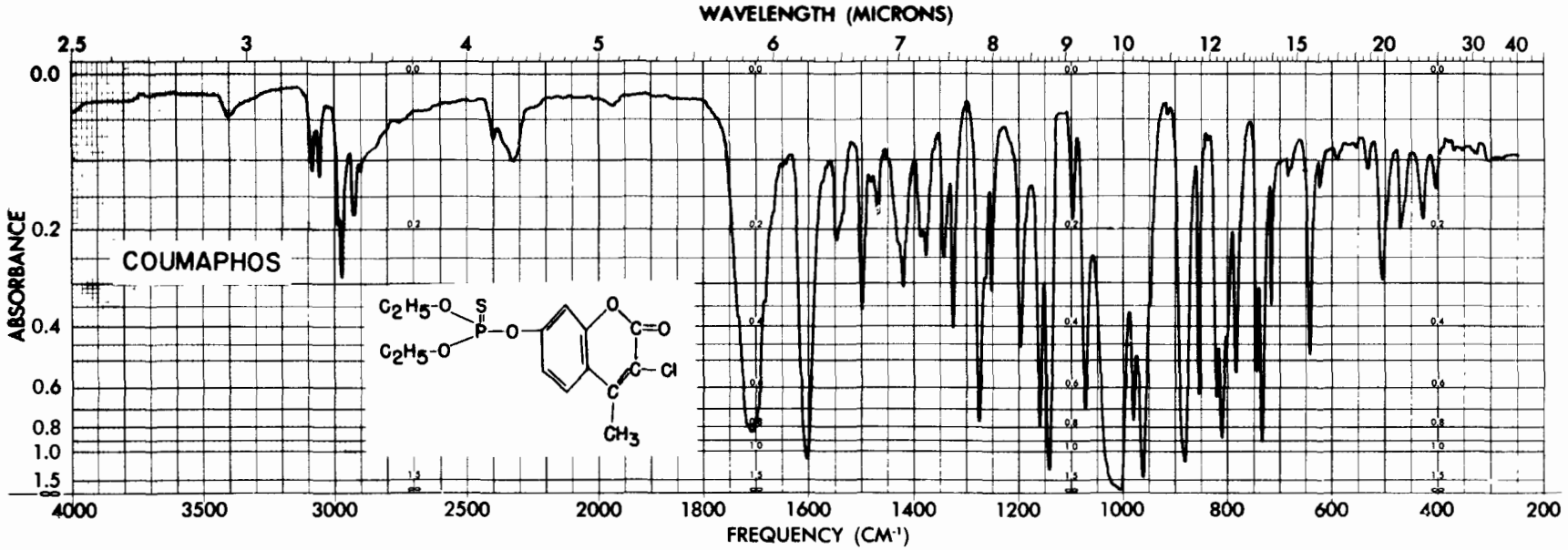

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
CHLORONEB
Cl
OCH3
CH3O
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

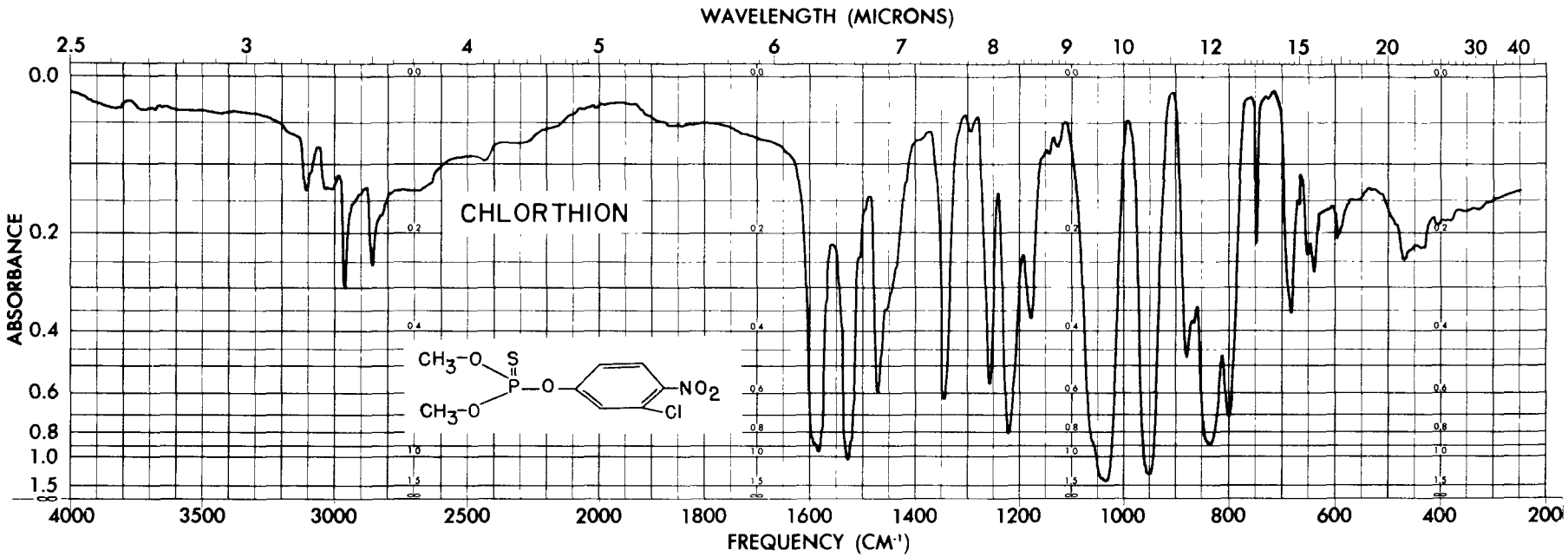

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
CHLOROPHACINONE
H-C=O
O
Cl
CH—C—CH
CH=O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

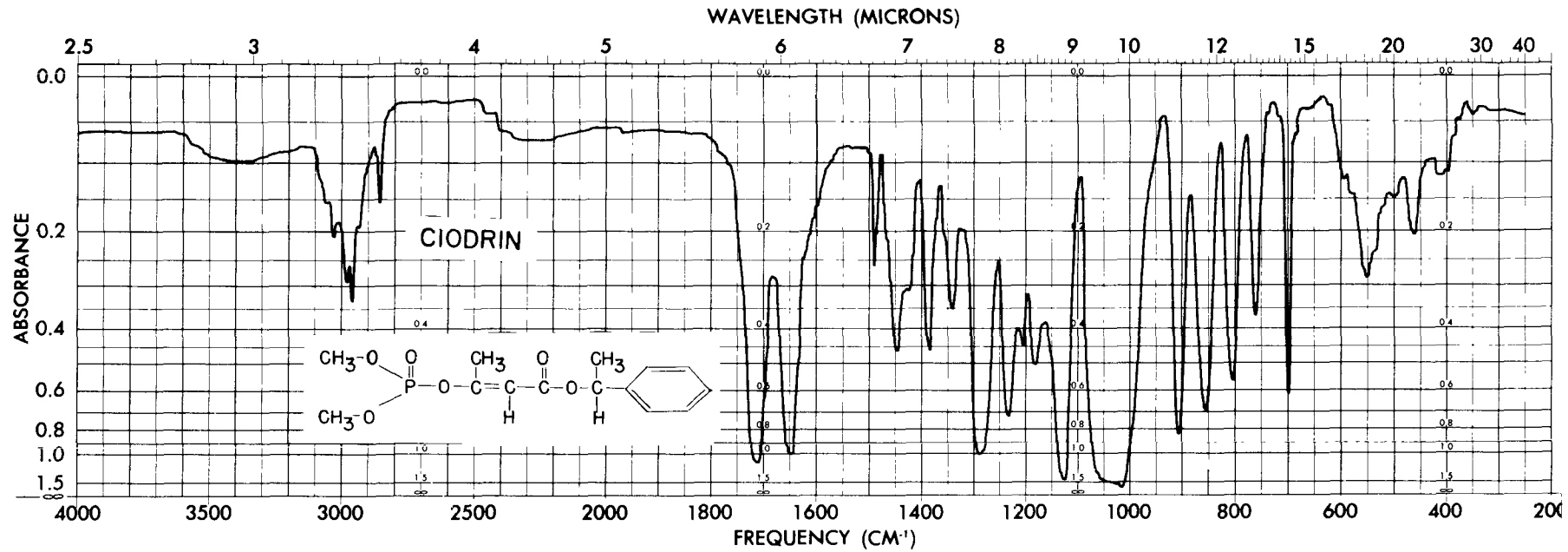

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
CHLOROTHALONIL
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CN
Cl
Cl
Cl
CN
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

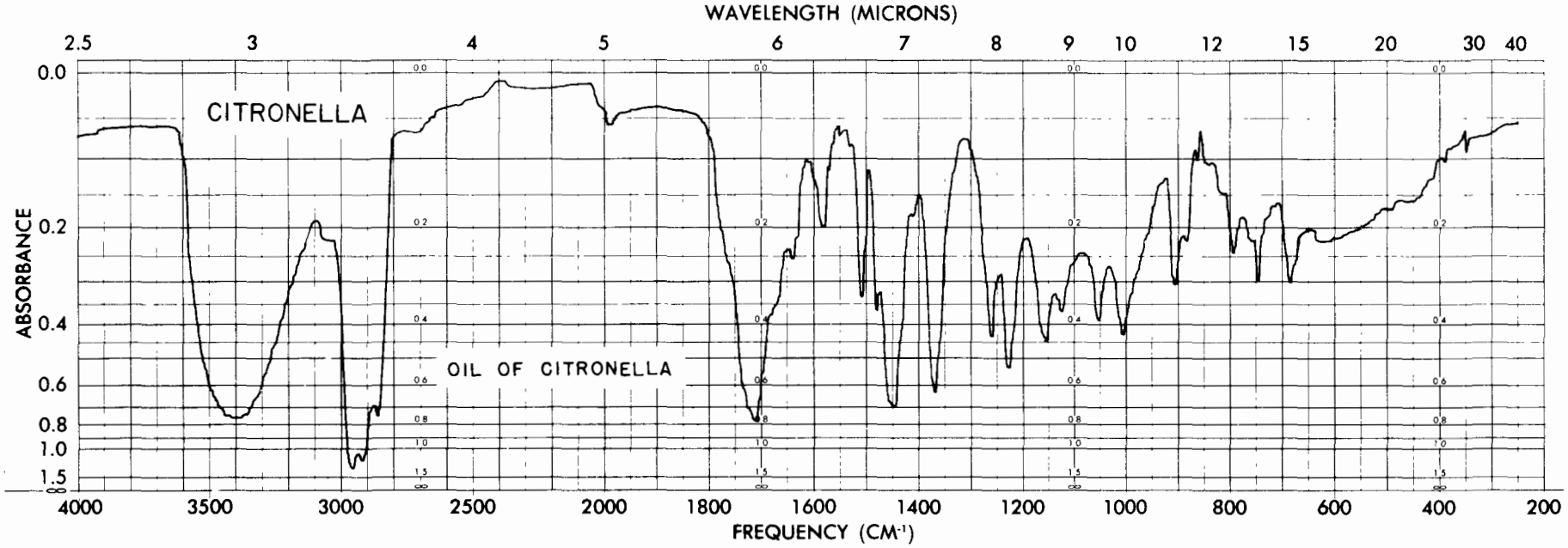

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
CHLORPROPHAM
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
O
NH–C–O–CH
CH3
CH3
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

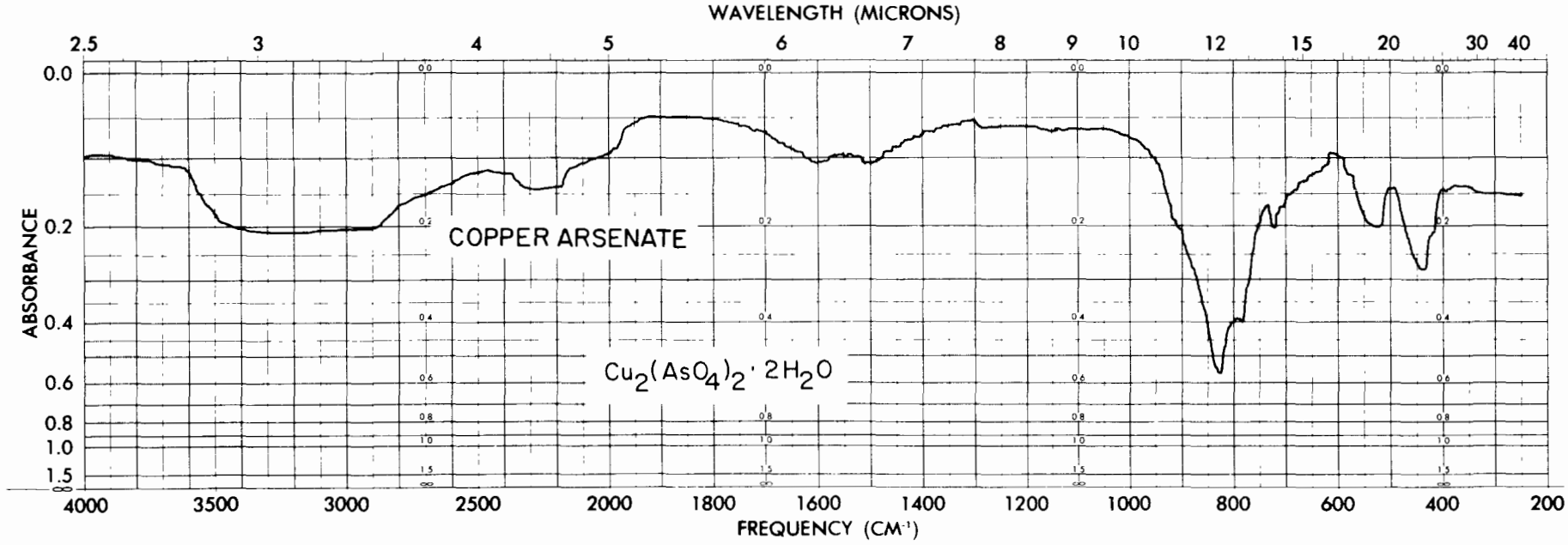

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CHLOROXURON
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

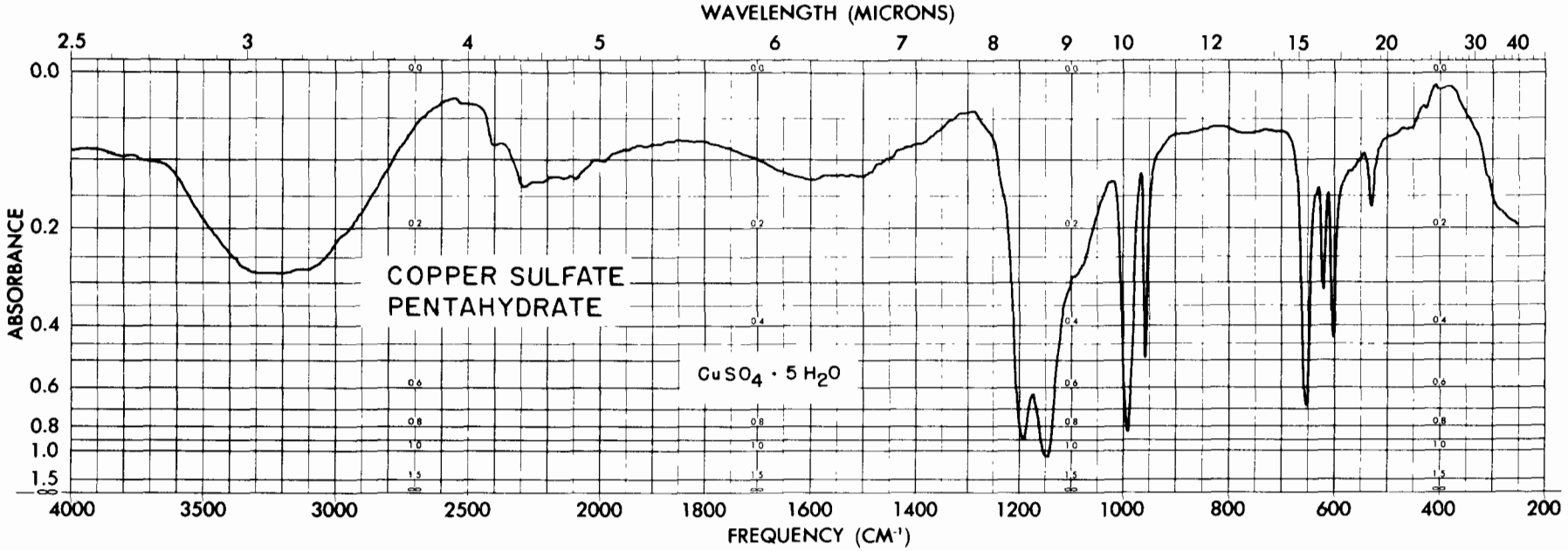

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
COUMAPHOS
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

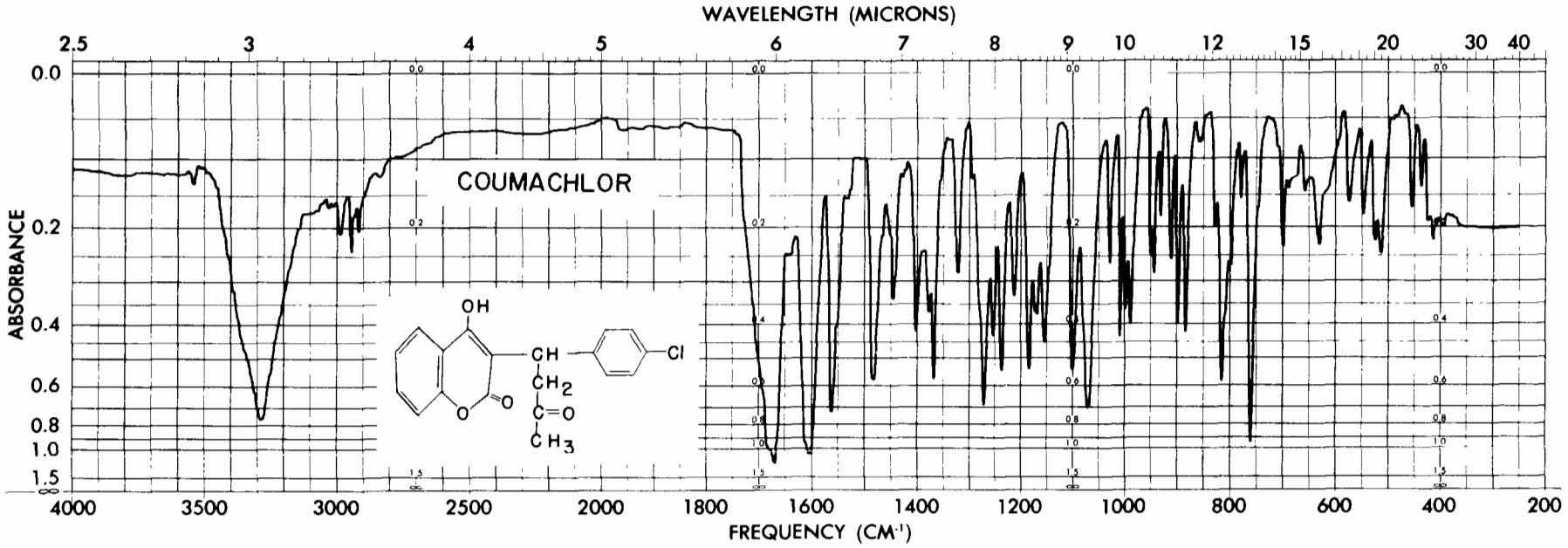

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CHLORTHION
CH_3-O
S
P
O
CH_3-O
NO_2
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

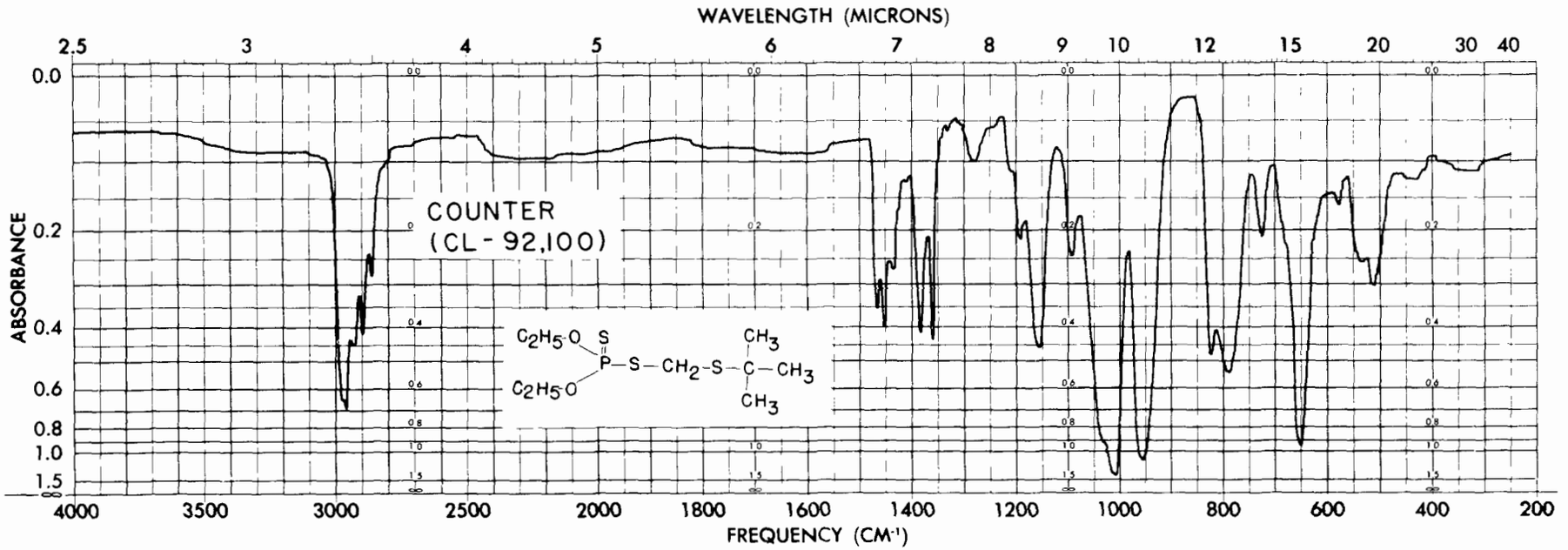

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CIODRIN
CH_3-O
O
P
O
CH_3-O
CH_3
C
H
O
C
O
CH_3
C
H
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

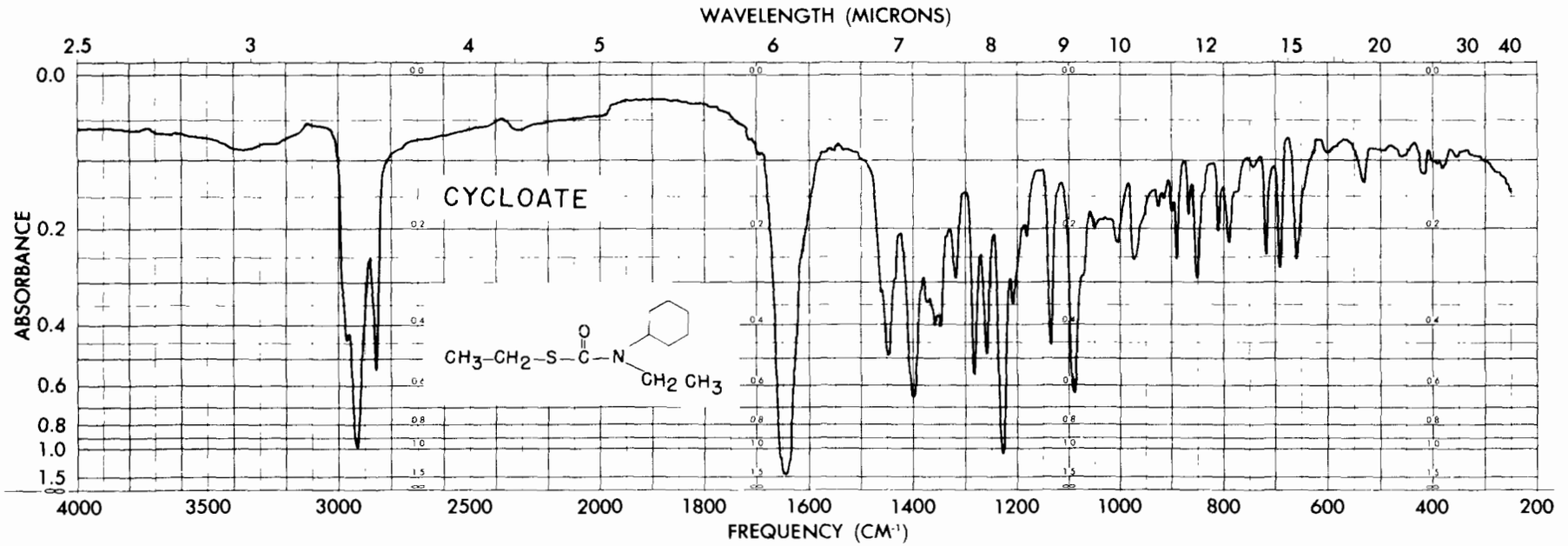

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
CITRONELLA
OIL OF CITRONELLA
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

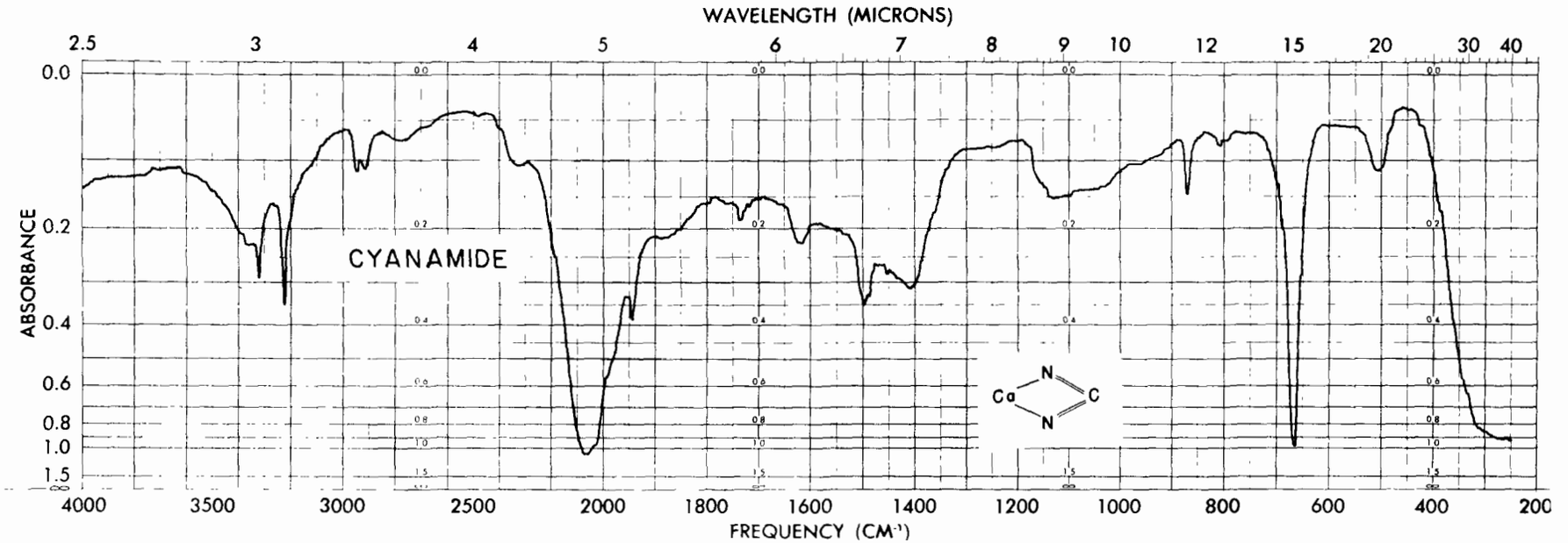

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
COPPER ARSENATE
Cu2(AsO4)2·2H2O
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

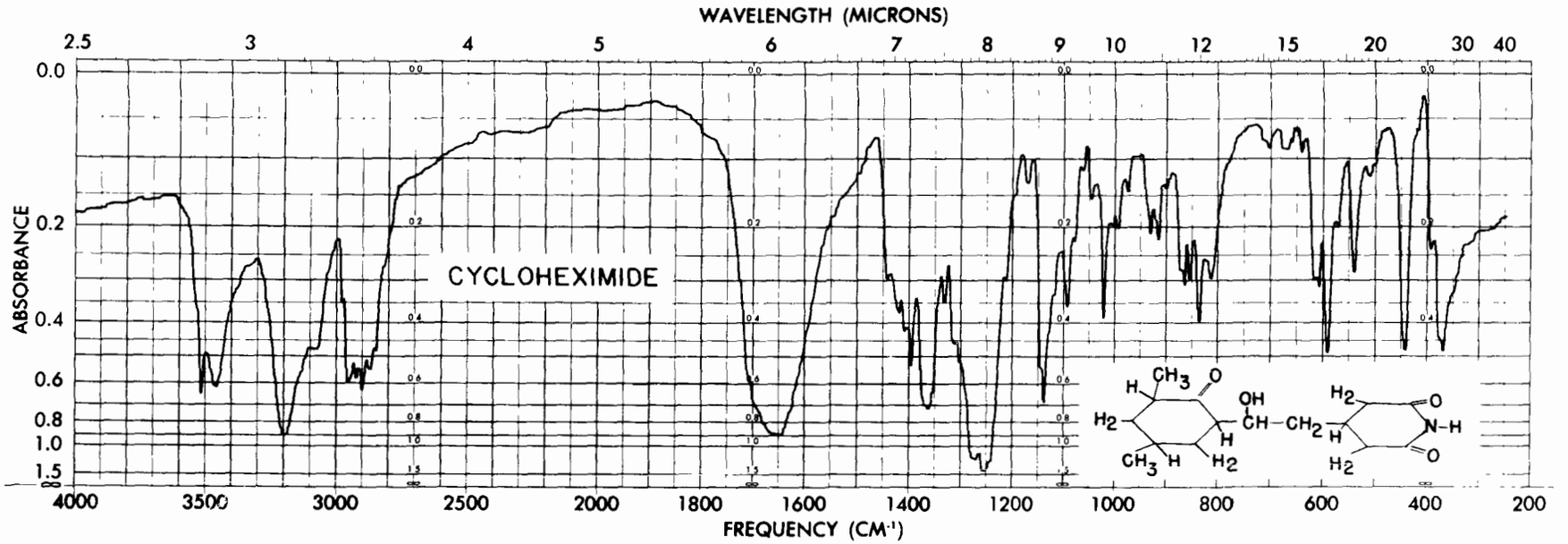

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
COPPER SULFATE
PENTAHYDRATE
$CuSO_4 \cdot 5H_2O$
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

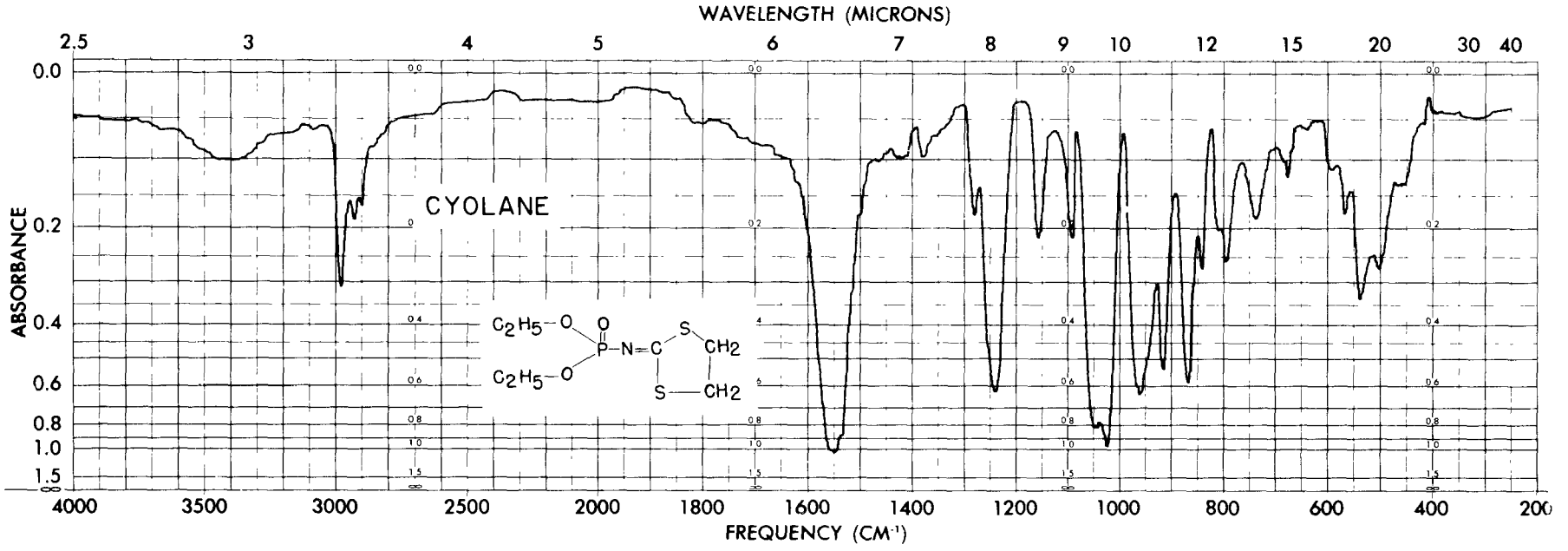

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
COUMACHLOR
OH
CH
CH_2
C=O
CH_3
Cl
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

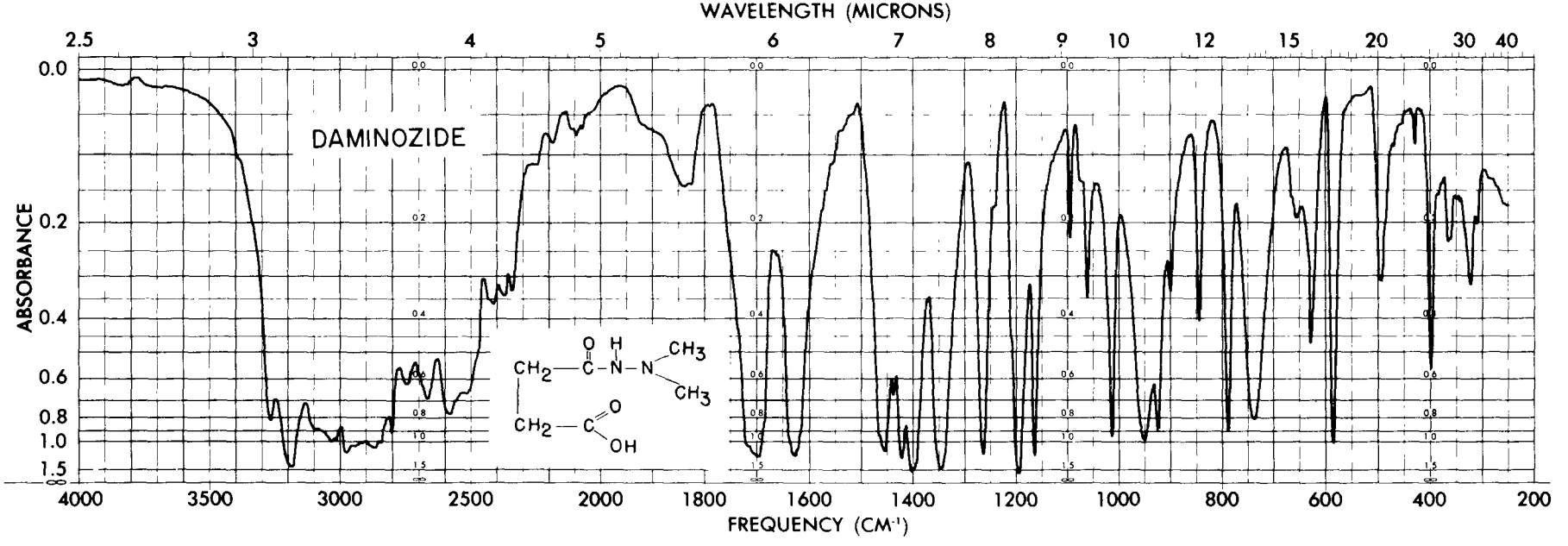

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
COUNTER
(CL-92,100)
C_2H_5O S
P–S–CH_2–S–C–CH_3
C_2H_5O
CH_3
CH_3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

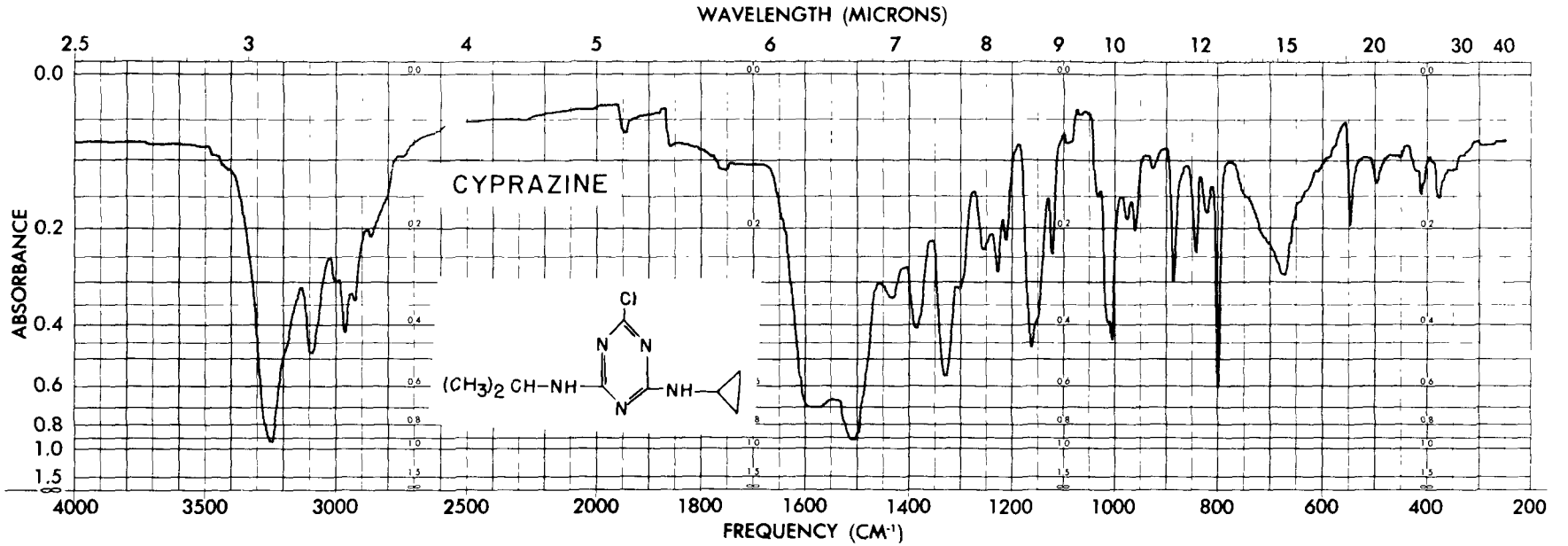

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CYCLOATE
O
CH_3–CH_2–S–C–N
CH_2 CH_3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

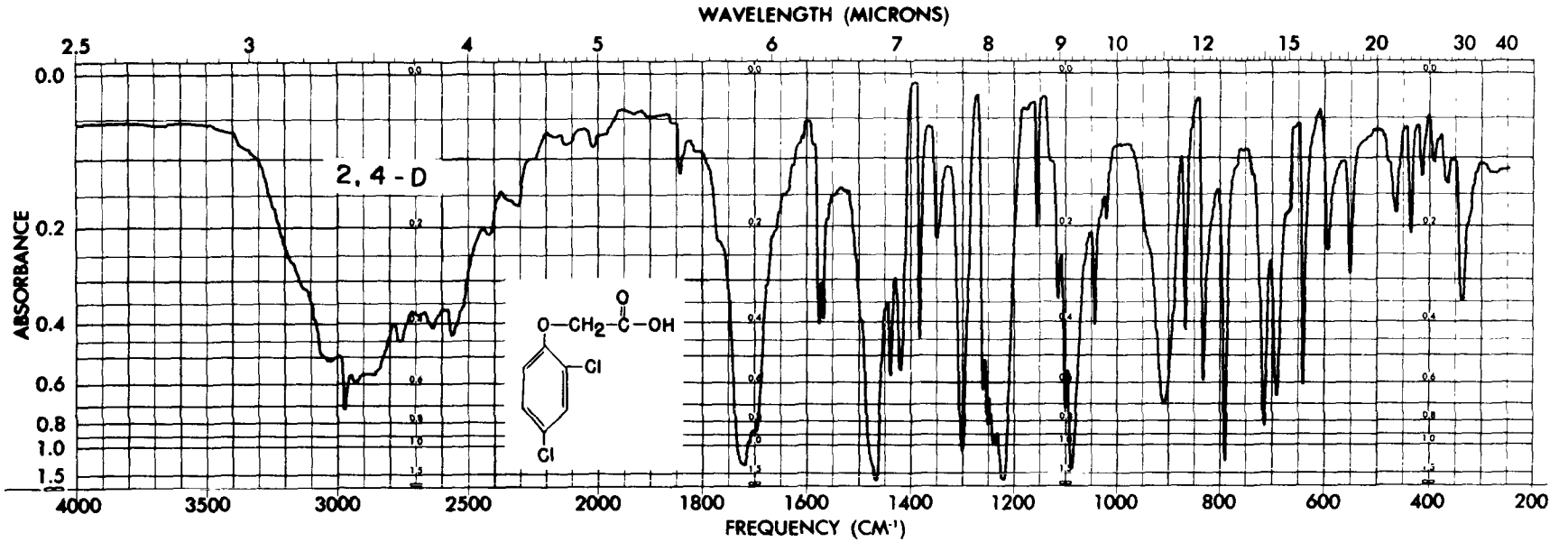

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CYANAMIDE
Ca
N
C
N
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

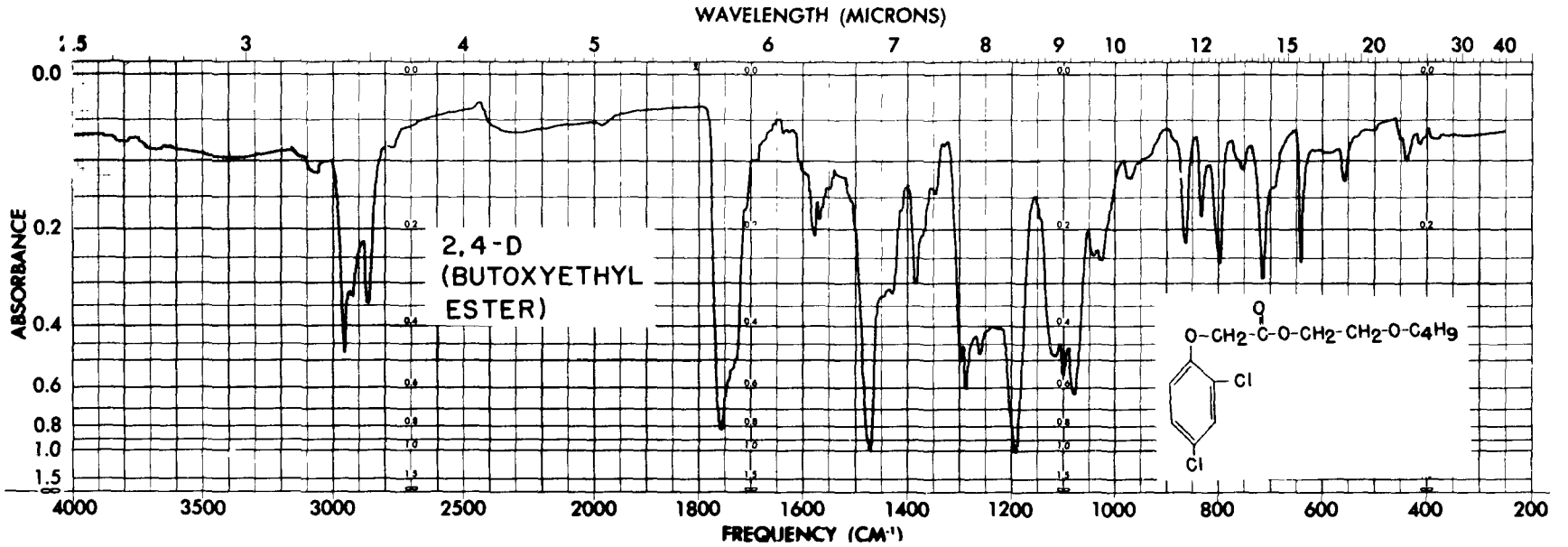

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CYCLOHEXIMIDE
H
CH3
O
OH
H2
CH
CH2
H
CH3
H
H2
H2
O
N-H
H
O
H2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

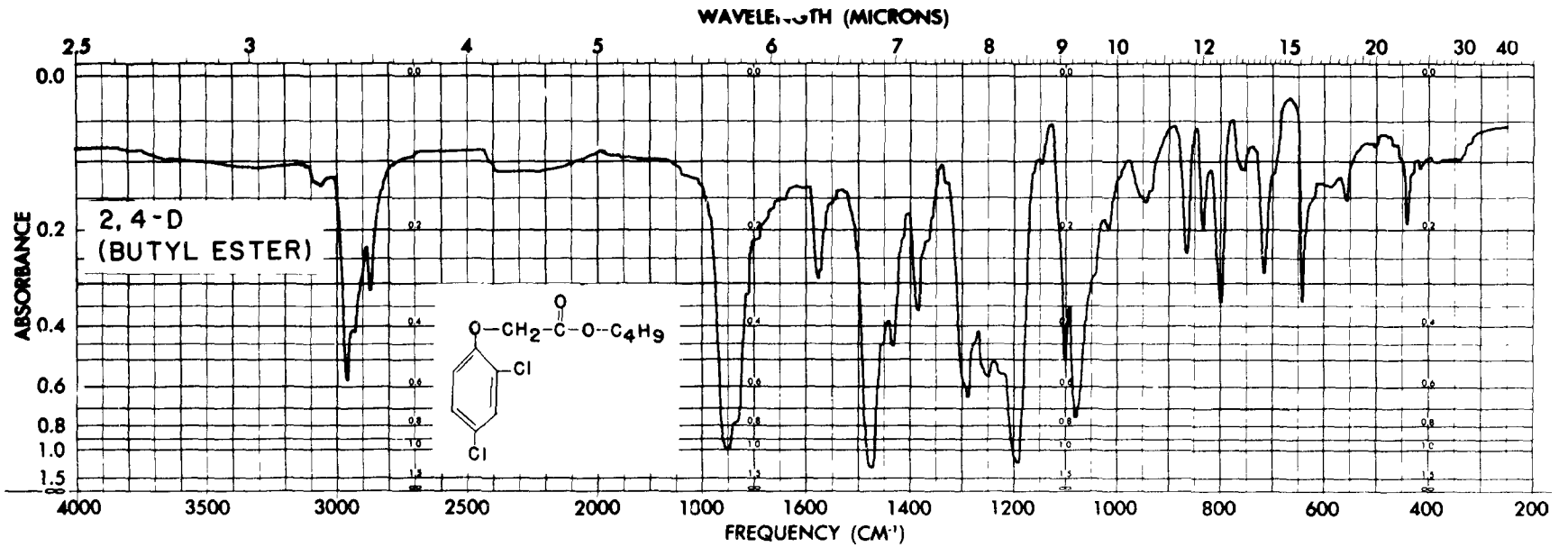

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CYOLANE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

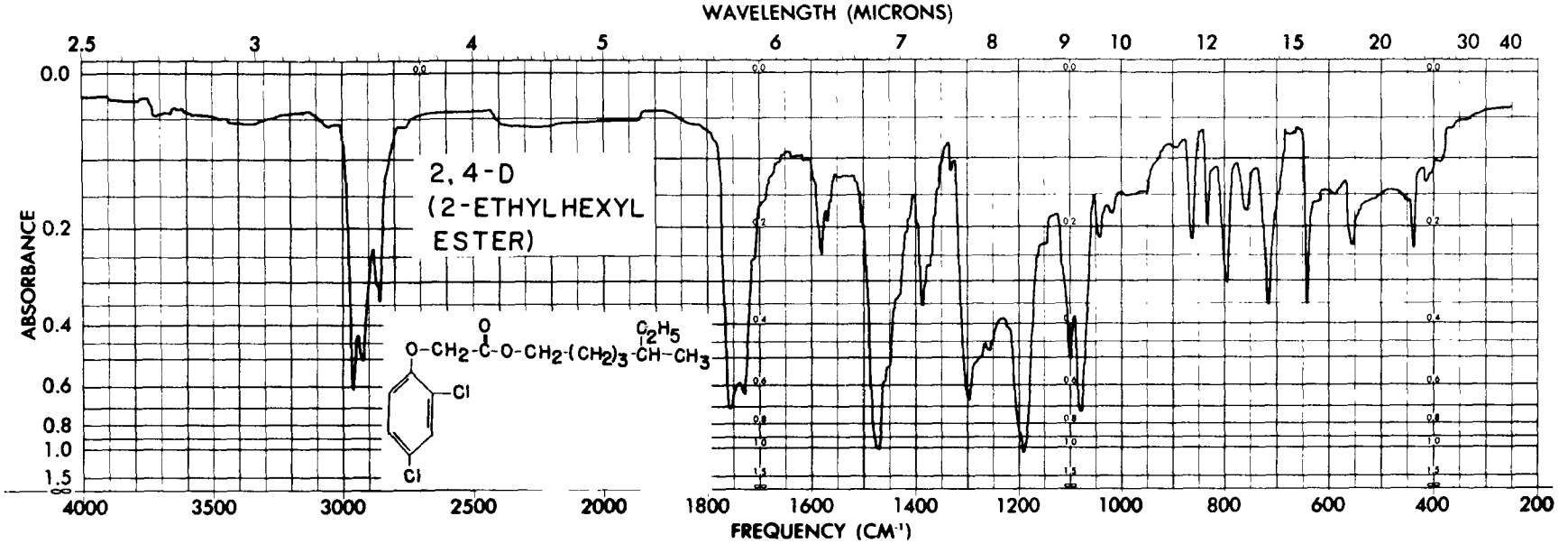

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DAMINOZIDE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

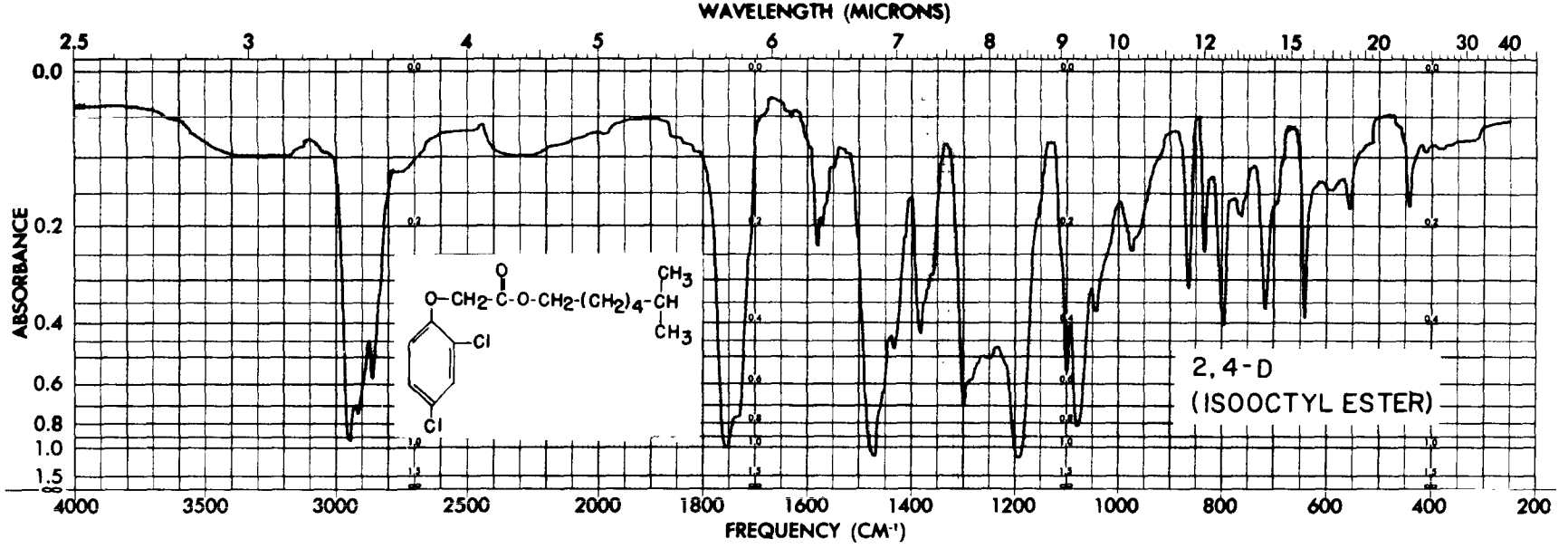

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CYPRAZINE
Cl
N
N
(CH3)2 CH–NH
NH
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

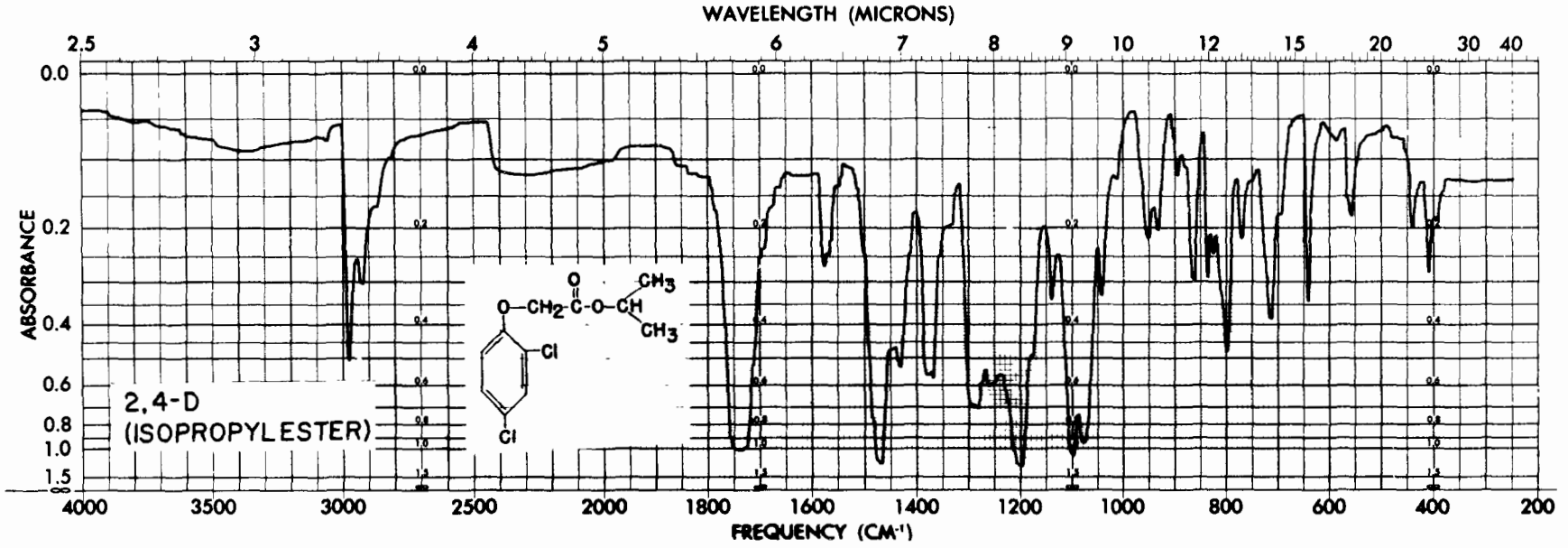

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
2,4-D
O
O–CH2–C–OH
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

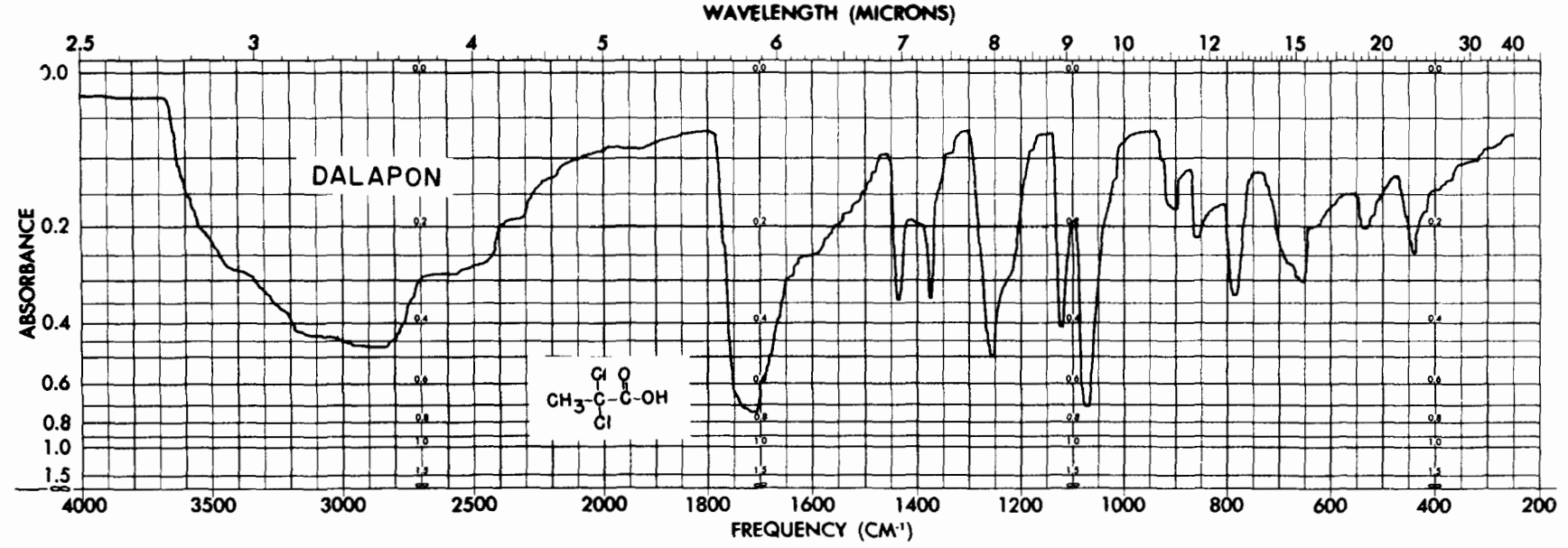

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
2,4-D
(BUTOXYETHYL
ESTER)
O
O-CH2-C-O-CH2-CH2-O-C4H9
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

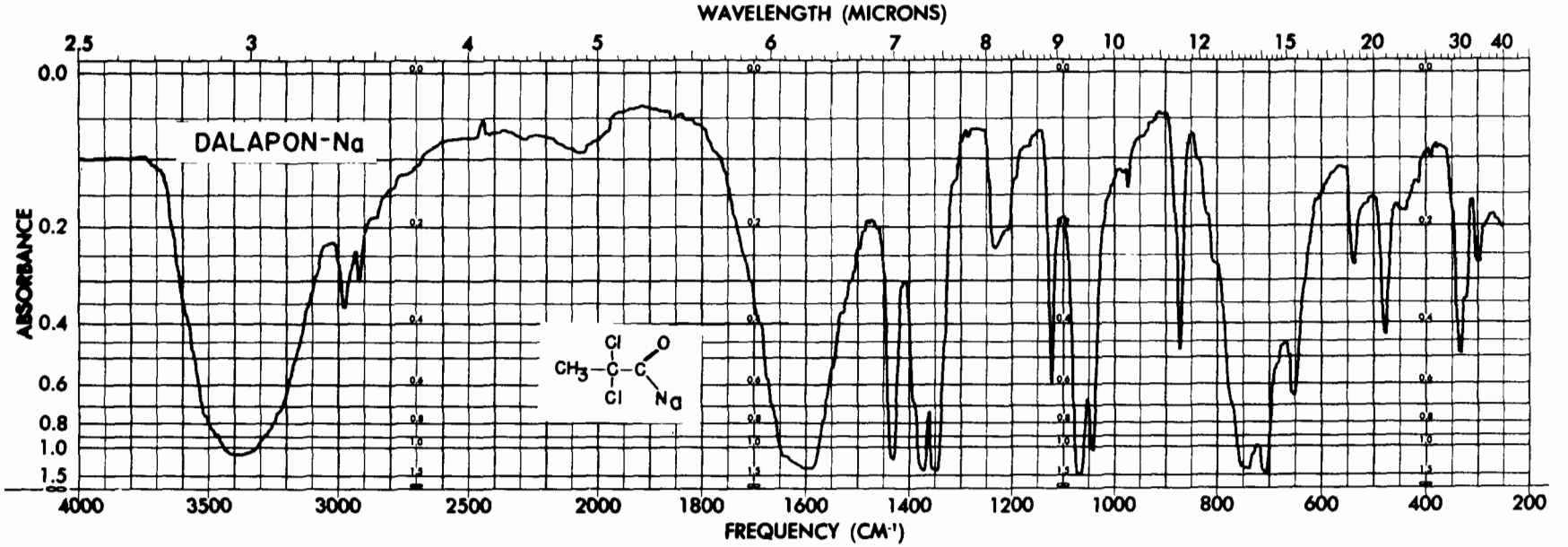

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
2,4-D
(BUTYL ESTER)
O
O-CH2-C-O-C4H9
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

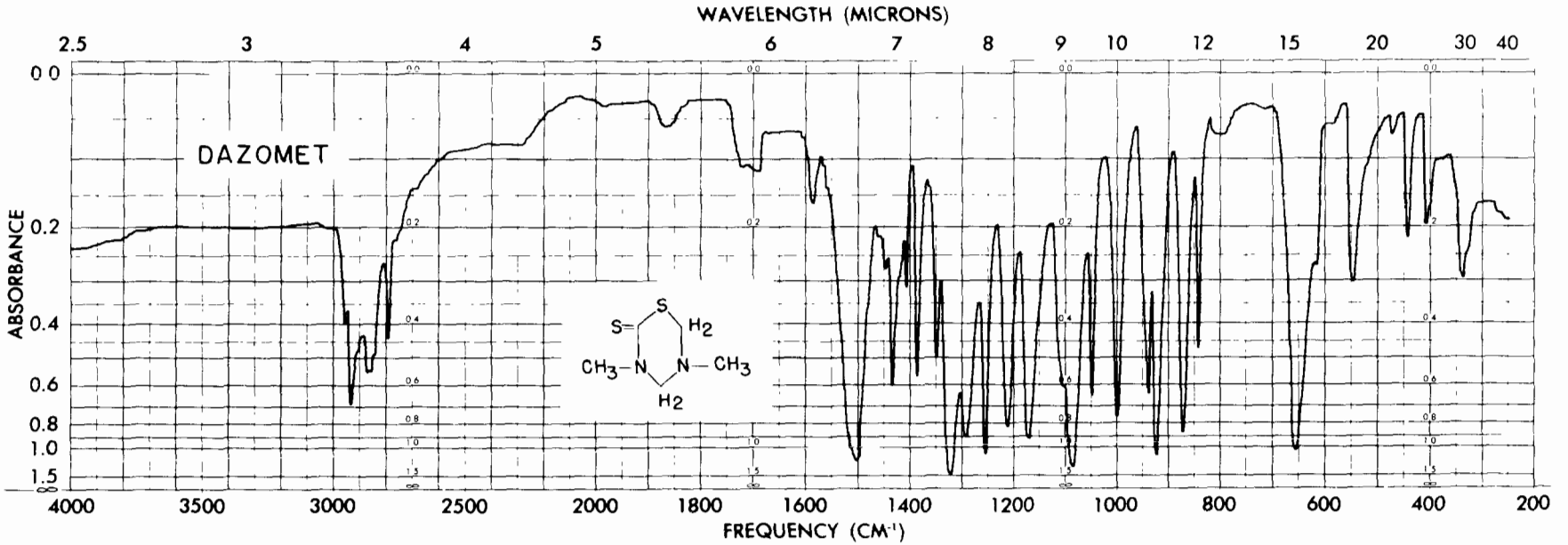

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
2, 4-D
(2-ETHYL HEXYL
ESTER)
O-CH2-C-O-CH2-(CH2)3-CH-CH3
C2H5
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

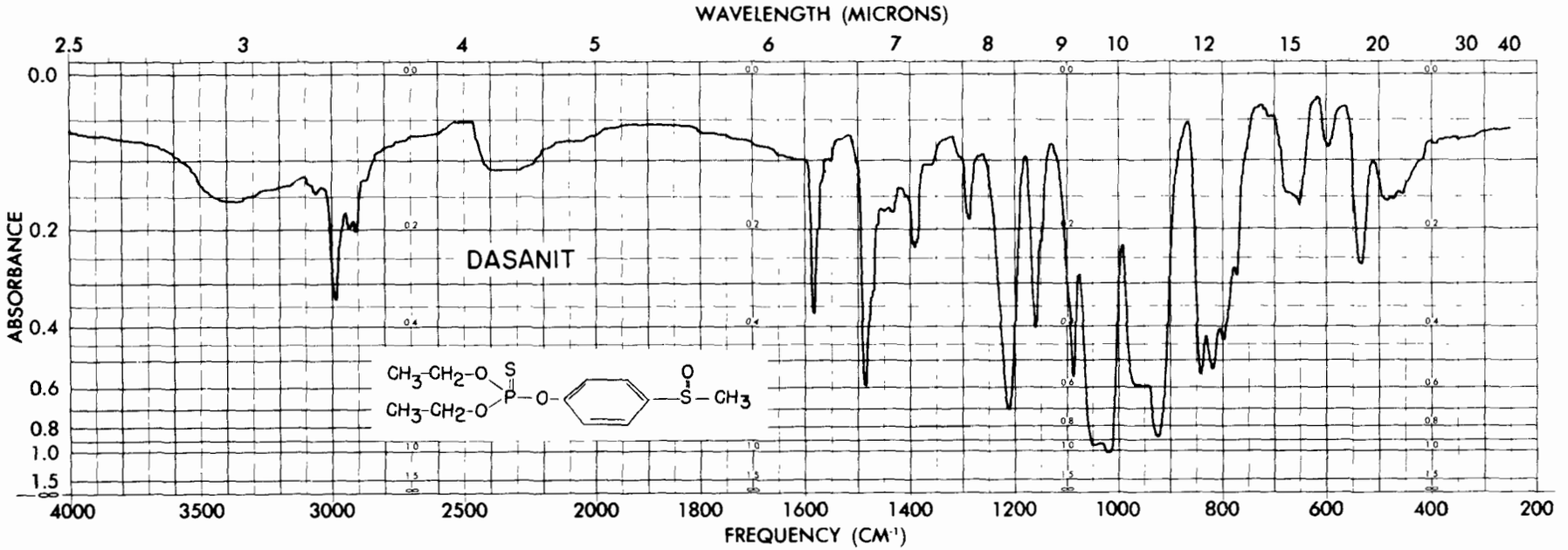

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
O-CH2-C-O-CH2-(CH2)4-CH
CH3
CH3
Cl
Cl
2, 4-D
(ISOOCTYL ESTER)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

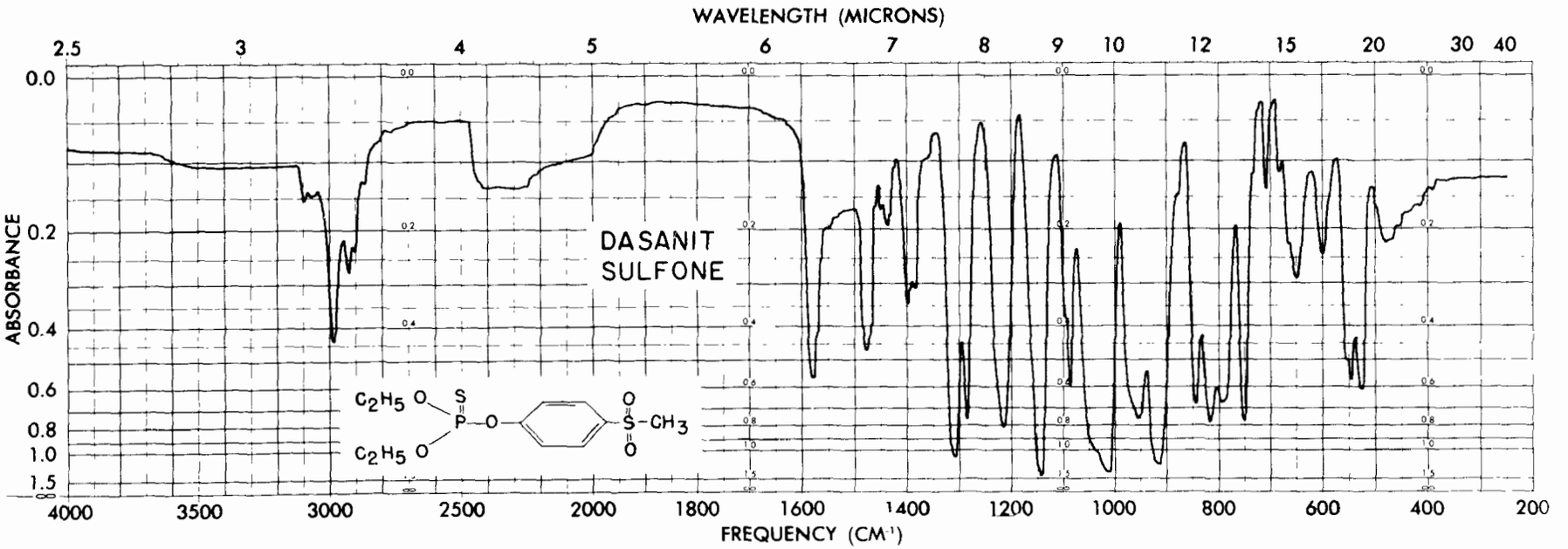

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
2,4-D
(ISOPROPYLESTER)
O
O—CH2-C-O-CH
CH3
CH3
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

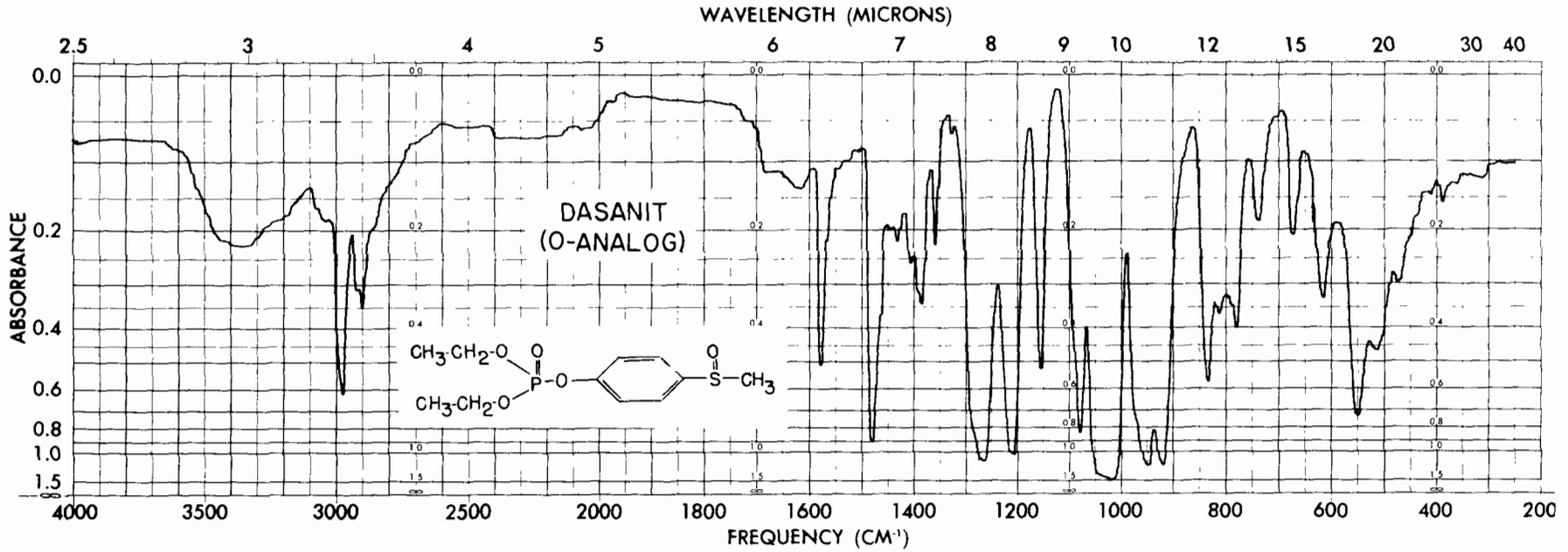

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DALAPON
Cl O
CH3-C-C-OH
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

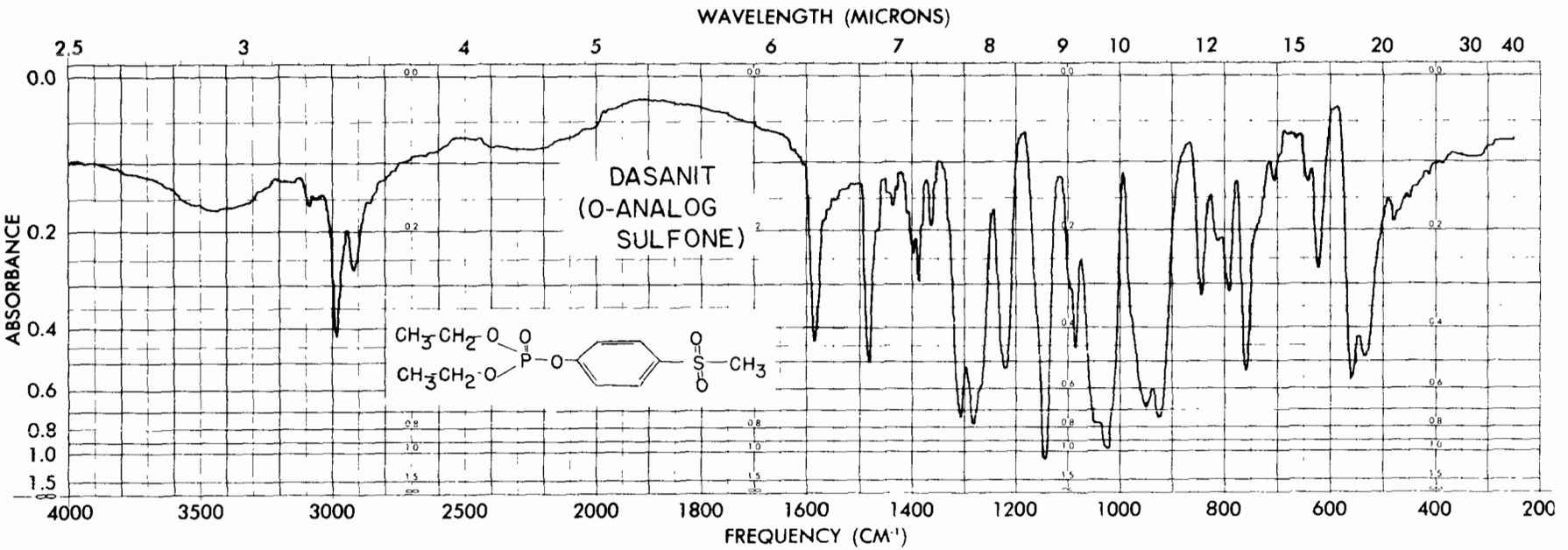

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
DALAPON-Na
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
Cl
O
CH3—C—C
Cl
Na
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

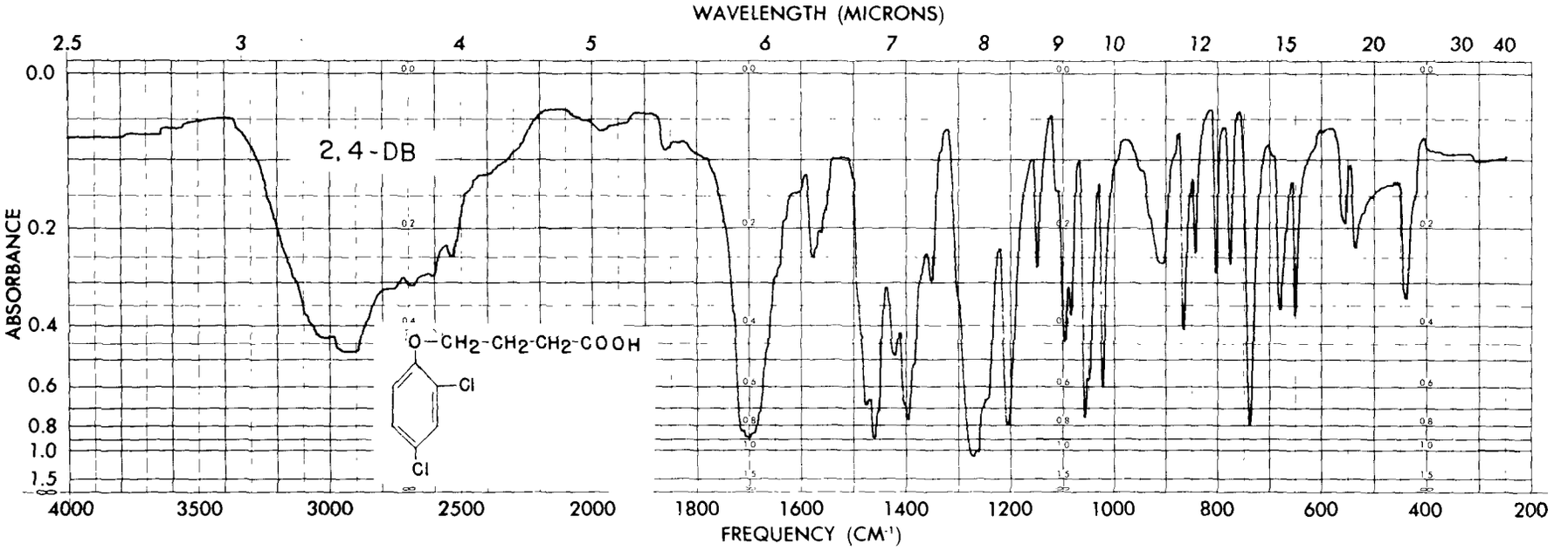

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
DAZOMET
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
S
S=
H2
CH3—N
N—CH3
H2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

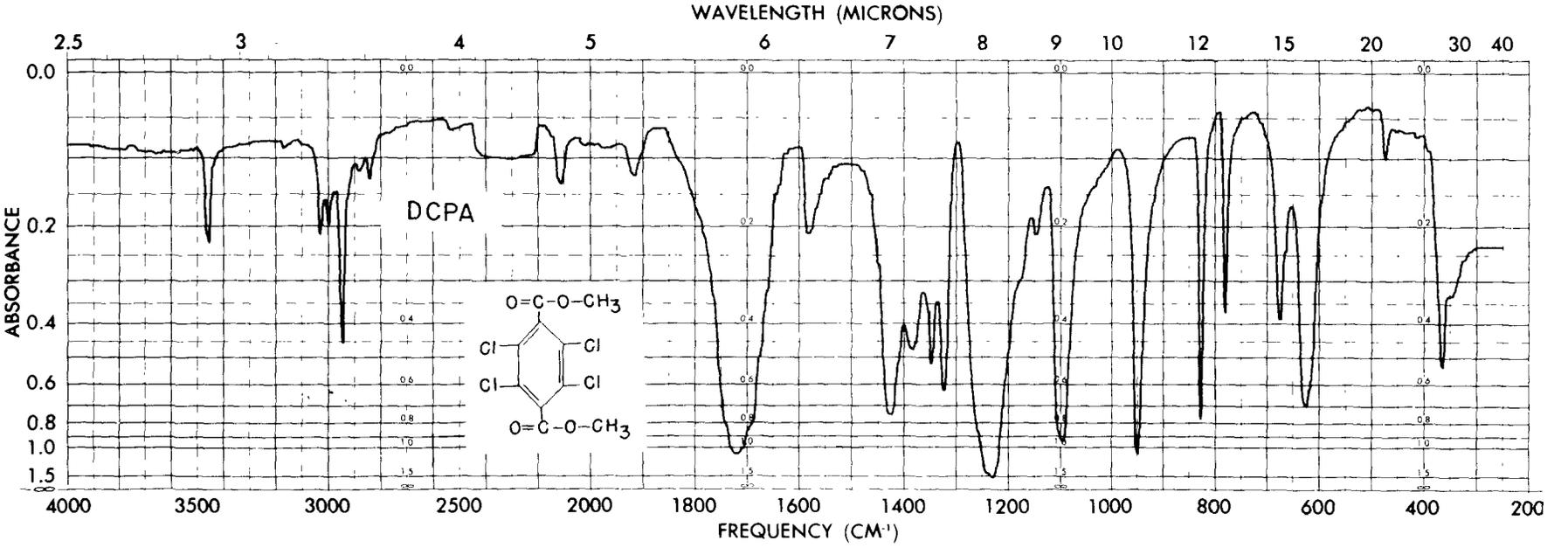

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
DASANIT
CH3-CH2-O
CH3-CH2-O
S
P
O
O
S
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

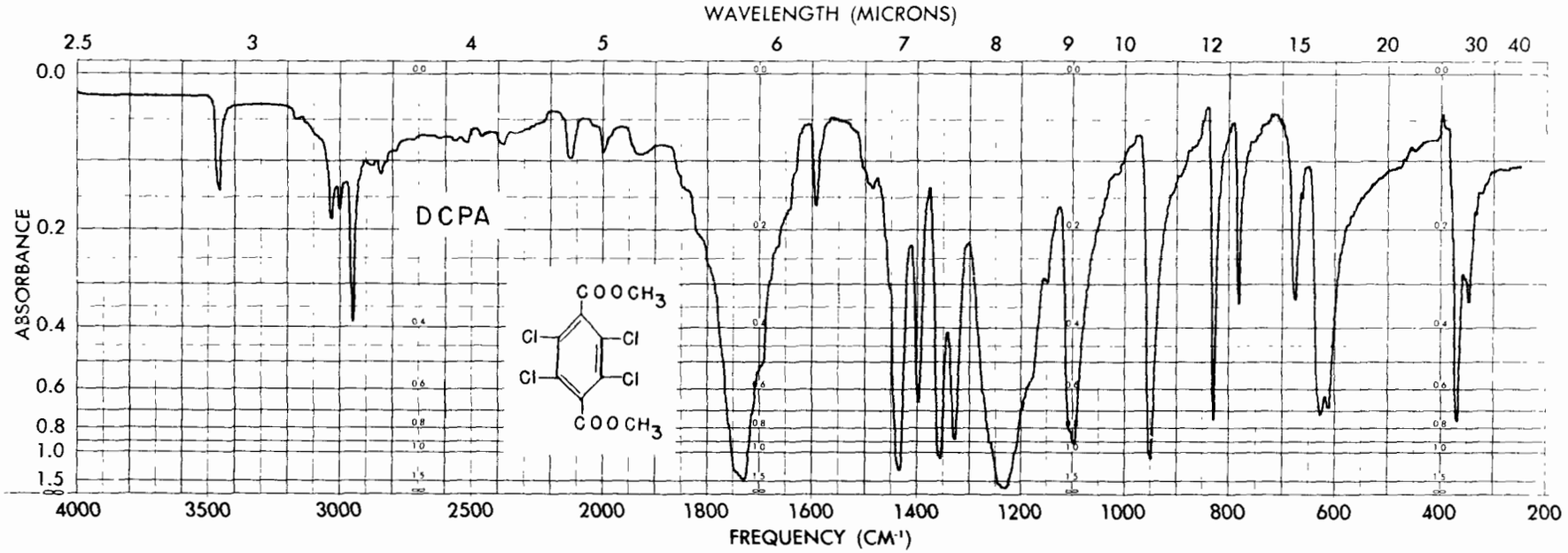

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
DASANIT
SULFONE
C2H5 O
C2H5 O
S
P
O
O
S
CH3
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

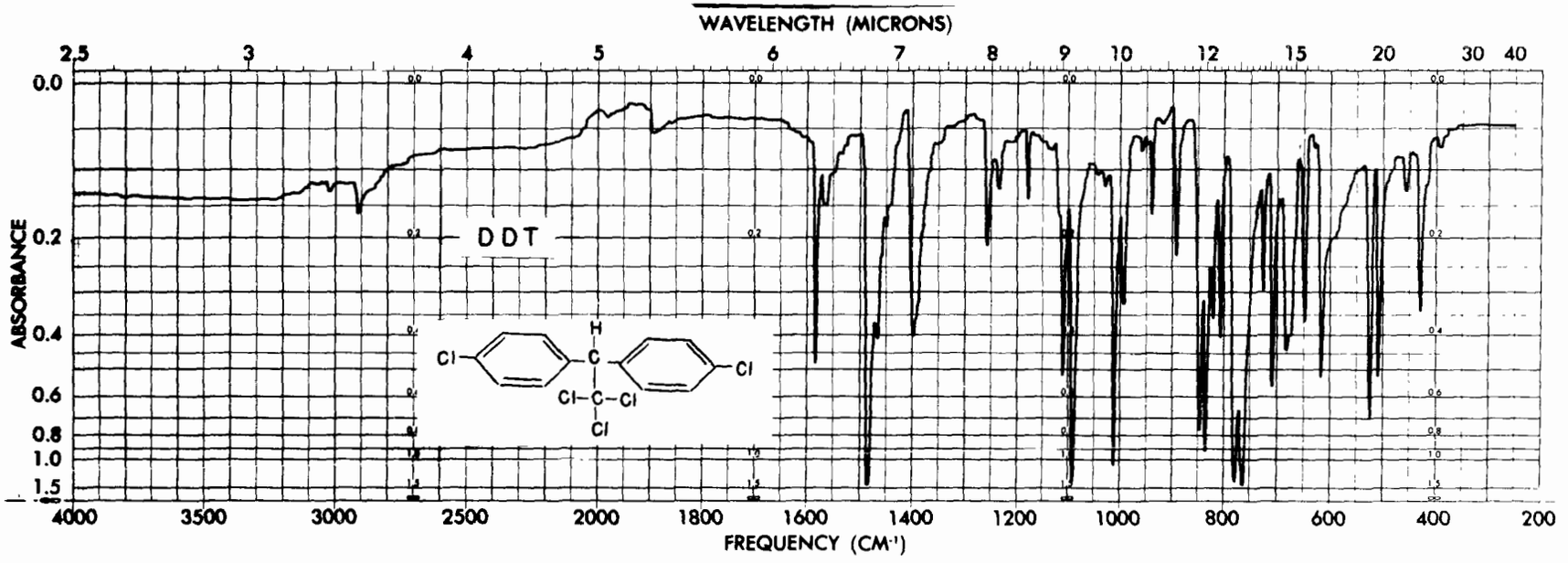

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DASANIT
(O-ANALOG)
CH3-CH2-O
CH3-CH2-O
P
O
S
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

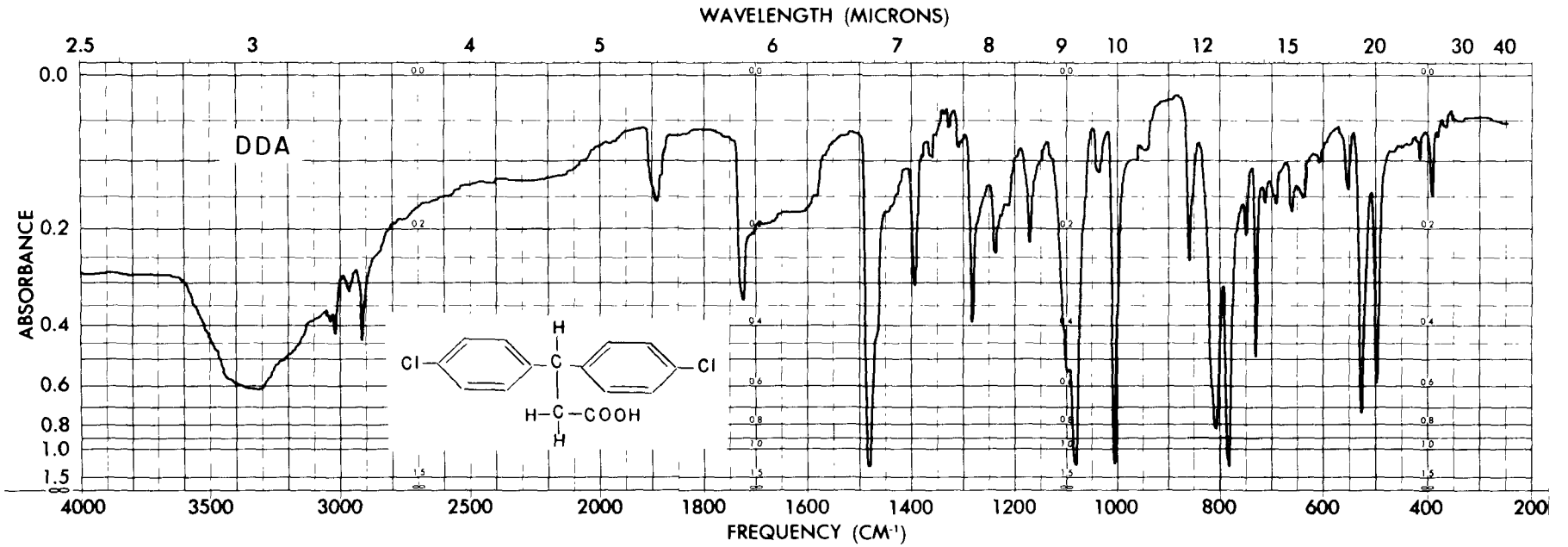

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DASANIT
(O-ANALOG
SULFONE)
CH3-CH2-O
CH3-CH2-O
P
O
S
O
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

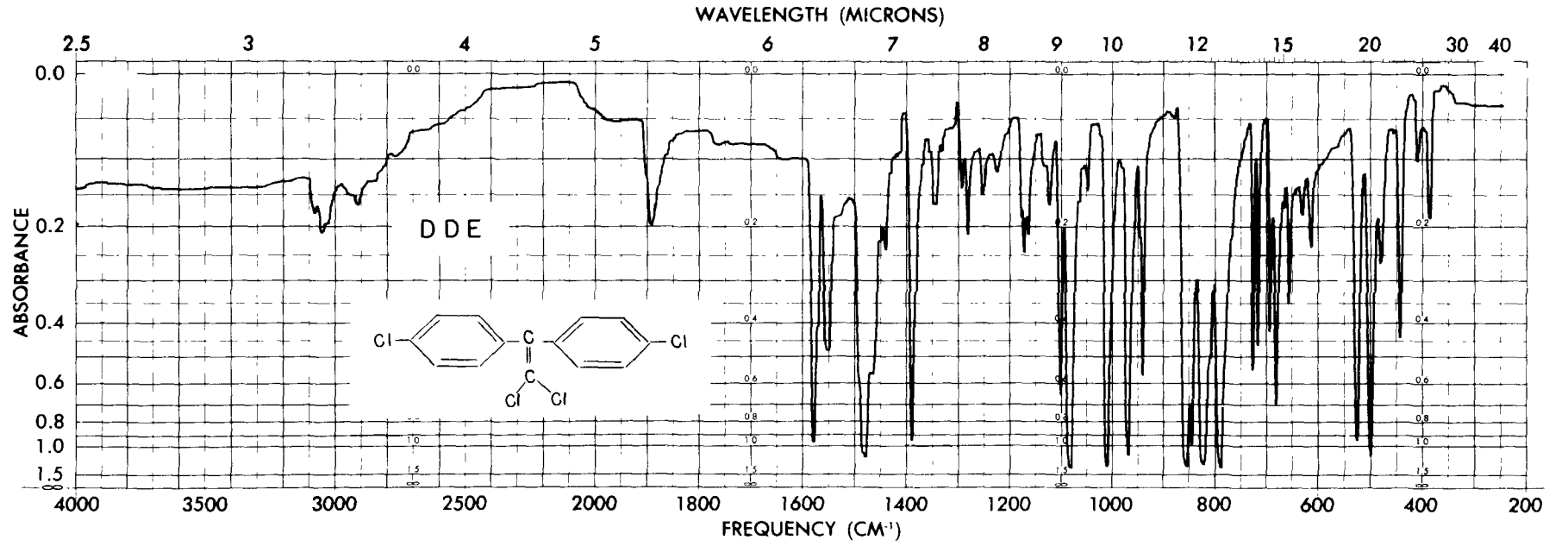

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
2,4-DB
O-CH2-CH2-CH2-COOH
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

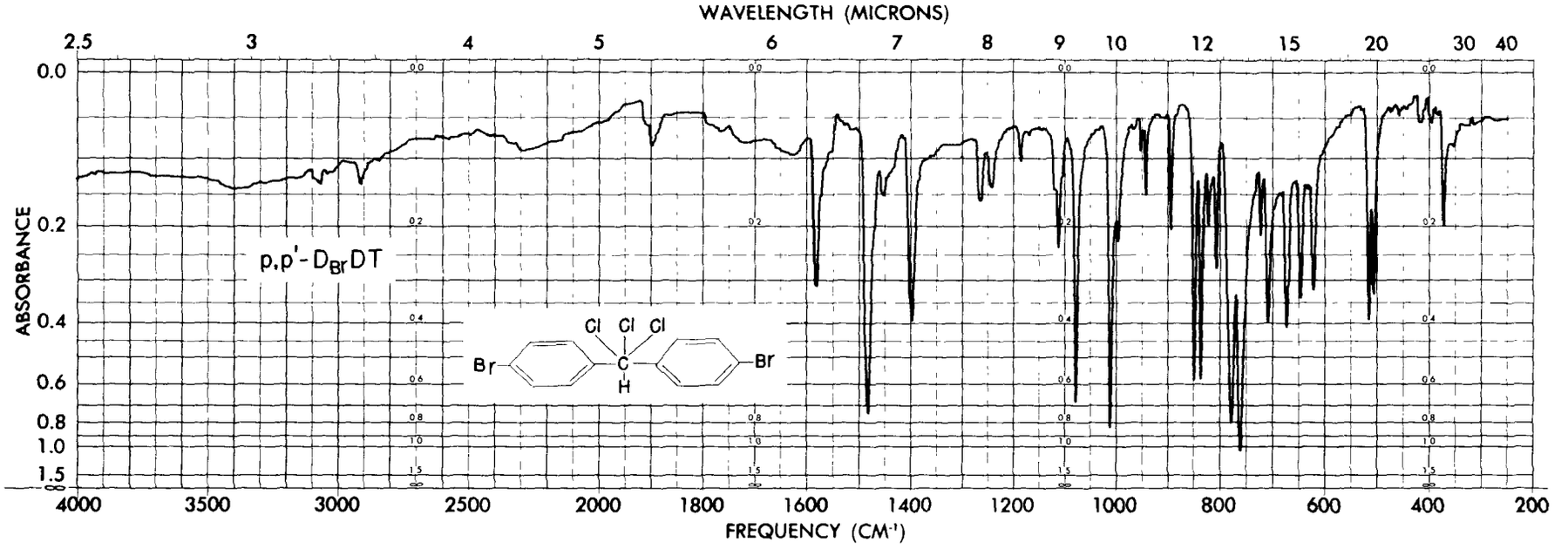

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DCPA
O=C-O-CH3
Cl
Cl
Cl
Cl
O=C-O-CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

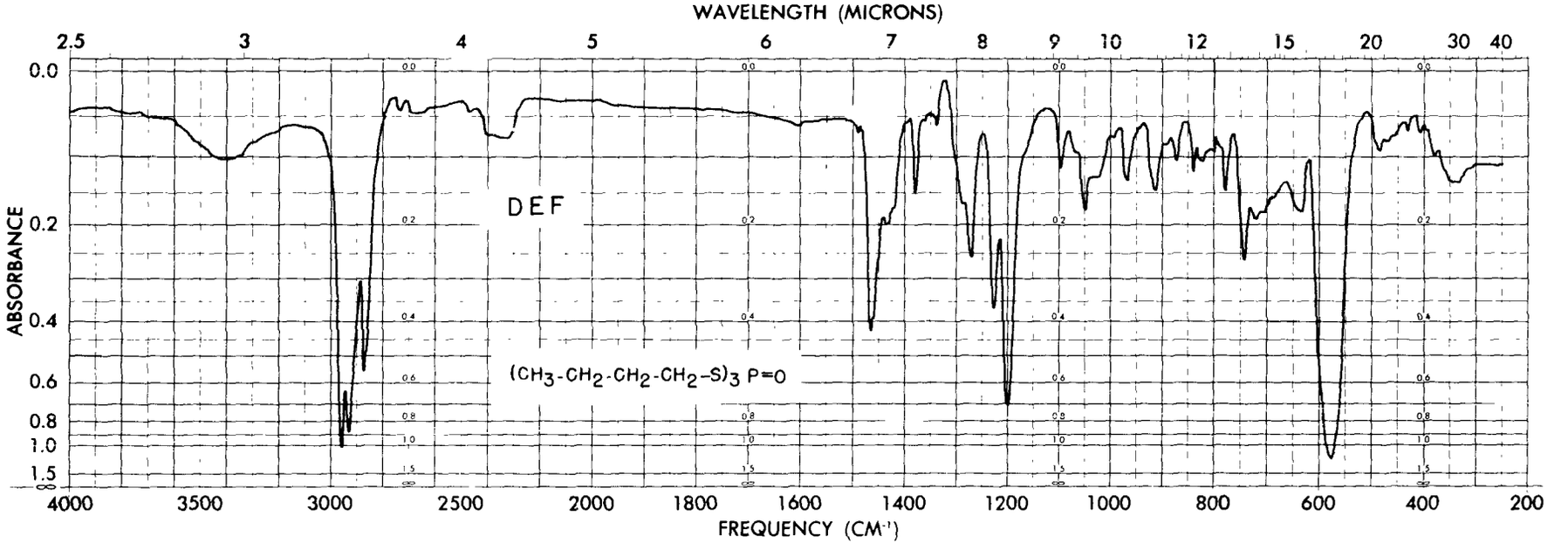

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DCPA
COOCH3
Cl
Cl
Cl
Cl
COOCH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

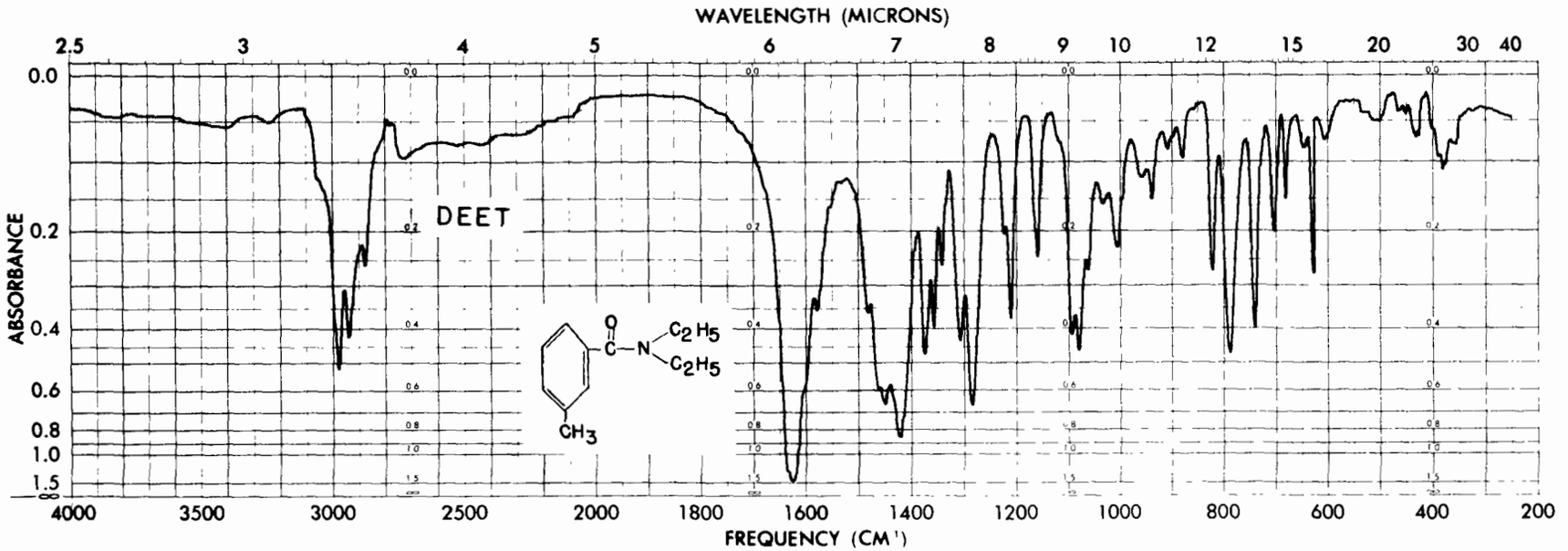

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DDT
H
C
Cl
Cl
Cl
C
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

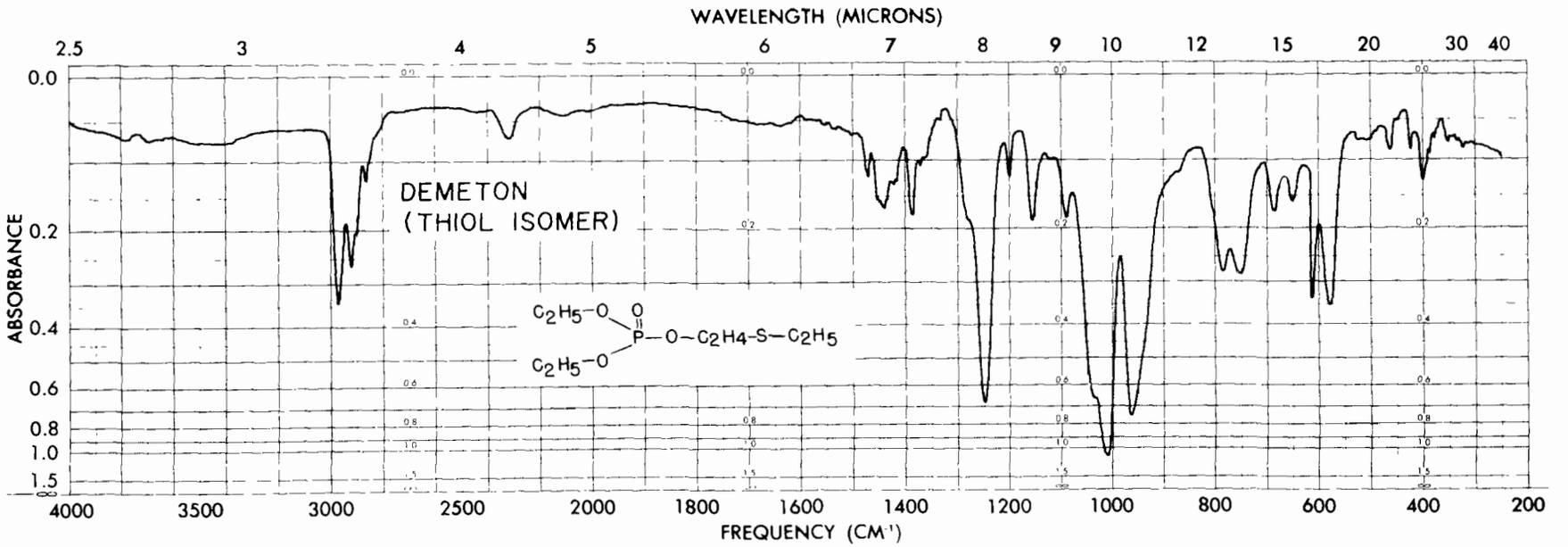

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
DDA
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
Cl
Cl
H
C
H–C–COOH
H
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

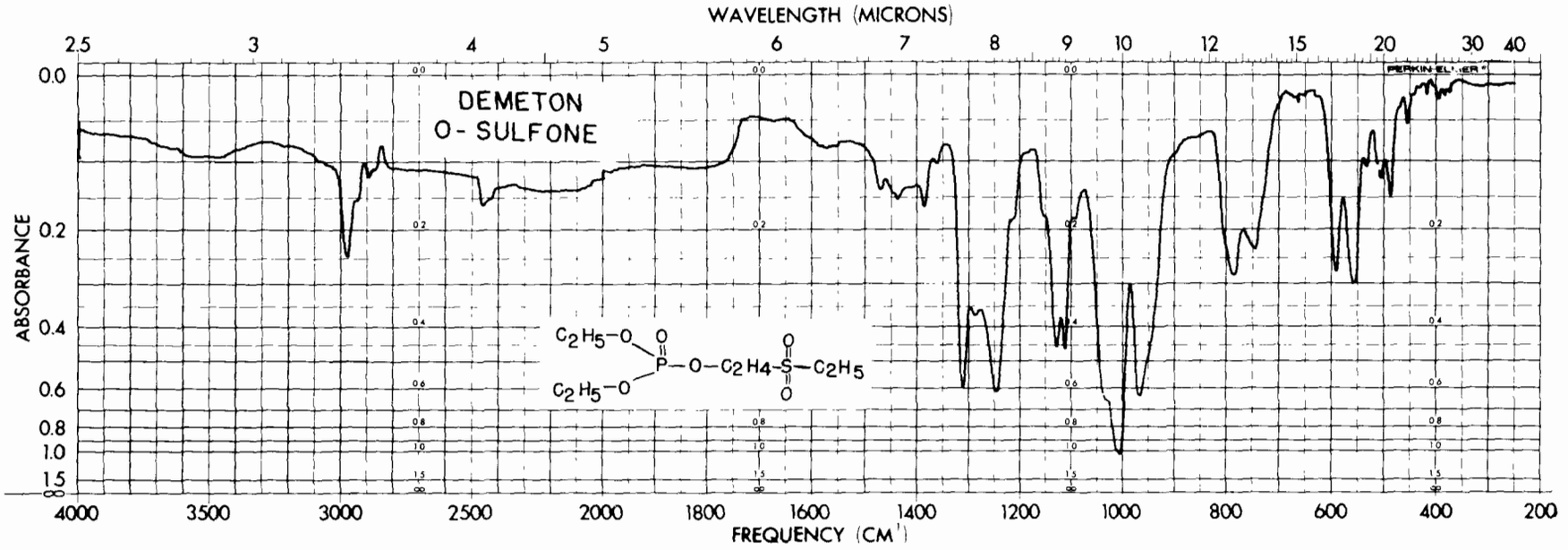

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
DDE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
Cl
Cl
C
C
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

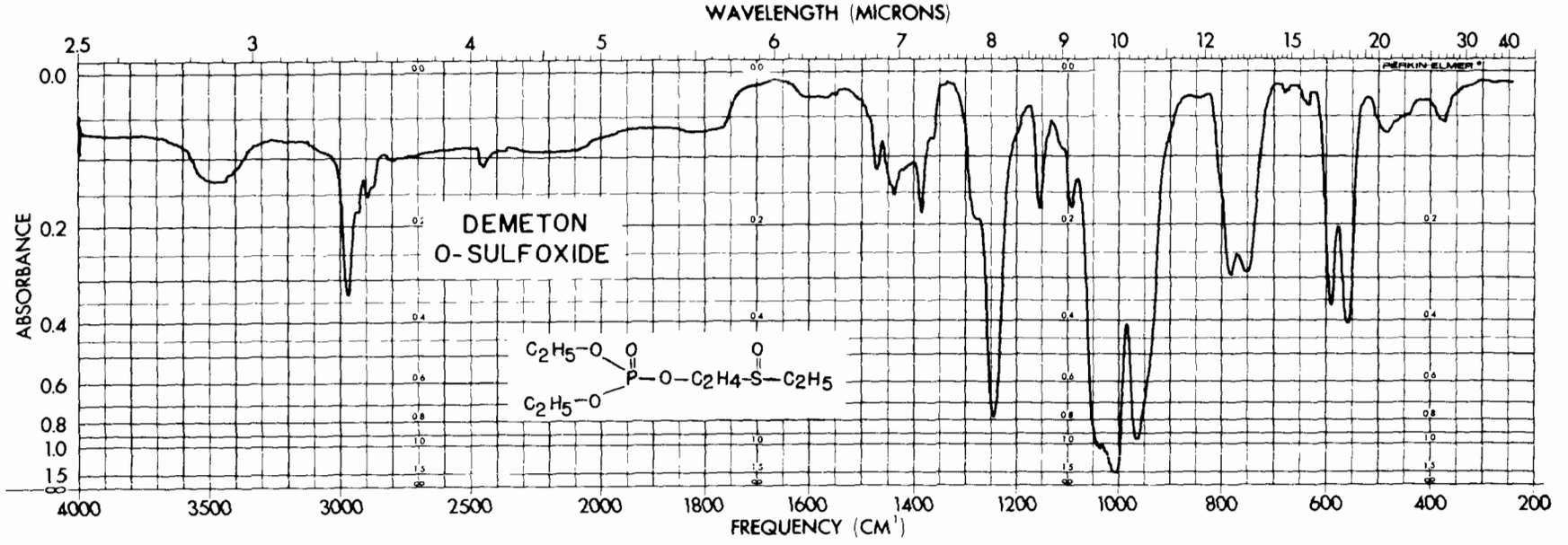

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
p,p'-DBrDT
Cl Cl Cl
Br
C
H
Br
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

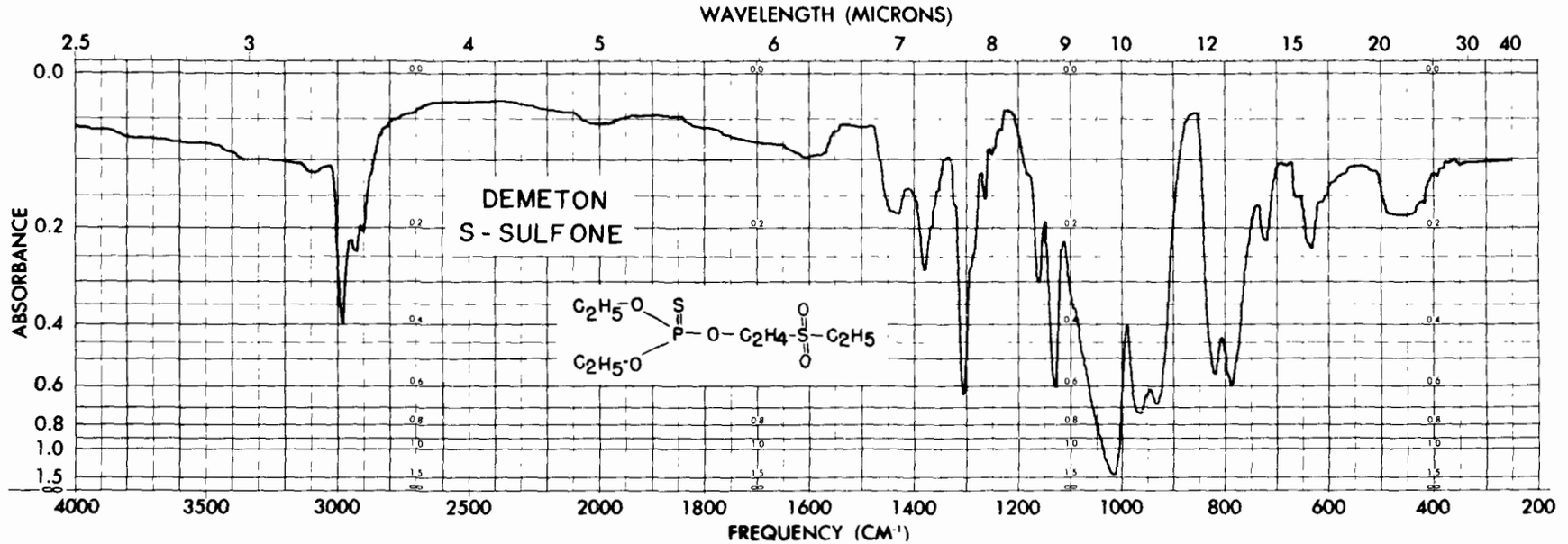

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DEF
(CH3-CH2-CH2-CH2-S)3 P=O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

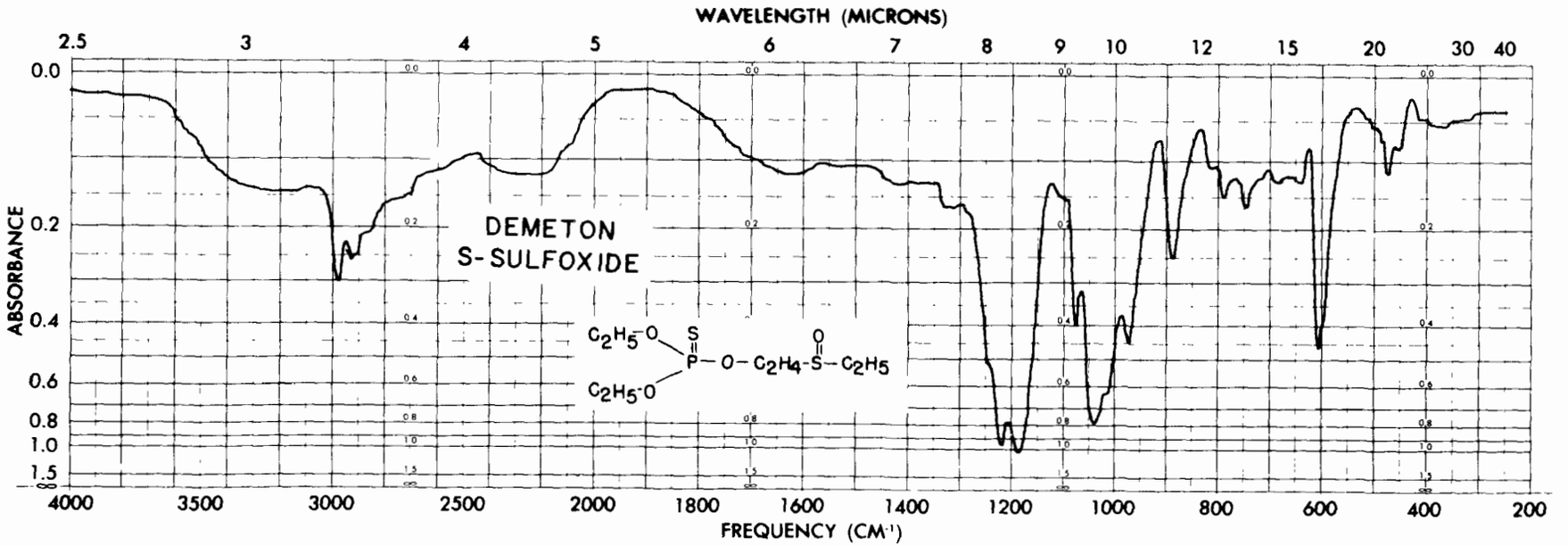

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DEET
O
C
N
C2H5
C2H5
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

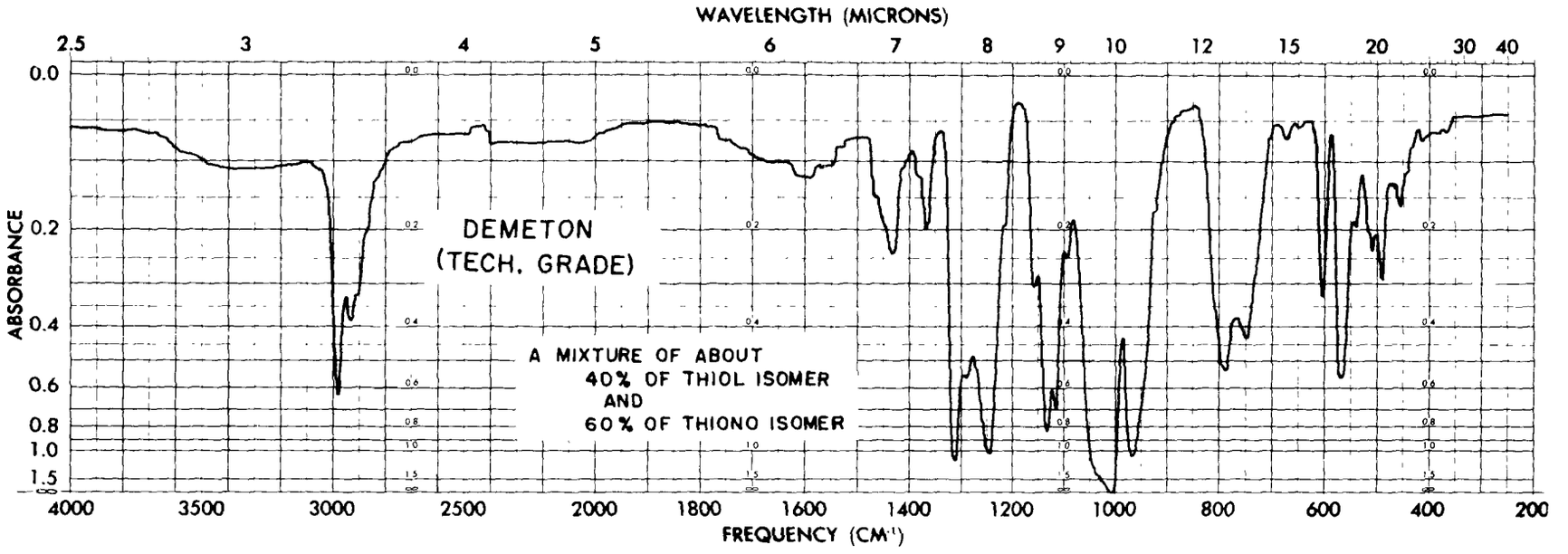

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DEMETON
(THIOL ISOMER)
C2H5-O
O
P
O-C2H4-S-C2H5
C2H5-O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

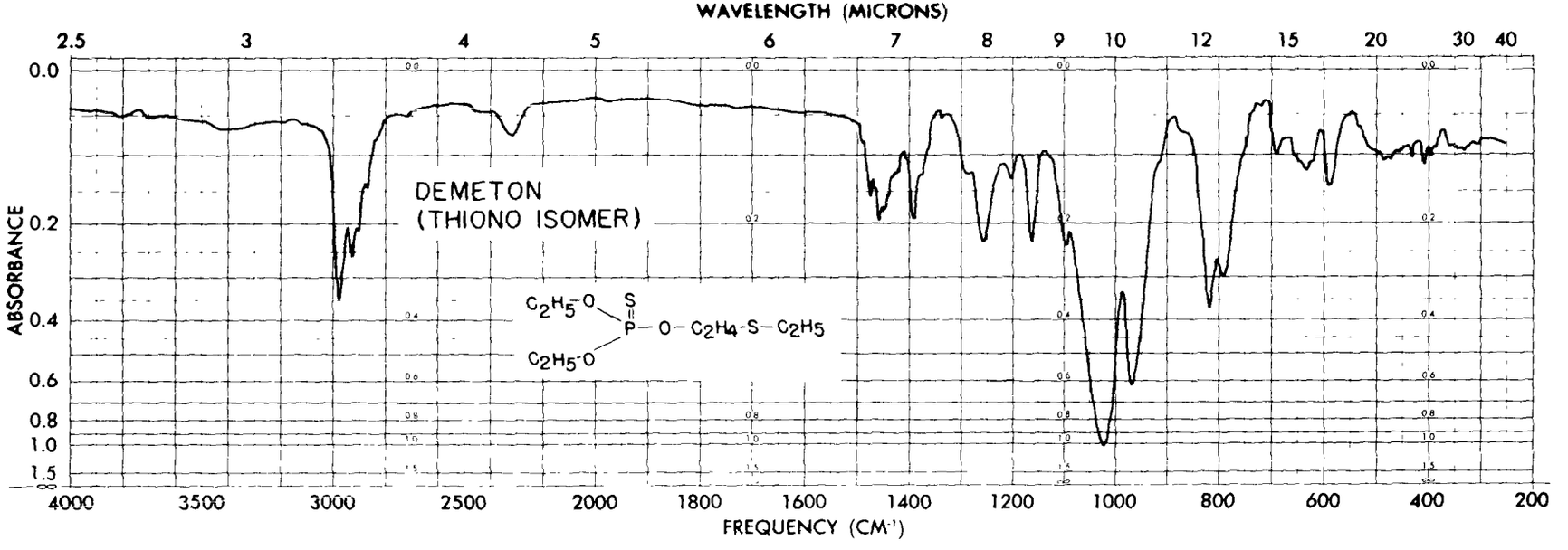

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
DEMETON
O- SULFONE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

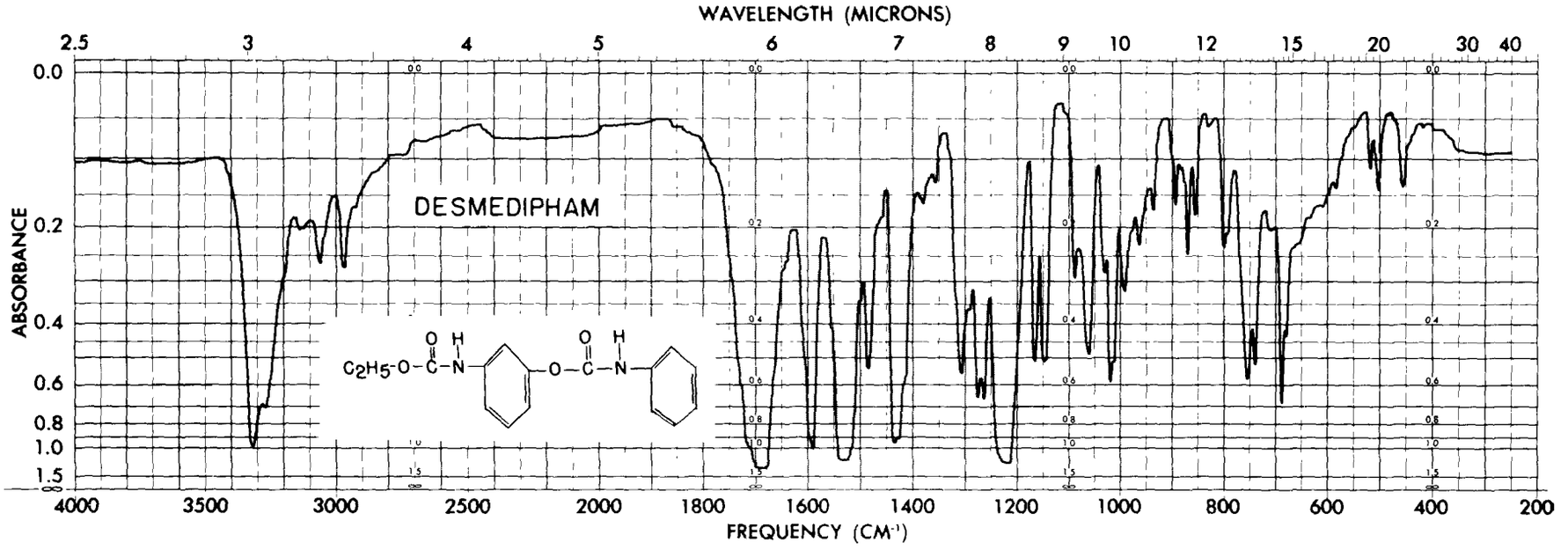

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
DEMETON
O-SULFOXIDE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

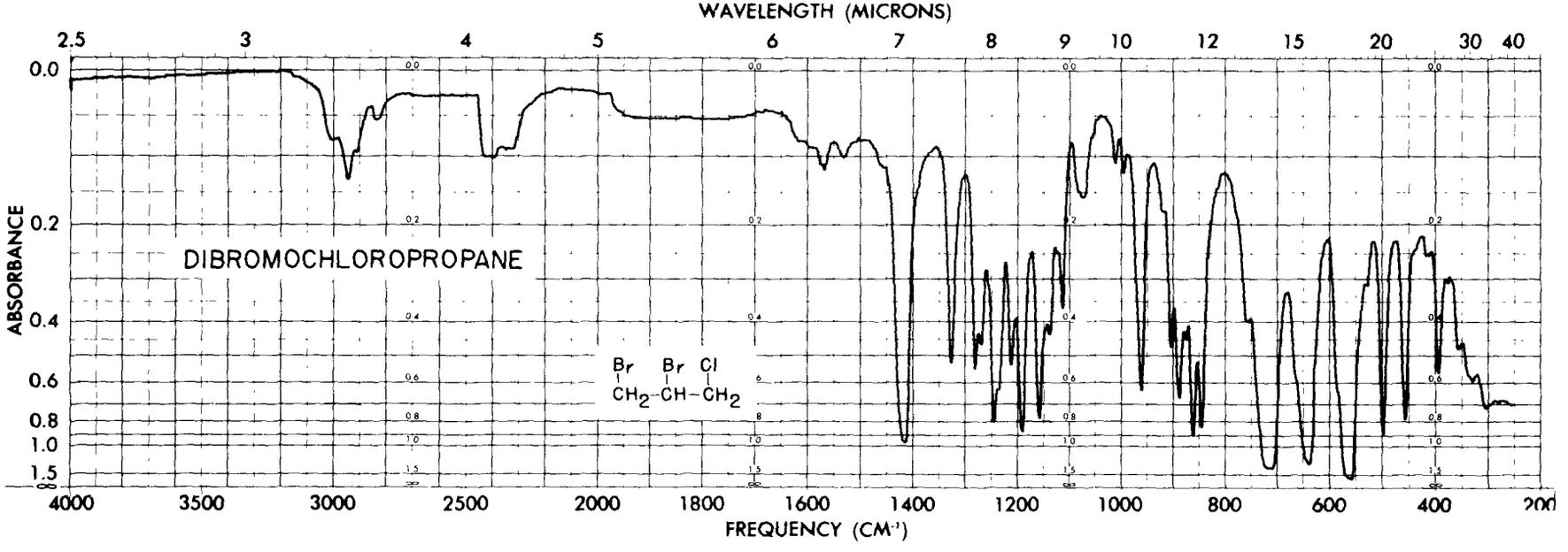

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DEMETON
S - SULFONE
C_2H_5-O
S
P
O
C_2H_5-O
$-O-C_2H_4-S-C_2H_5$
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

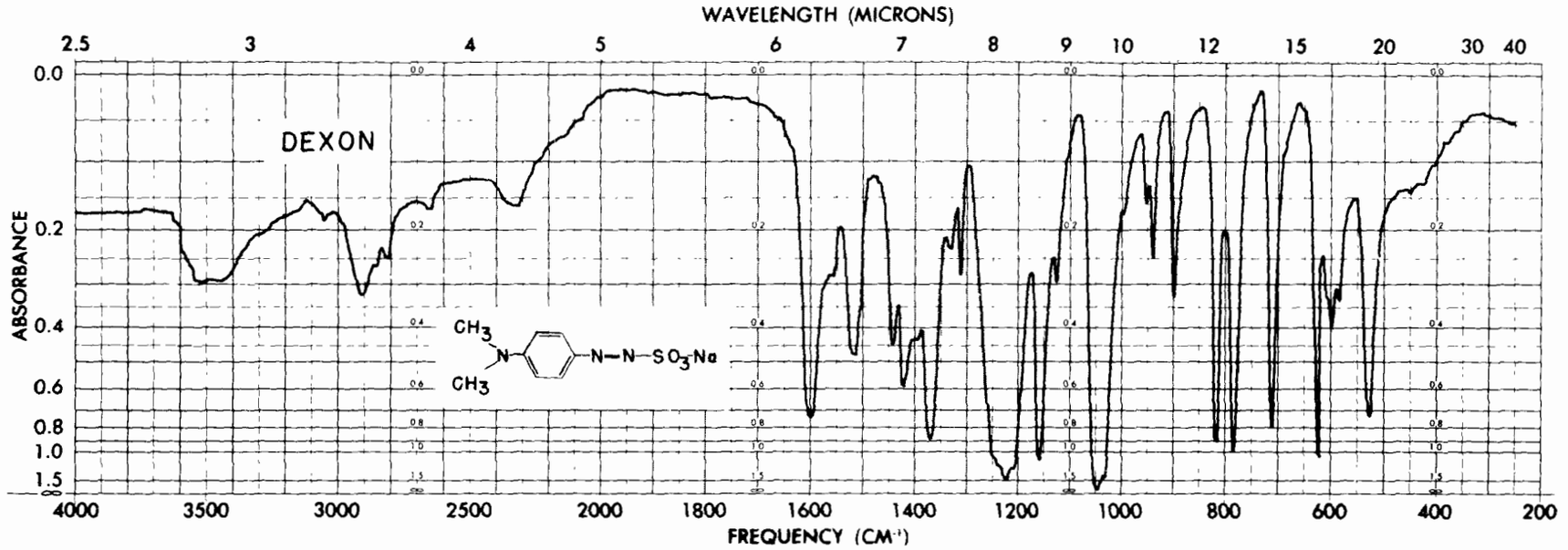

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DEMETON
S-SULFOXIDE
C_2H_5-O
S
P
O
C_2H_5-O
$-O-C_2H_4-S-C_2H_5$
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

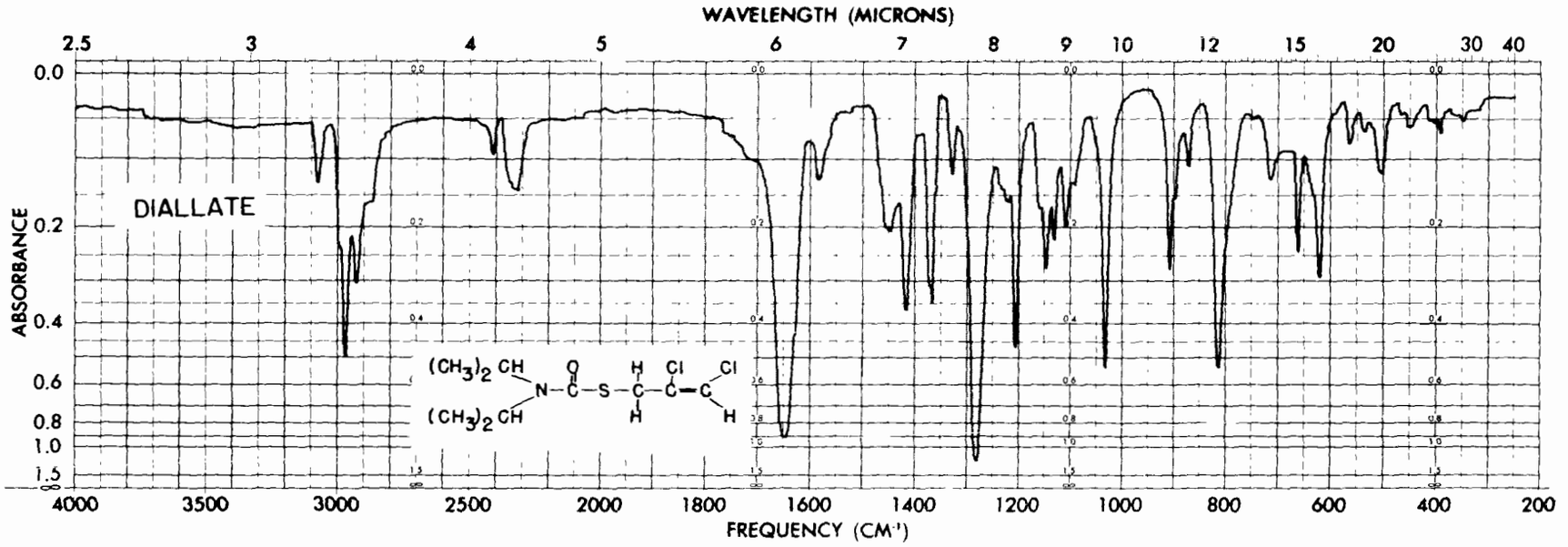

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DEMETON
(TECH. GRADE)
A MIXTURE OF ABOUT
40% OF THIOL ISOMER
AND
60% OF THIONO ISOMER
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

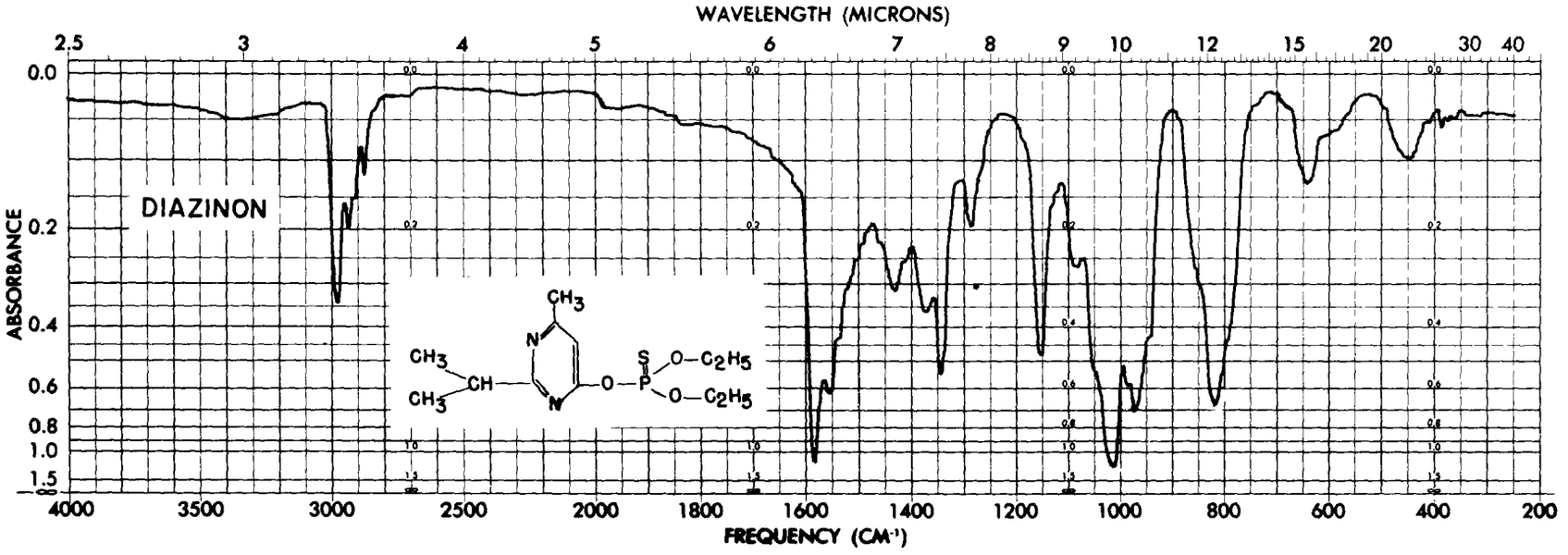

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DEMETON
(THIONO ISOMER)
C2H5-O
S
P
O-C2H4-S-C2H5
C2H5-O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

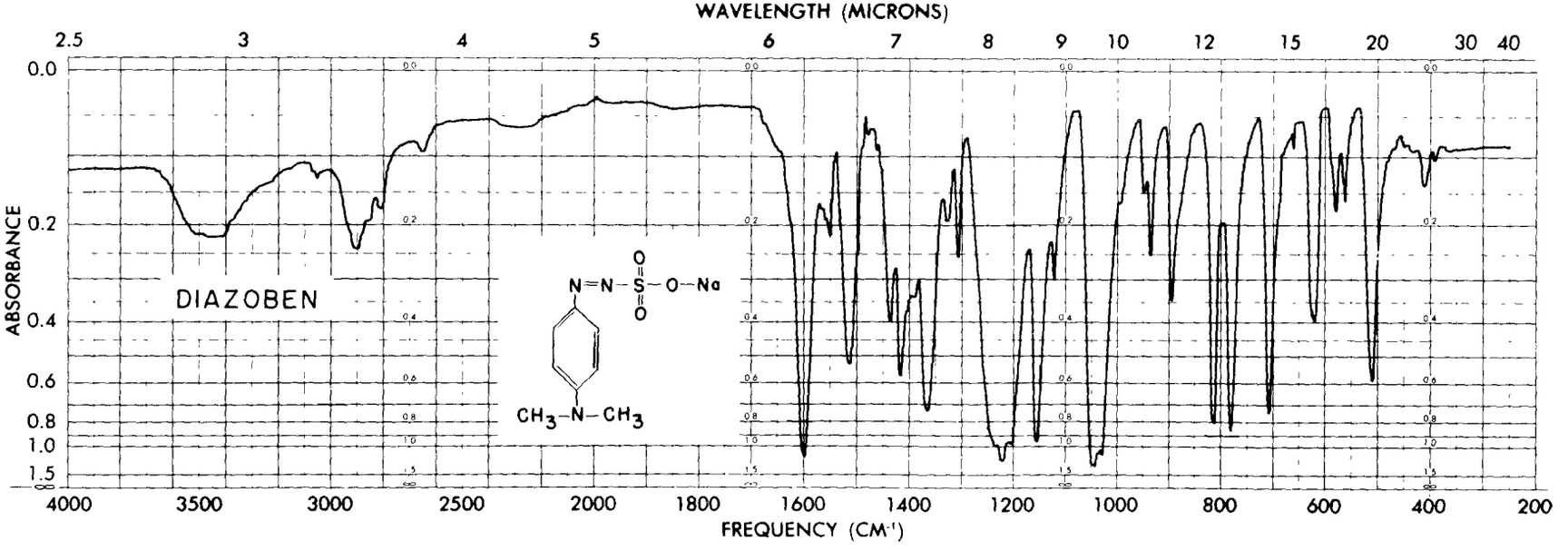

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DESMEDIPHAM
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

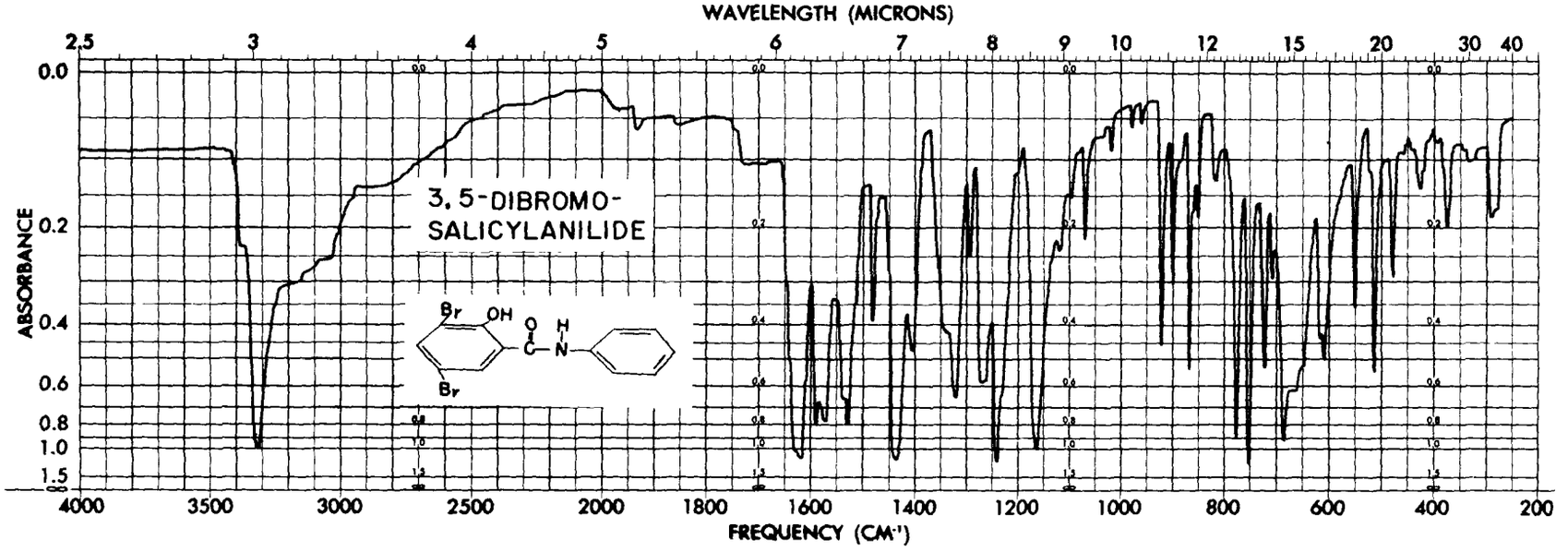

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIBROMOCHLOROPROPANE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
FREQUENCY (CM⁻¹)

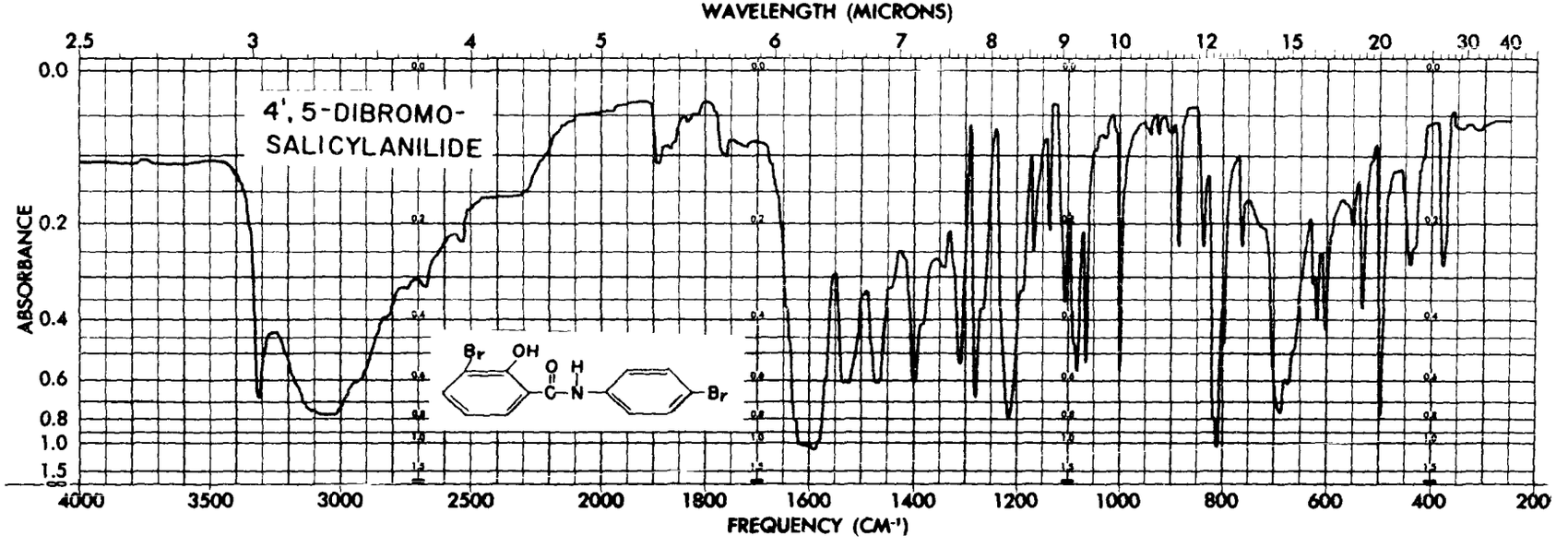

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
DEXON
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CH3
N
CH3
N—N—SO3Na
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

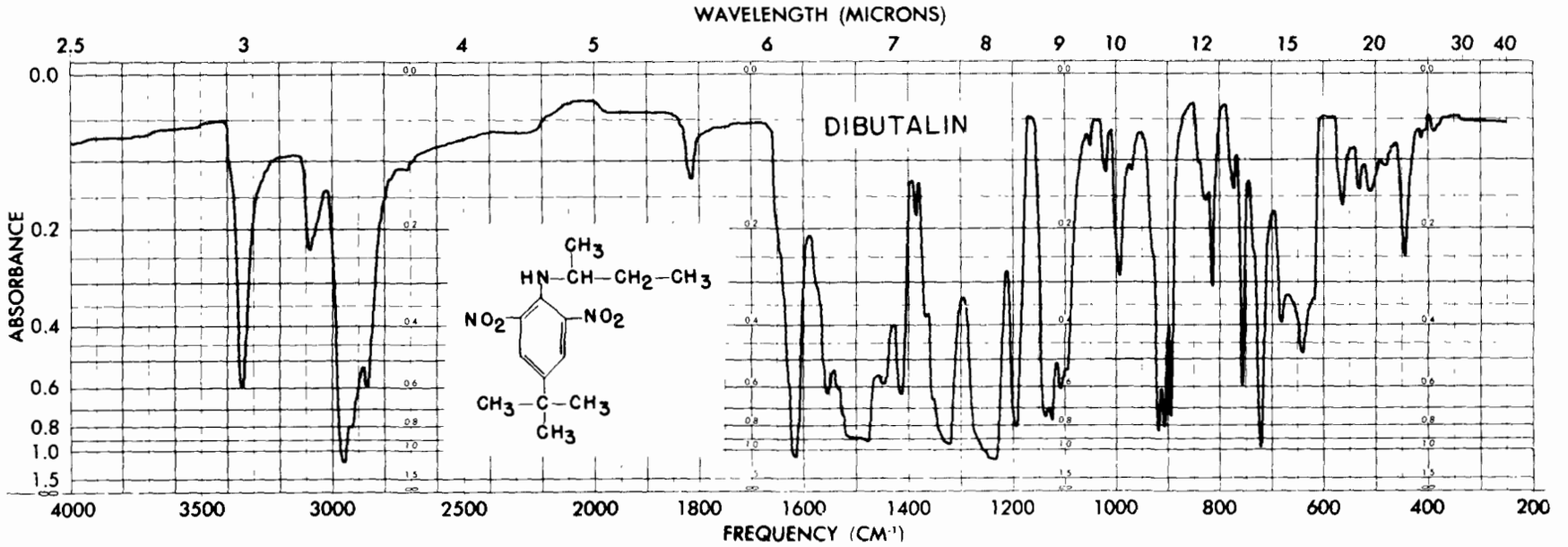

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
DIALLATE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
(CH3)2 CH
N—C—S—C—C=C
(CH3)2 CH
O
H
Cl
Cl
H
H
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

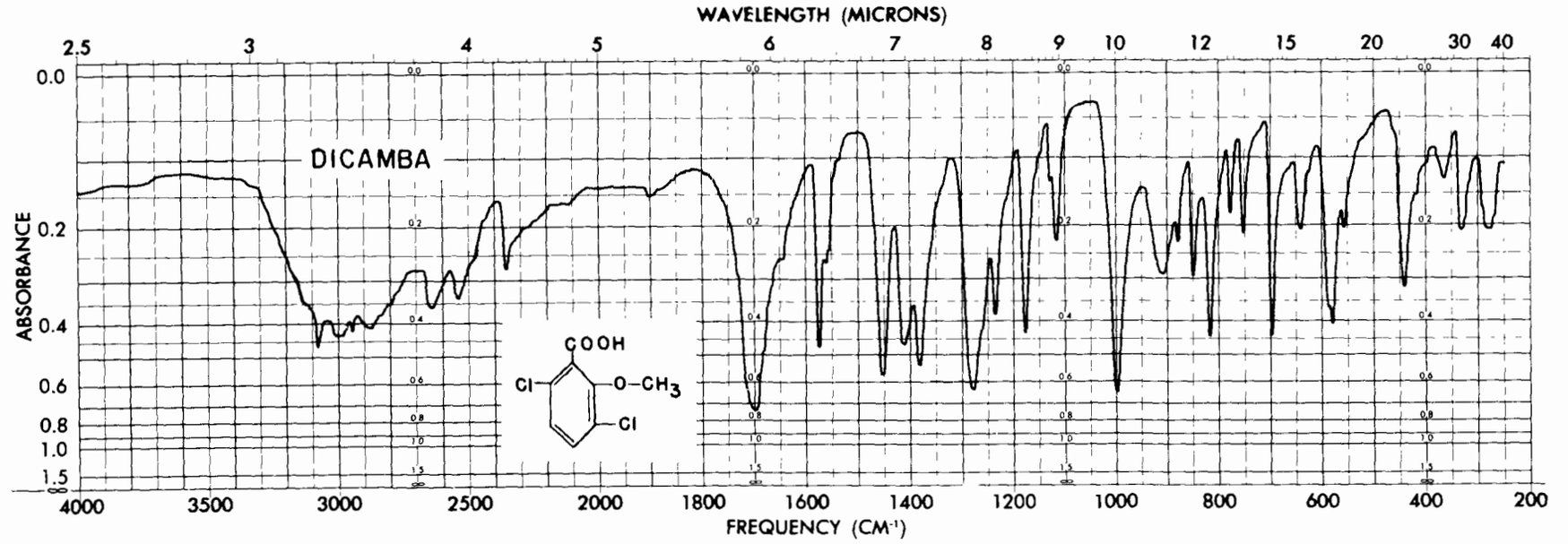

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
DIAZINON
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

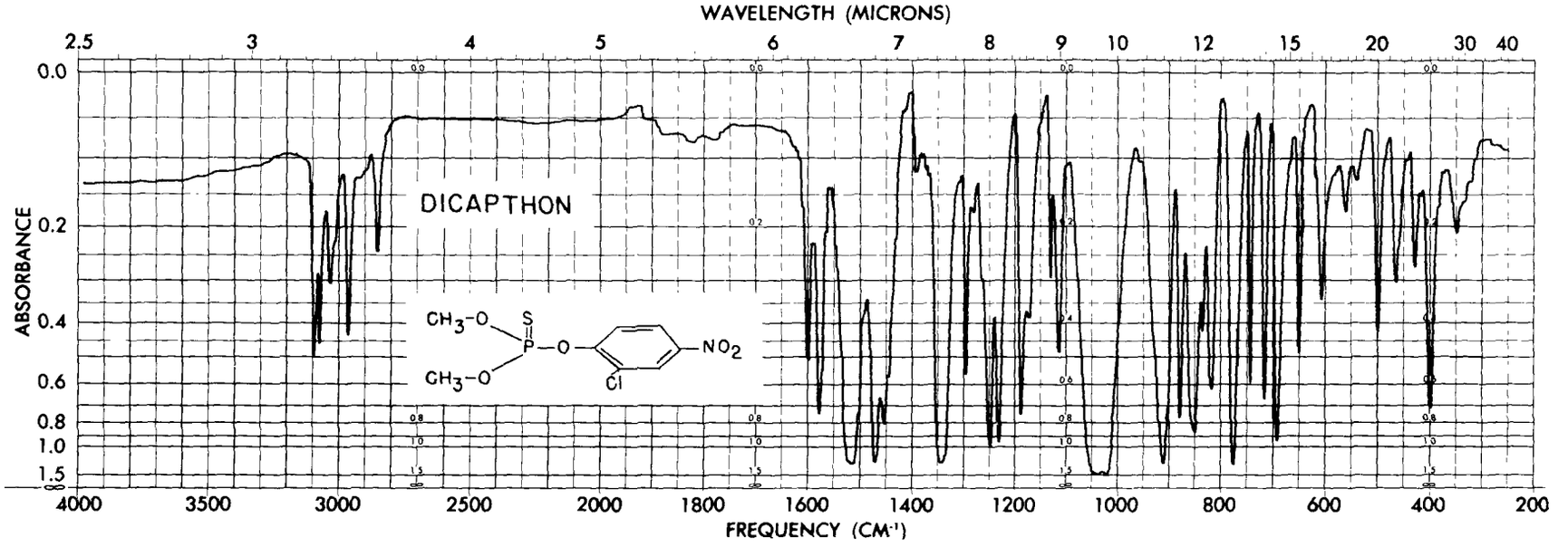

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
DIAZOBEN
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

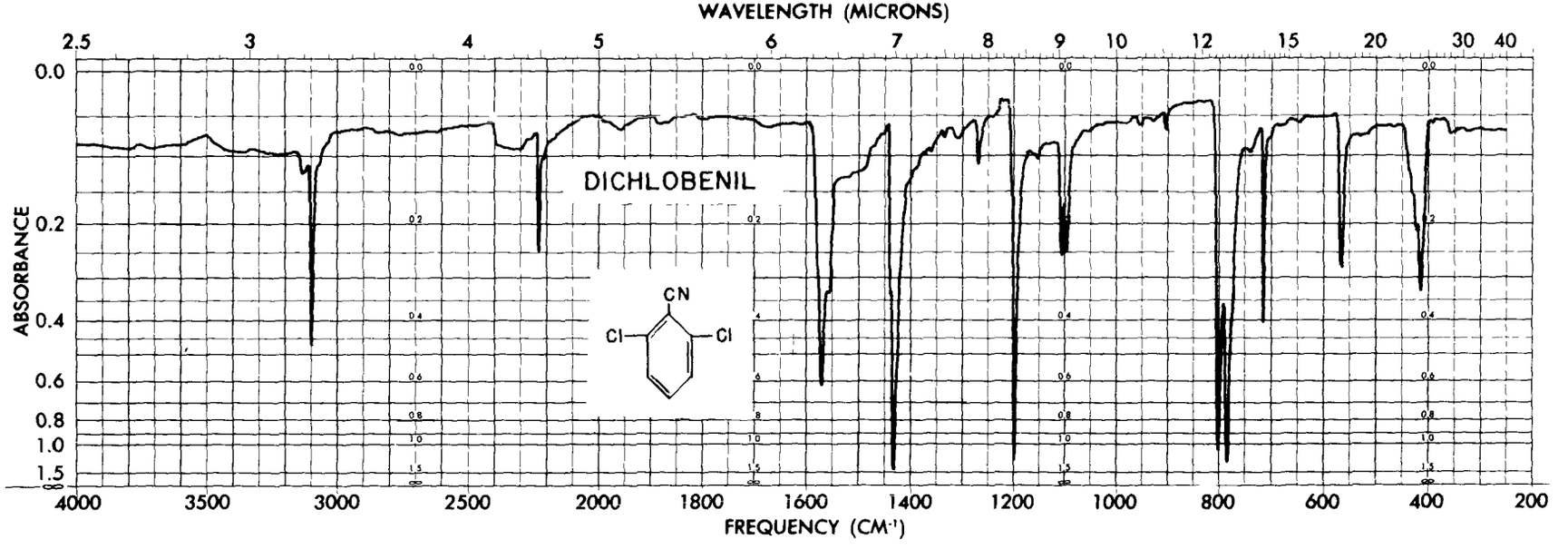

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
3, 5-DIBROMO-
SALICYLANILIDE
Br
OH
O
H
C
N
Br
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

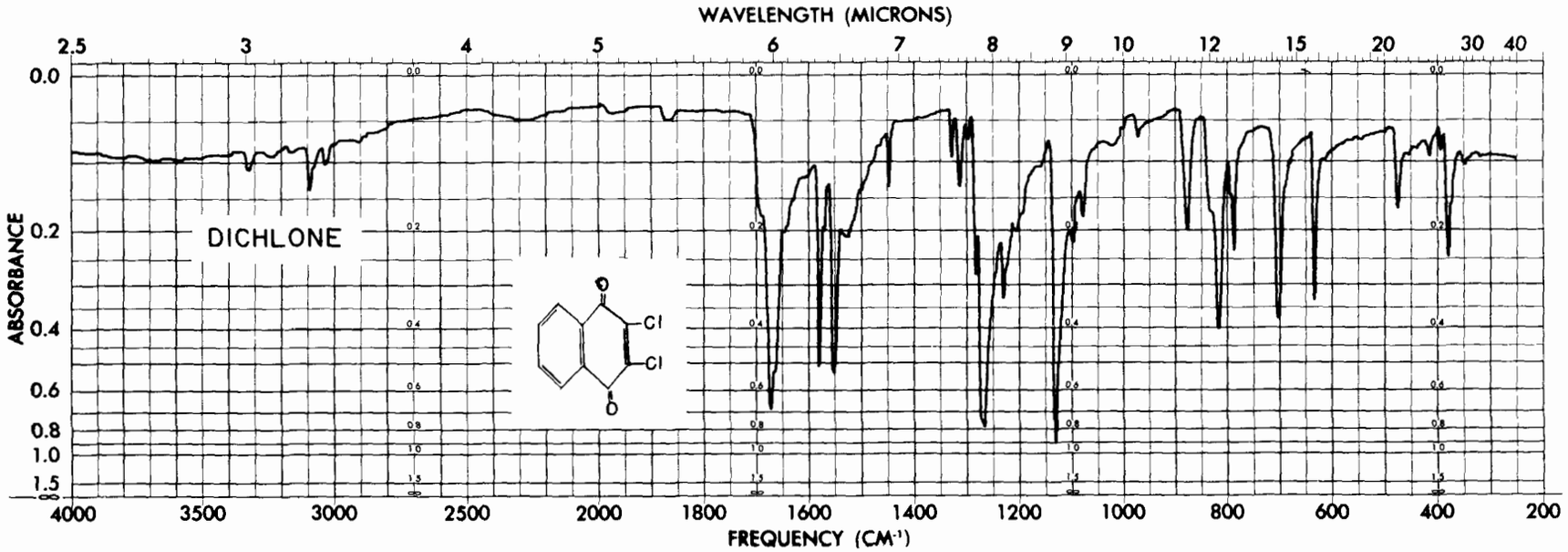

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
4', 5-DIBROMO-
SALICYLANILIDE
Br
OH
O
H
C
N
Br
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

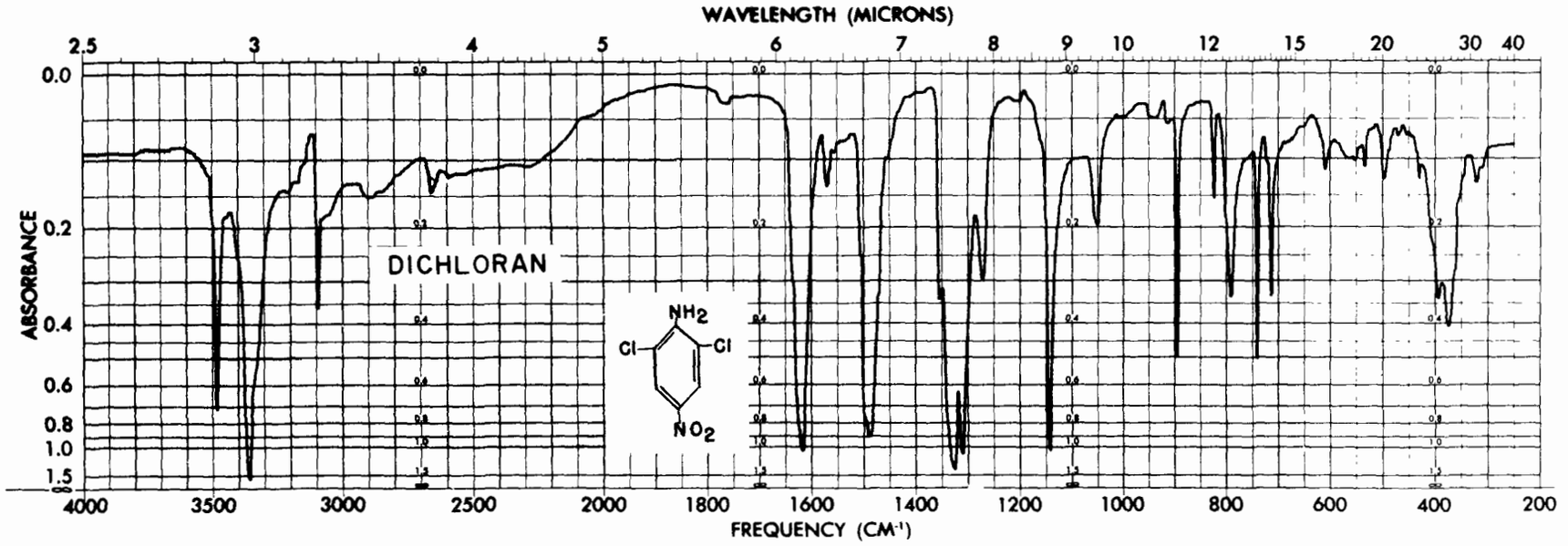

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
DIBUTALIN
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)
CH3
HN–CH–CH2–CH3
NO2
NO2
CH3–C–CH3
CH3

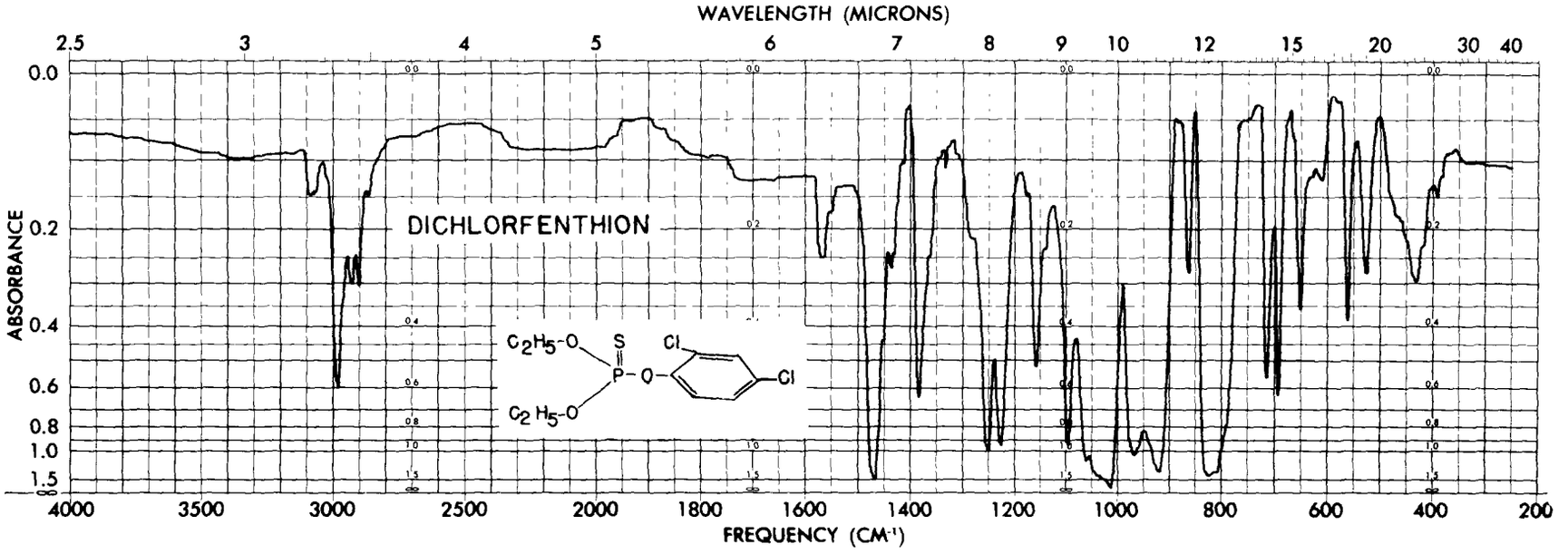

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
DICAMBA
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)
COOH
Cl
O–CH3
Cl

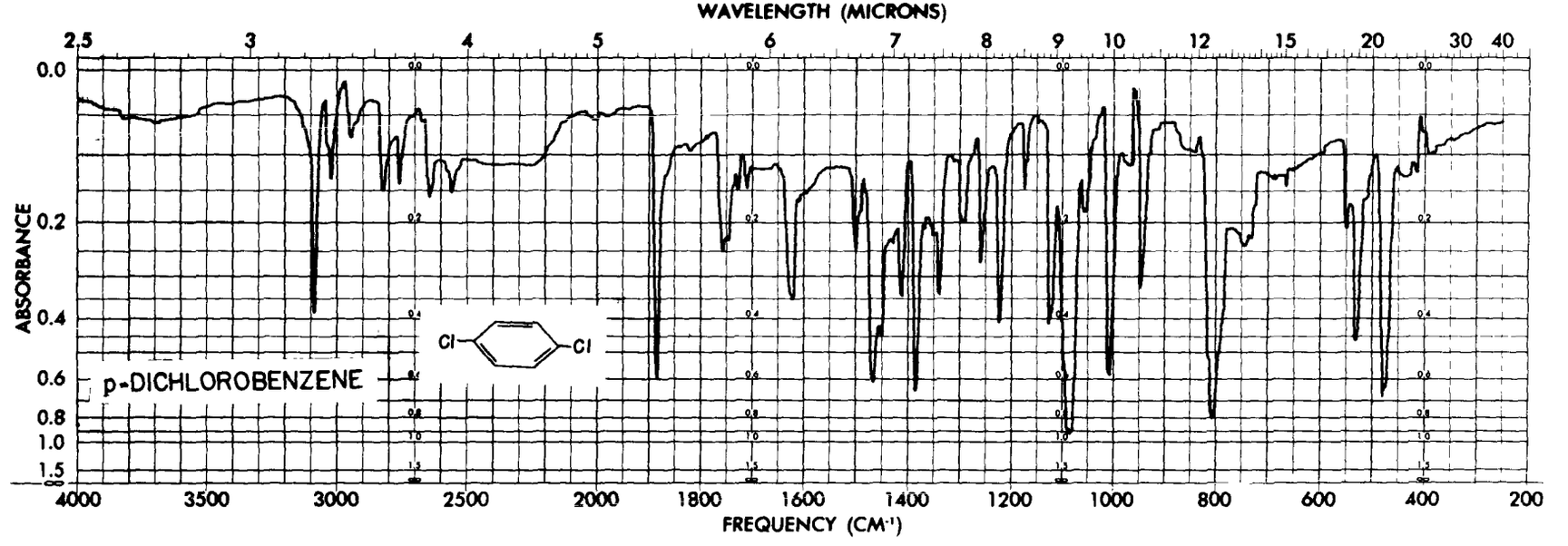

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DICAPTHON
CH3-O
S
P
O
CH3-O
NO2
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

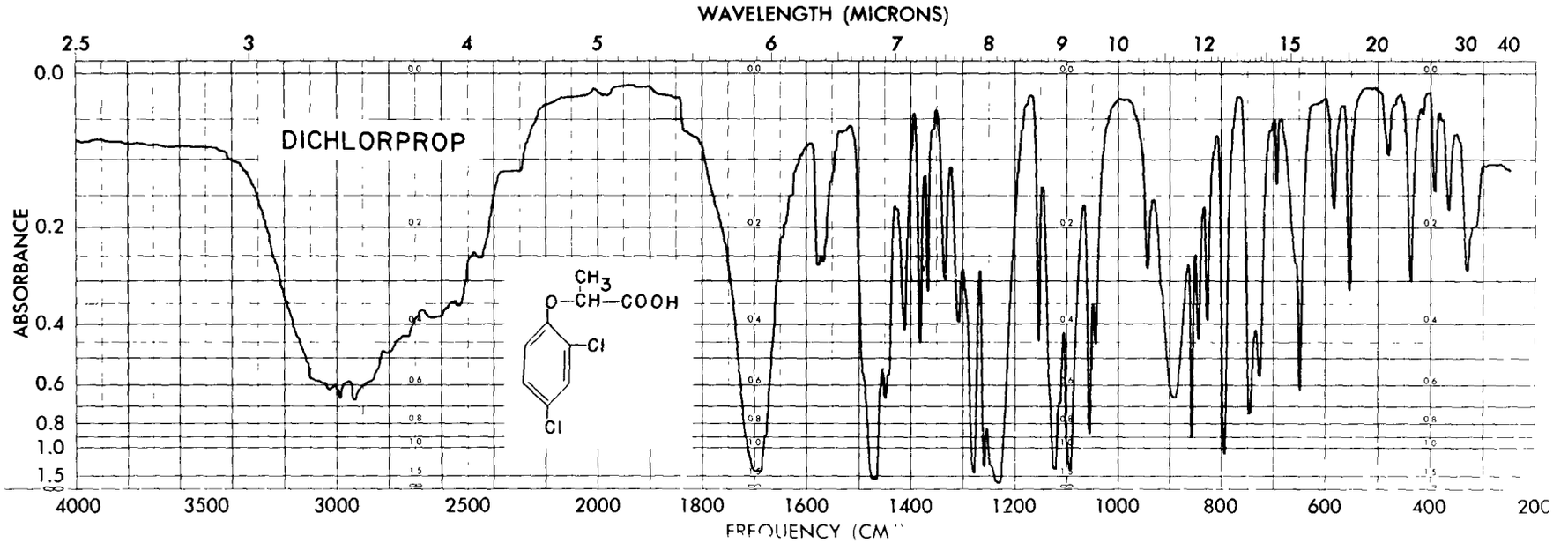

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DICHLOBENIL
CN
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

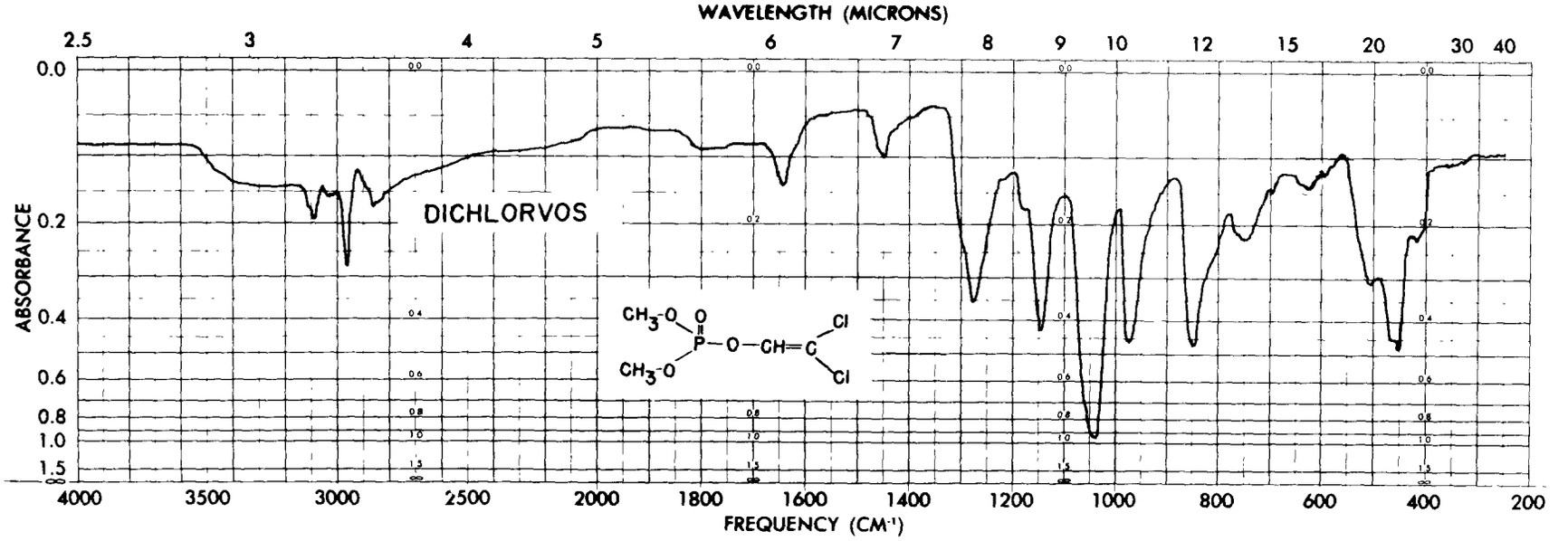

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
DICHLONE
Cl
Cl
O
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

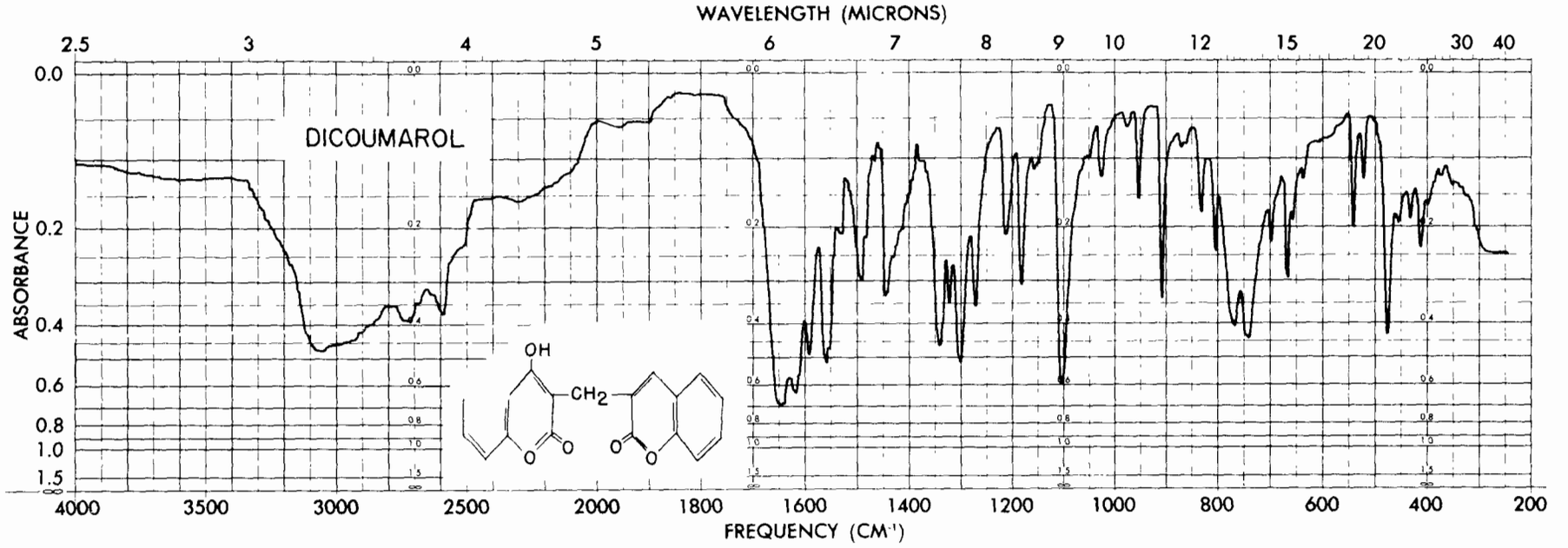

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
DICHLORAN
NH2
Cl
Cl
NO2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

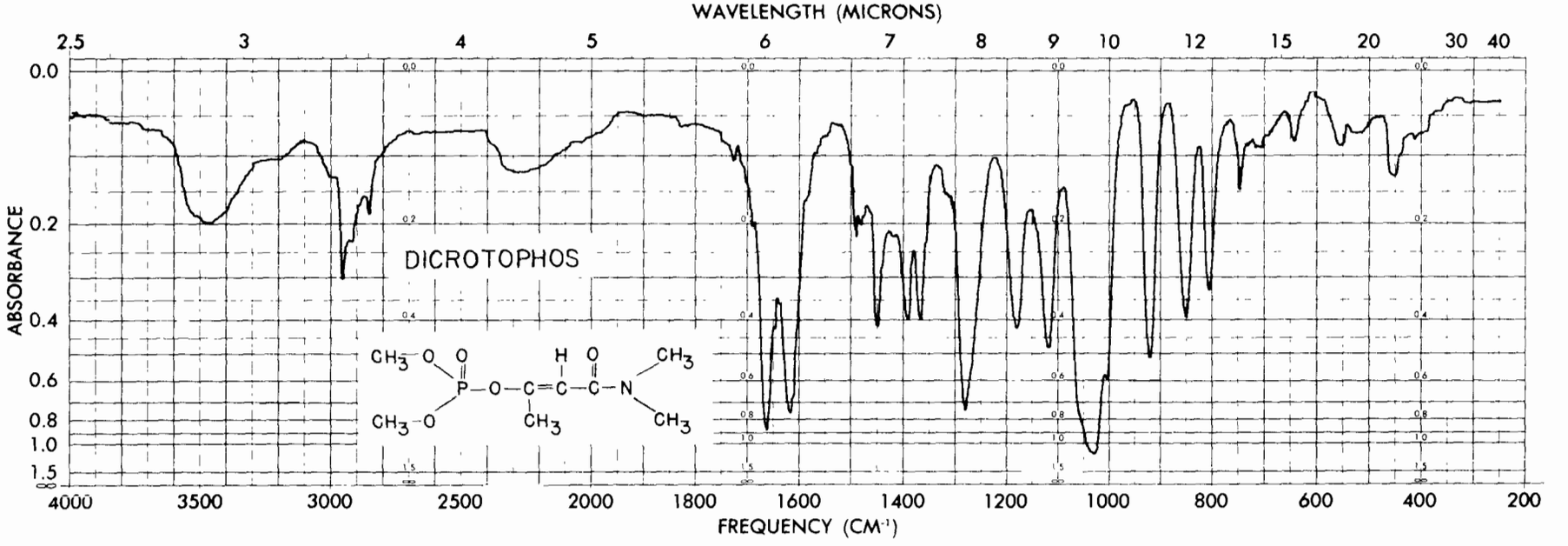

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DICHLORFENTHION
C_2H_5-O
S
P-O-
Cl
Cl
C_2H_5-O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

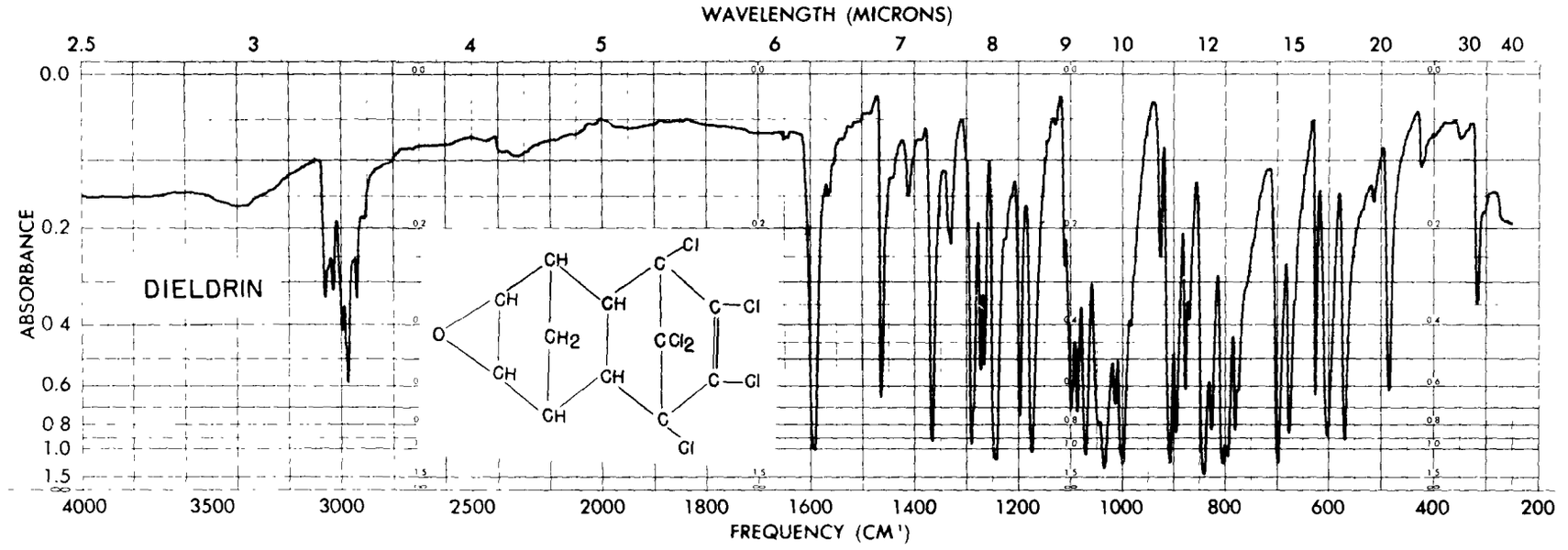

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
p-DICHLOROBENZENE
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

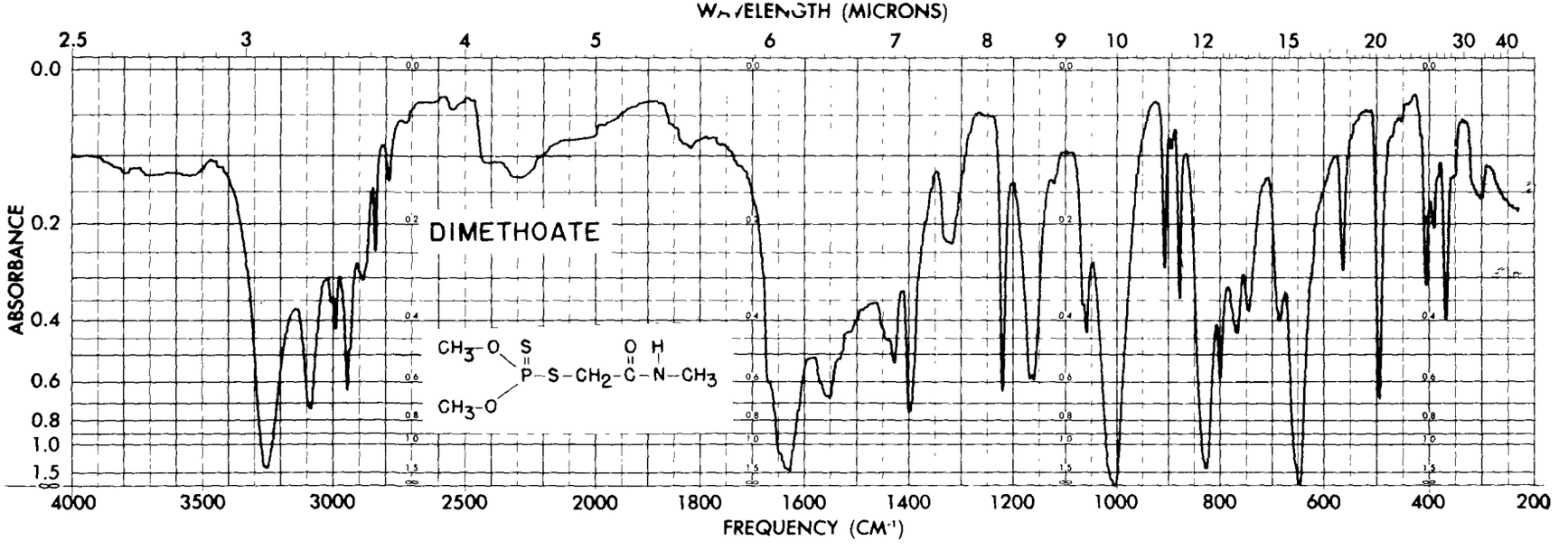

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
DICHLORPROP
CH3
O–CH–COOH
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM

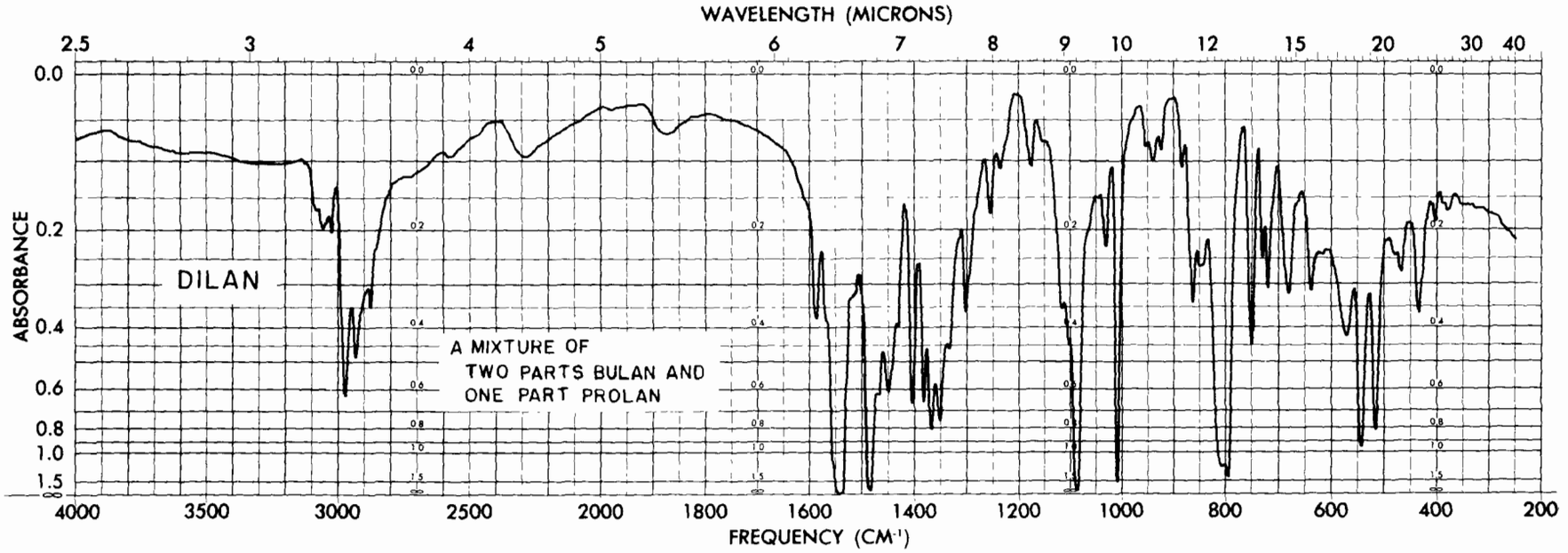

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
DICHLORVOS
CH3-O
O
P
O
CH=C
Cl
Cl
CH3-O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

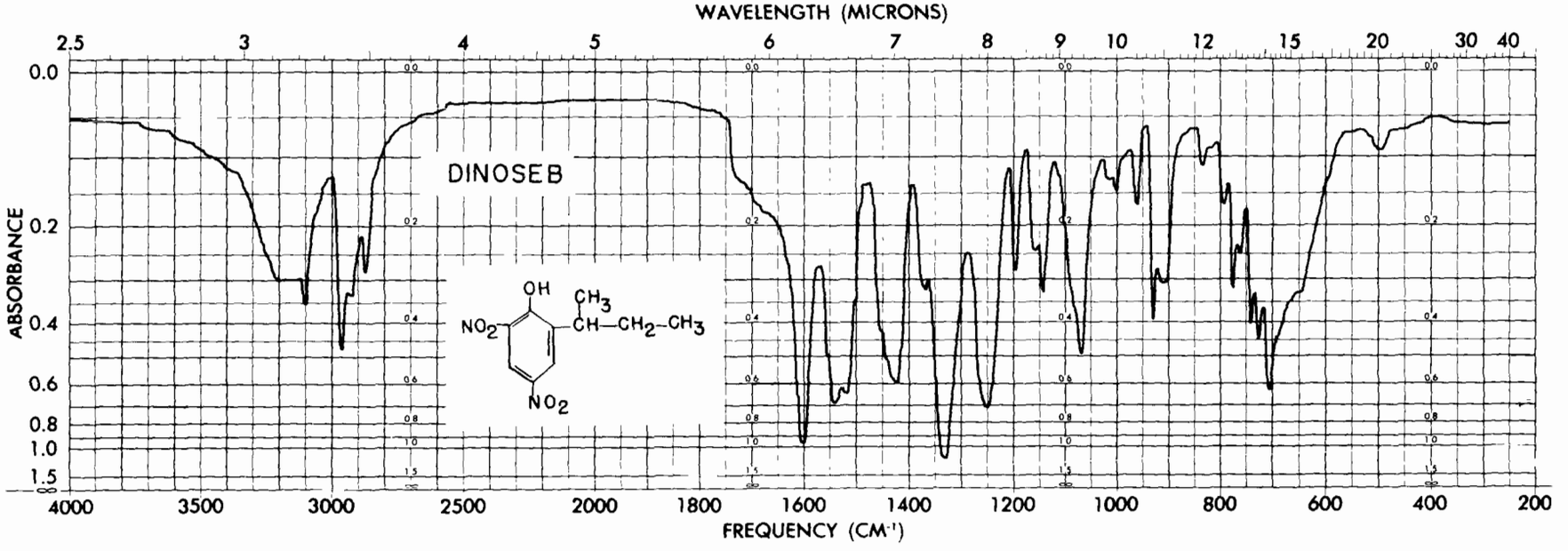

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
DICOUMAROL
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
OH
CH2
O
O
O
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

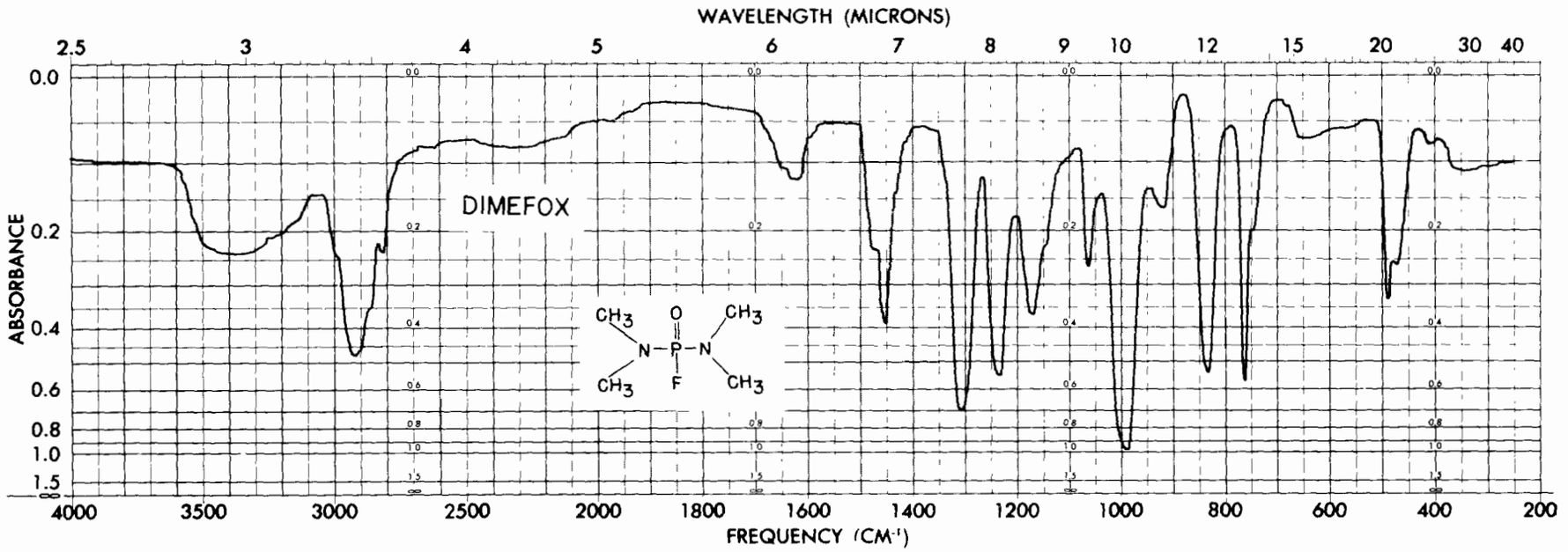

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
DICROTOPHOS
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CH3
O
O
H
O
CH3
P
O
C
C
C
N
CH3
O
CH3
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

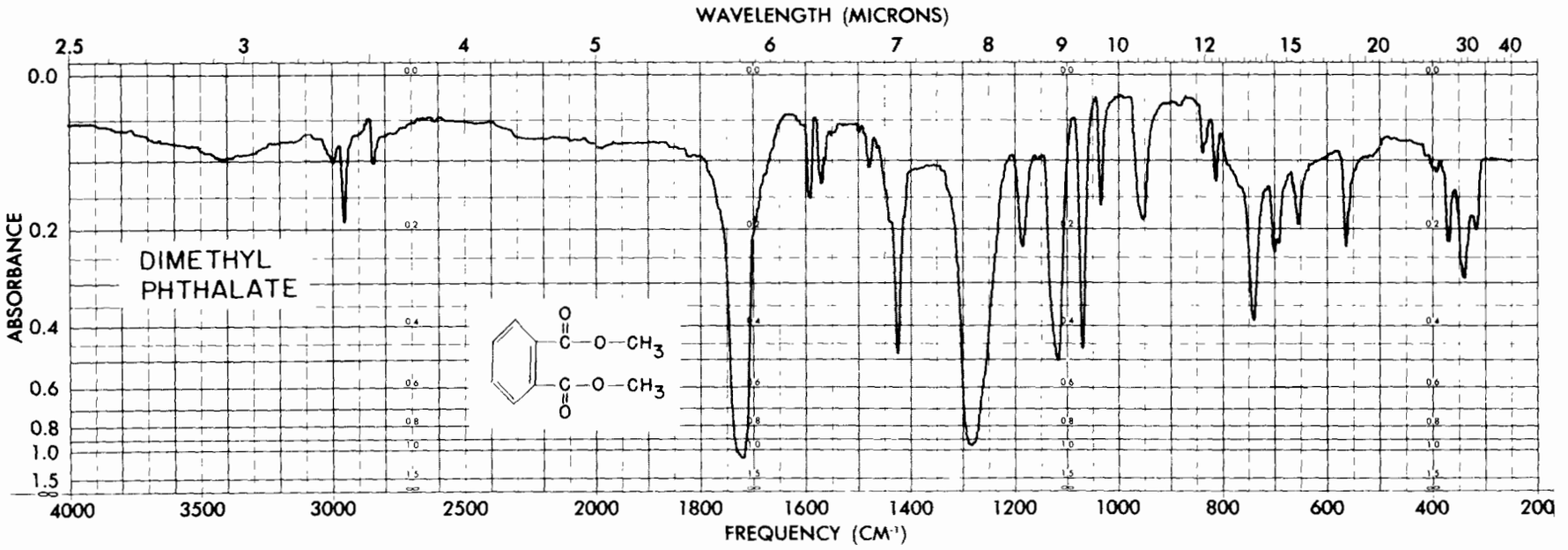

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIELDRIN
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

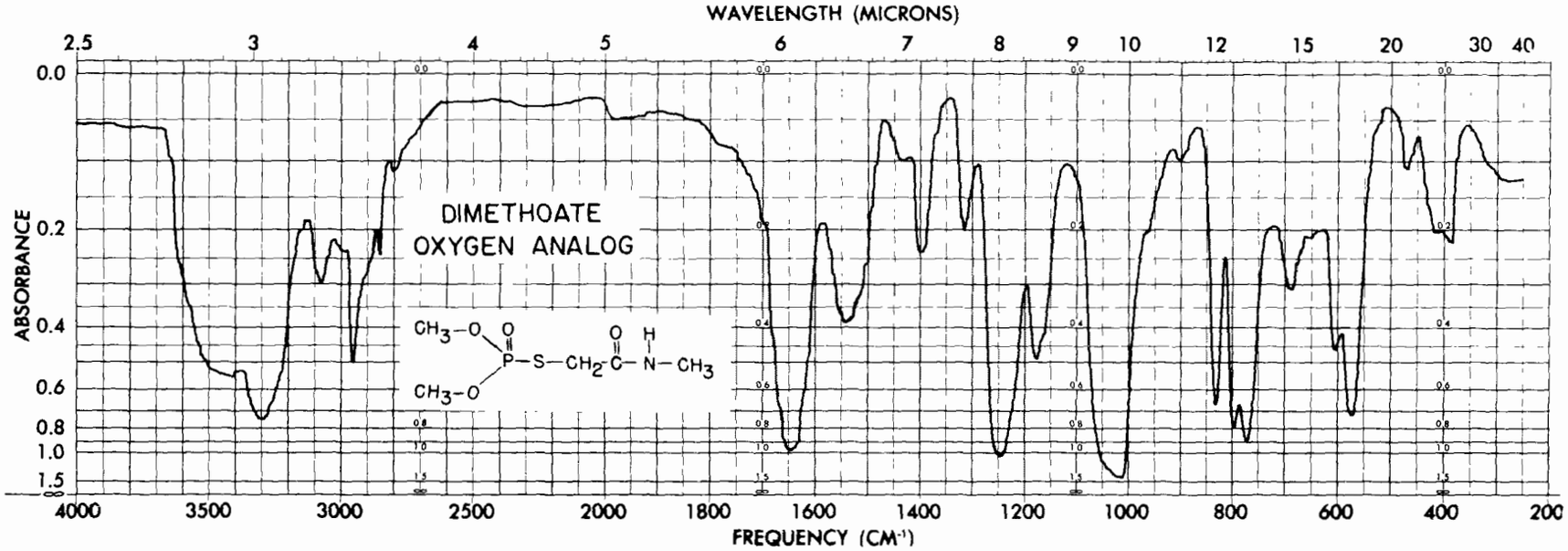

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIMETHOATE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

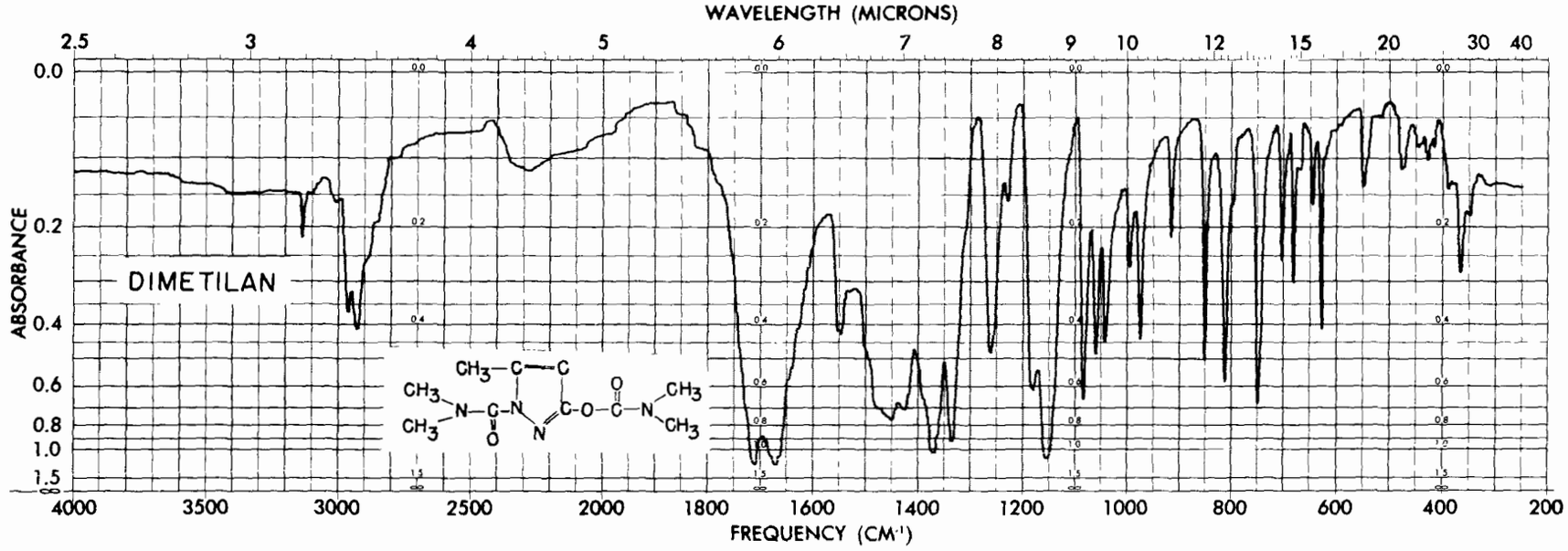

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DILAN
A MIXTURE OF
TWO PARTS BULAN AND
ONE PART PROLAN
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

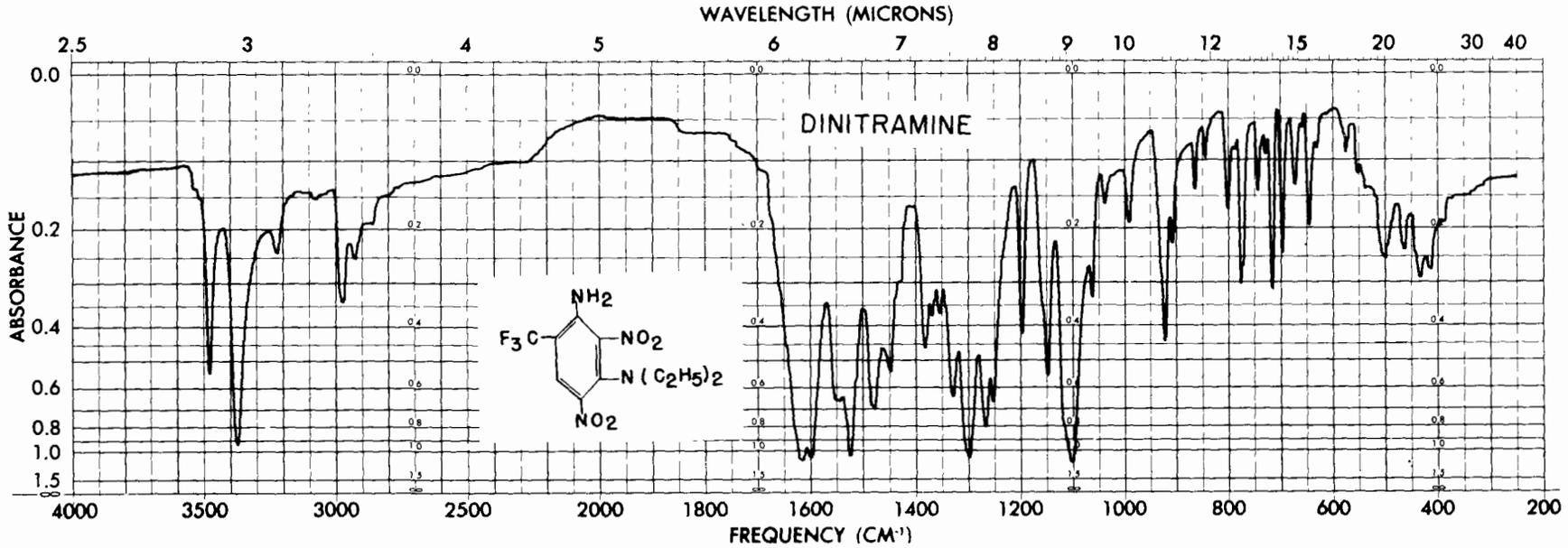

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DINOSEB
OH
CH3
NO2
CH—CH2—CH3
NO2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

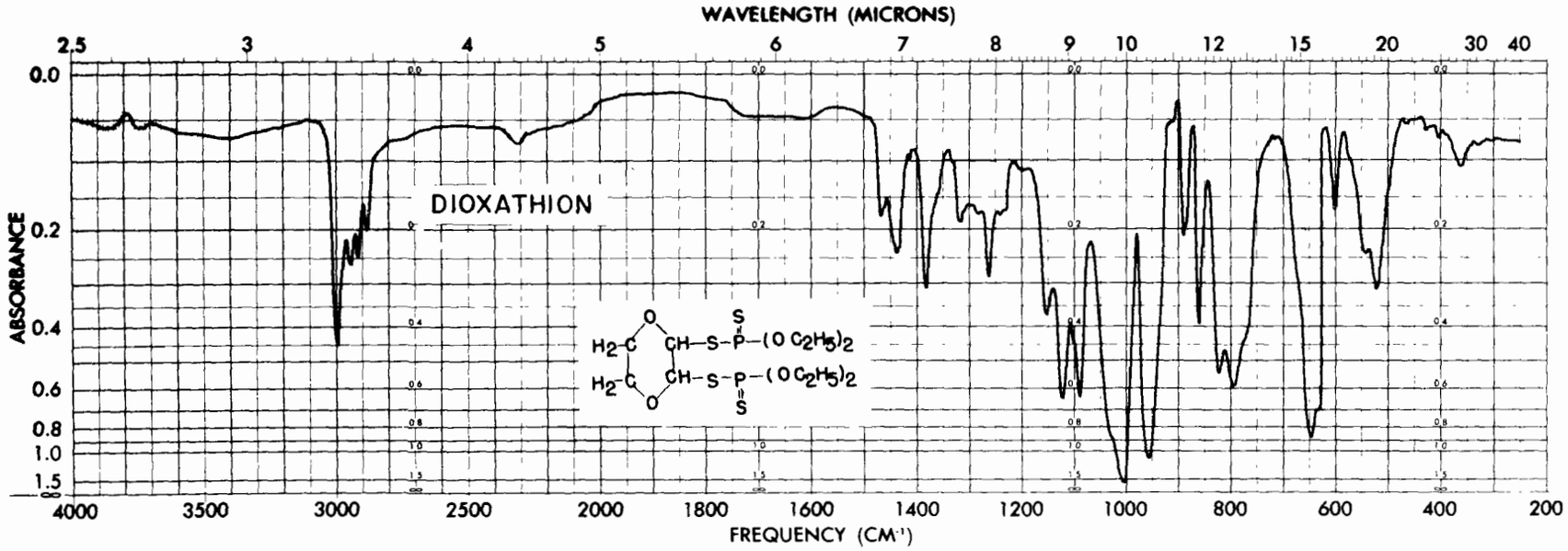

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIMEFOX
CH3
O
CH3
N
P
N
CH3
F
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

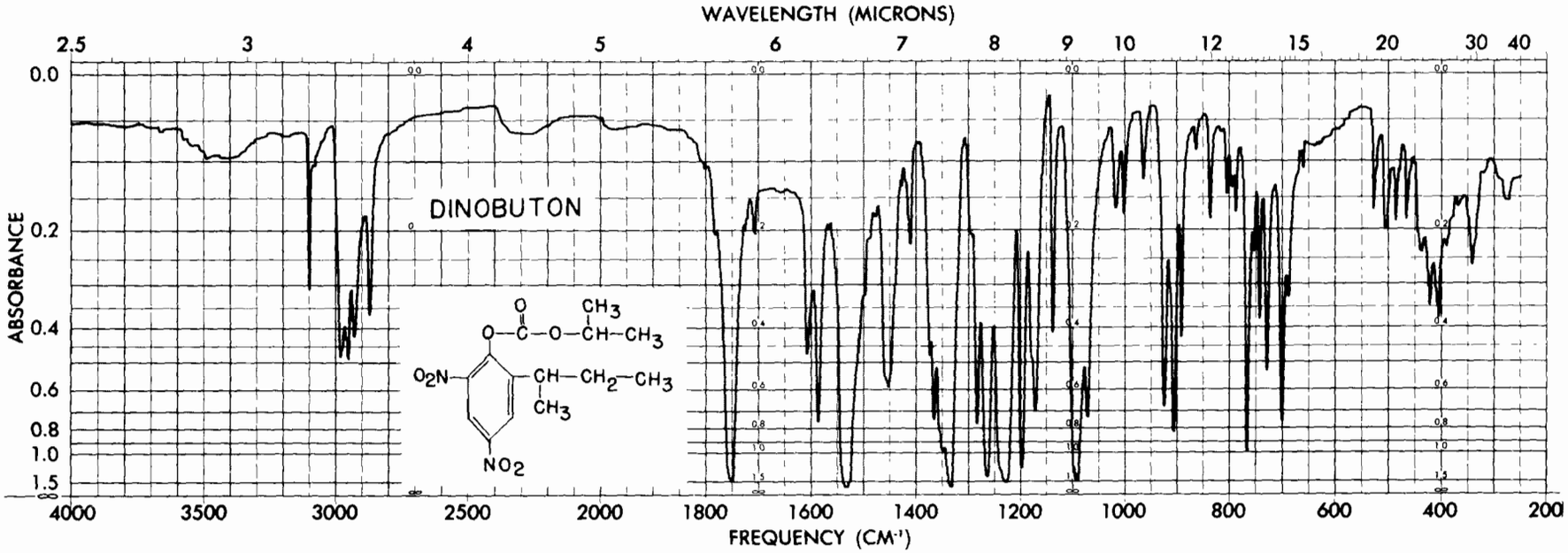

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIMETHYL
PHTHALATE
O
C
O
CH3
C
O
CH3
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

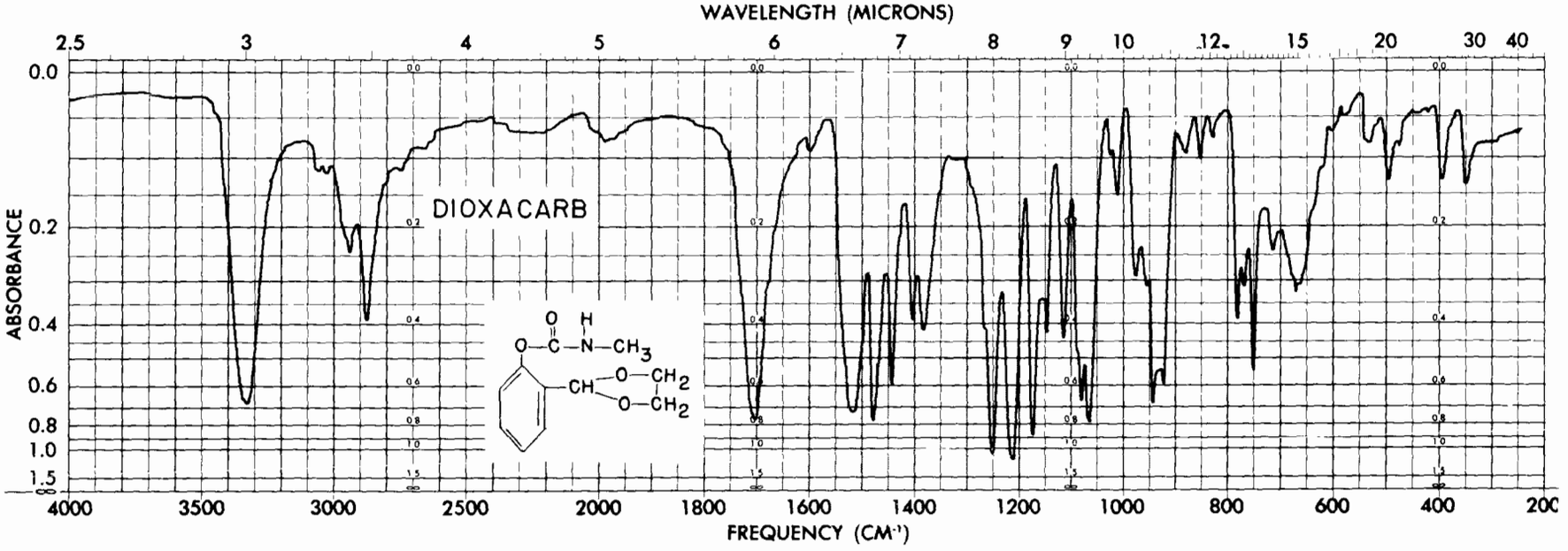

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIMETHOATE
OXYGEN ANALOG
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

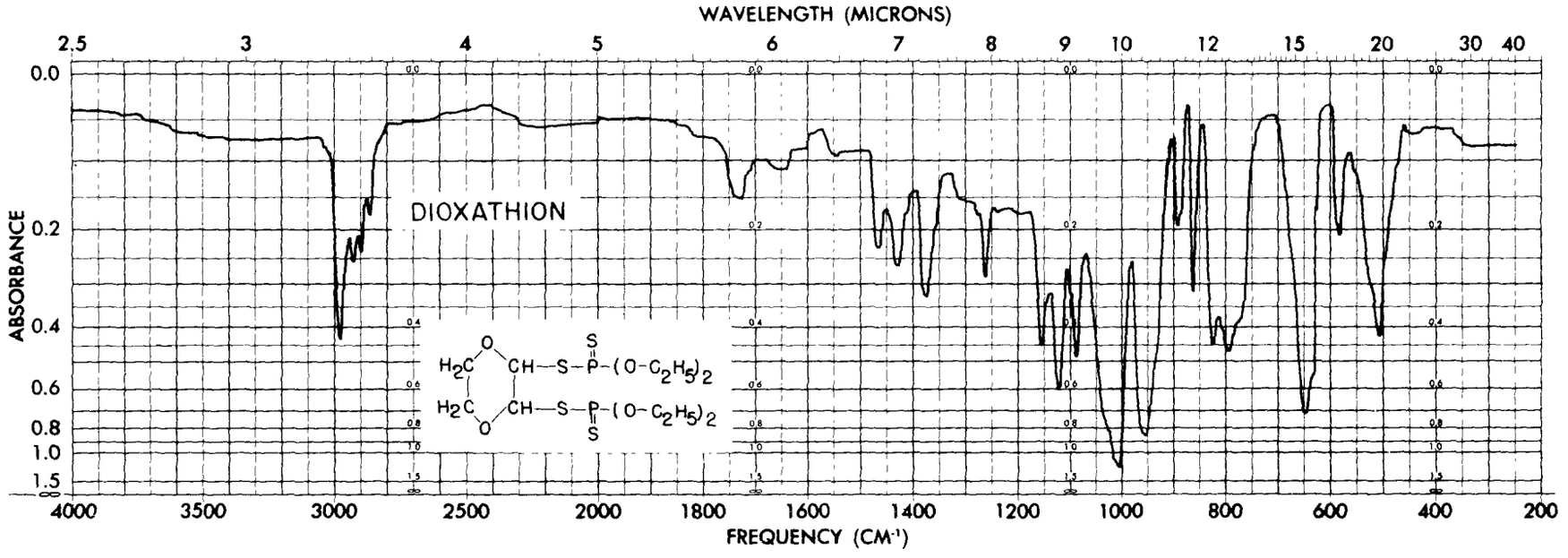

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIMETILAN
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

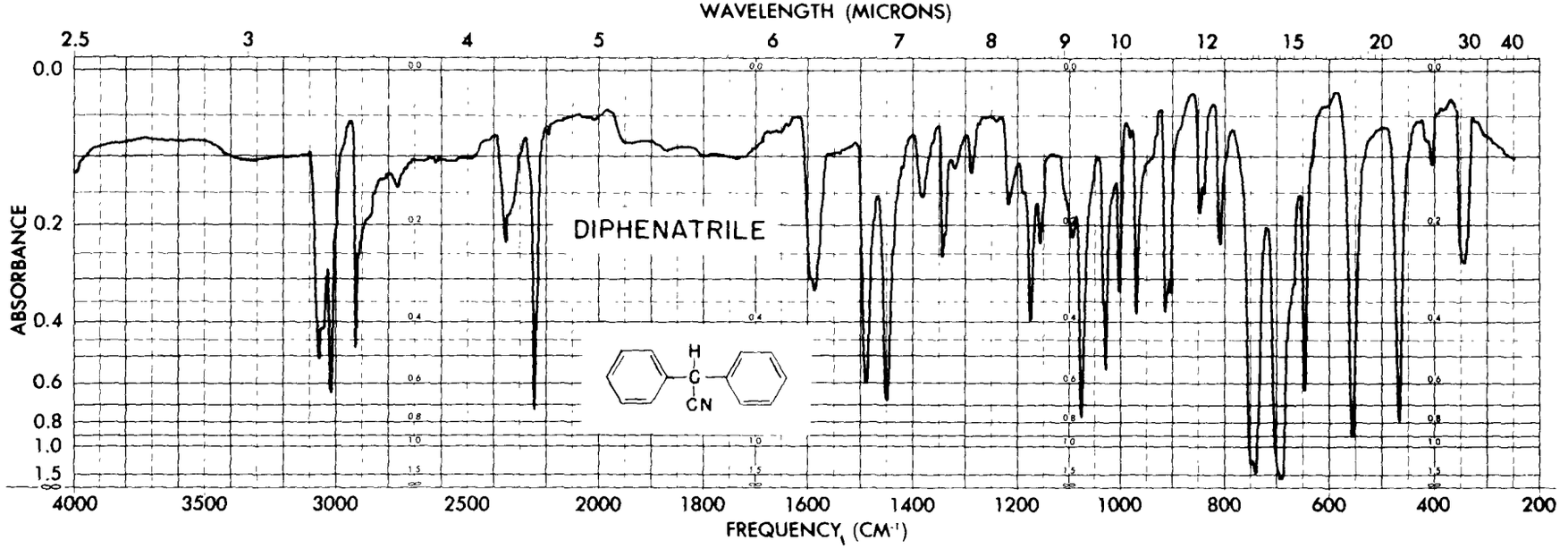

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
DINITRAMINE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
NH2
F3C
NO2
N(C2H5)2
NO2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

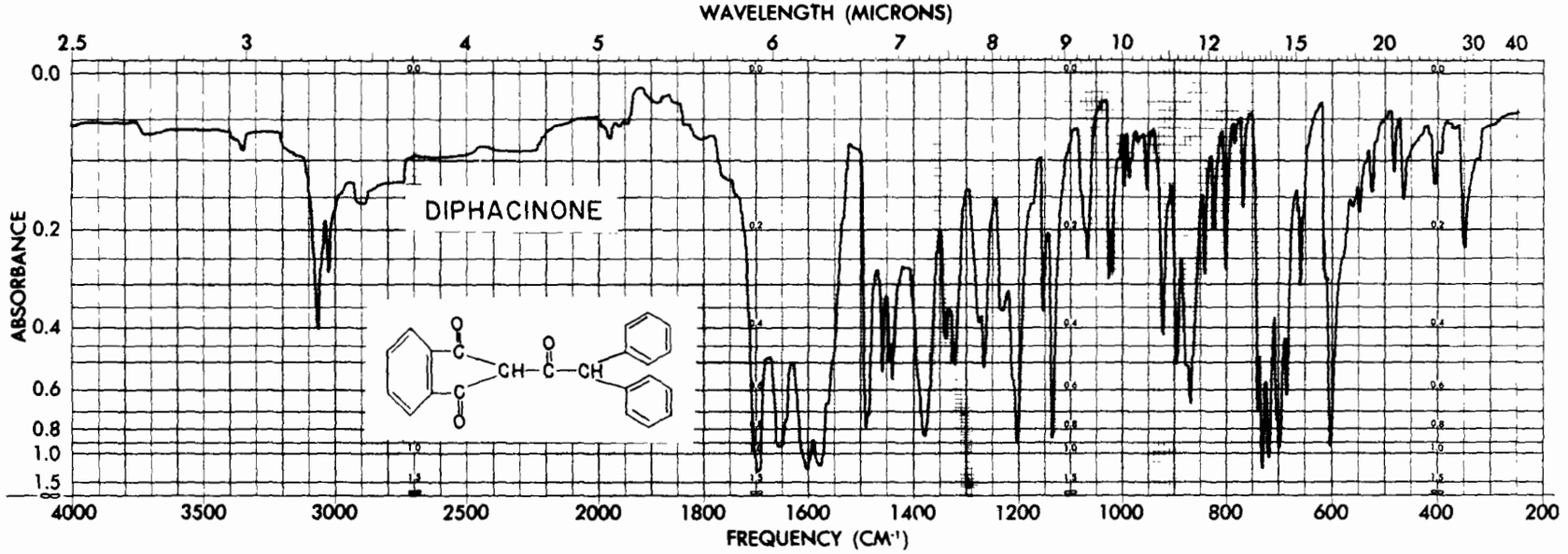

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
DIOXATHION
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
O
S
H2C
CH-S-P-(OC2H5)2
H2C
CH-S-P-(OC2H5)2
O
S
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

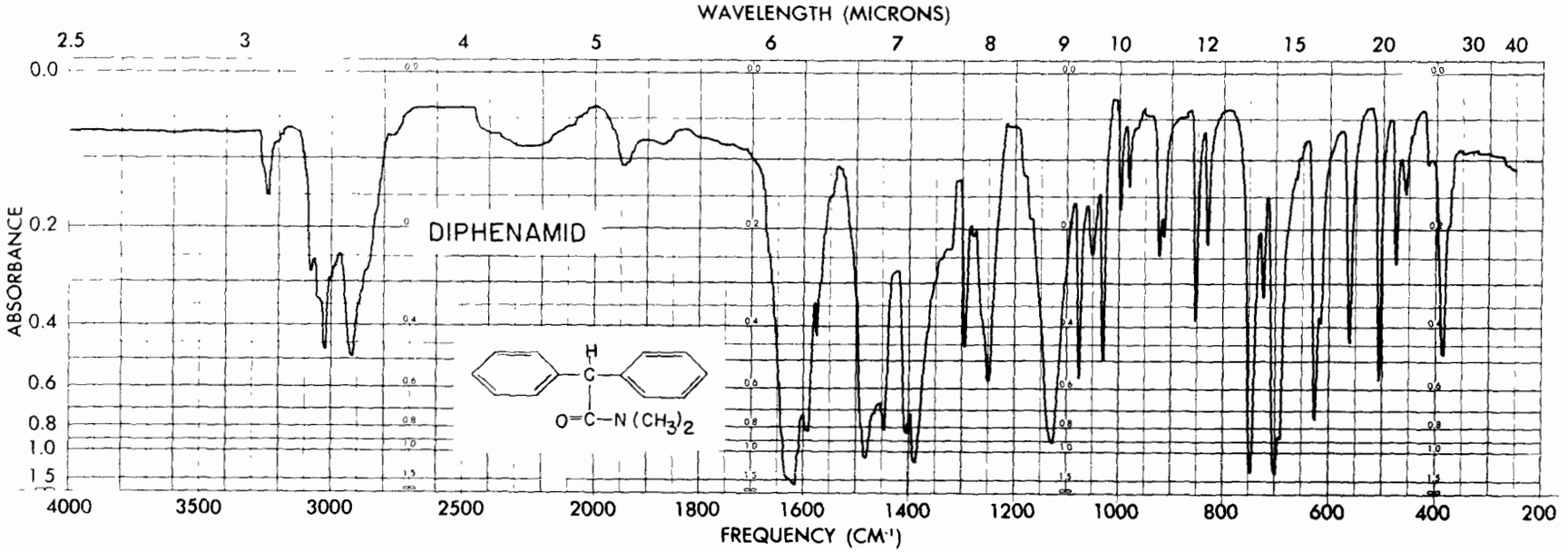

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DINOBUTON
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
FREQUENCY (CM⁻¹)

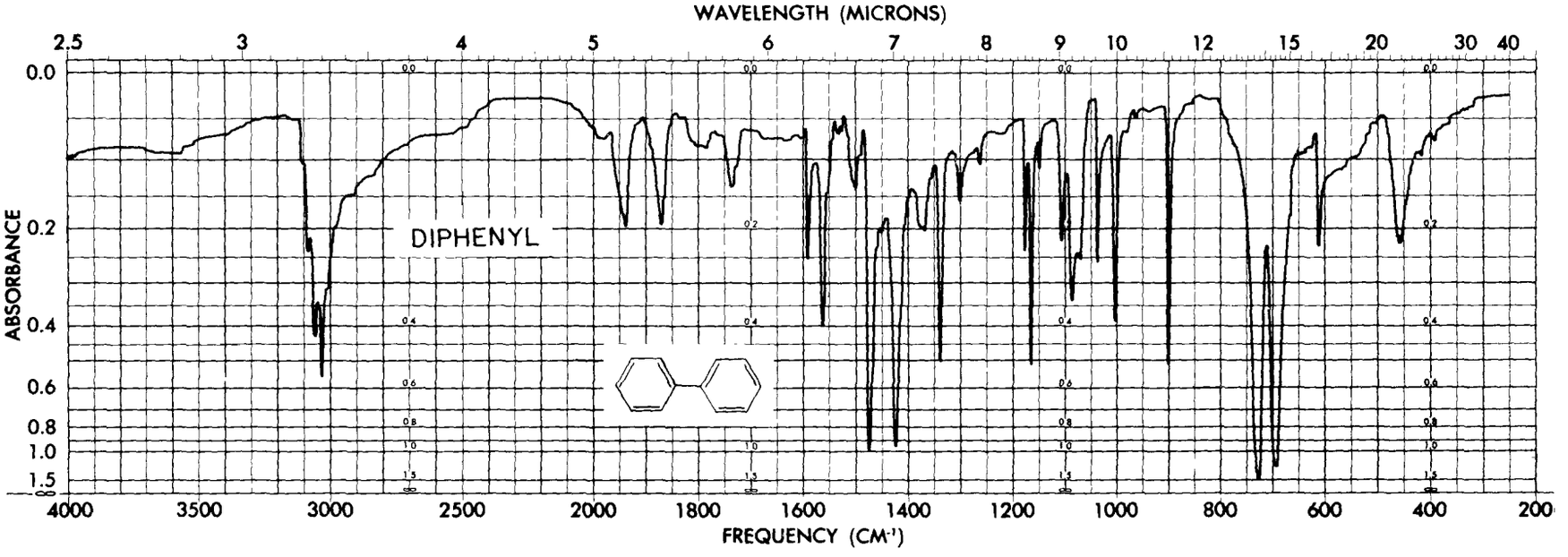

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIOXACARB
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
FREQUENCY (CM⁻¹)

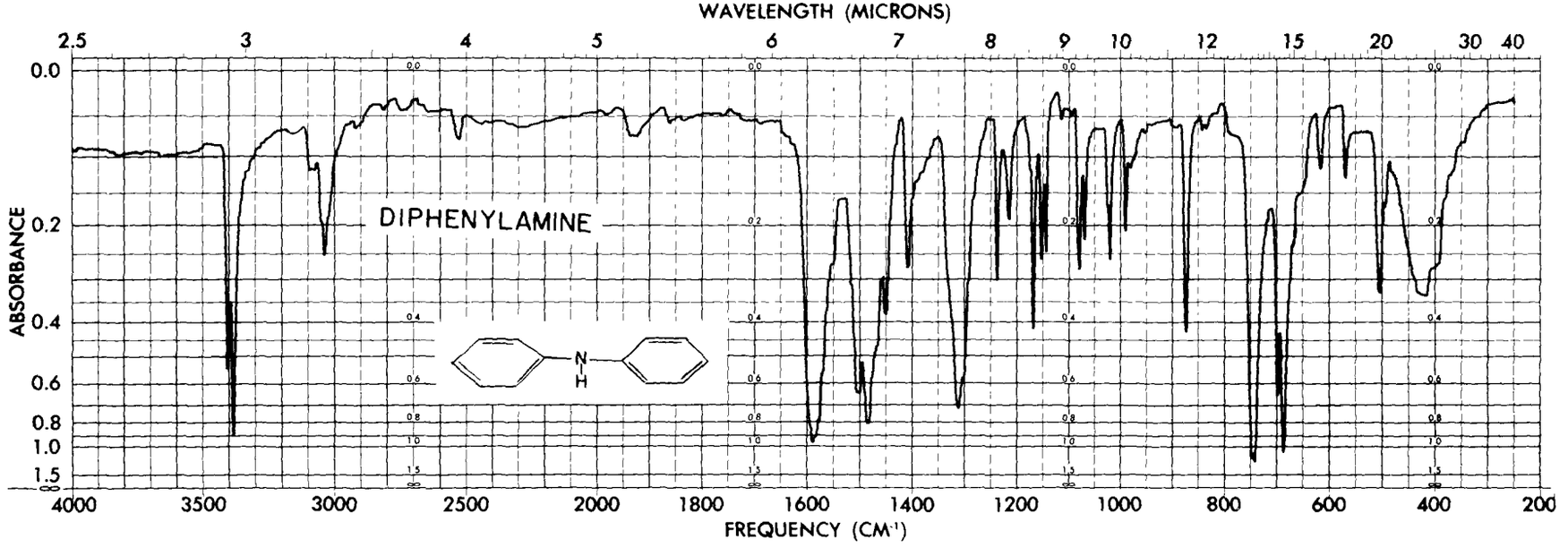

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIOXATHION
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

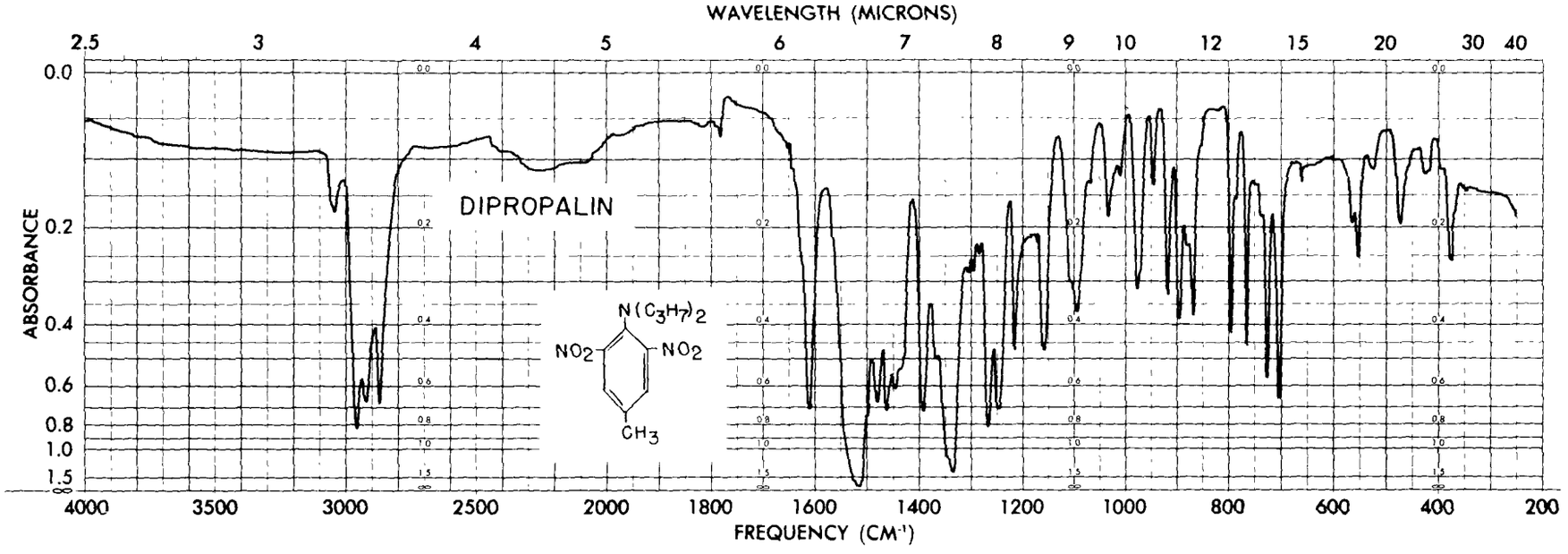

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIPHENATRILE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY, (CM⁻¹)

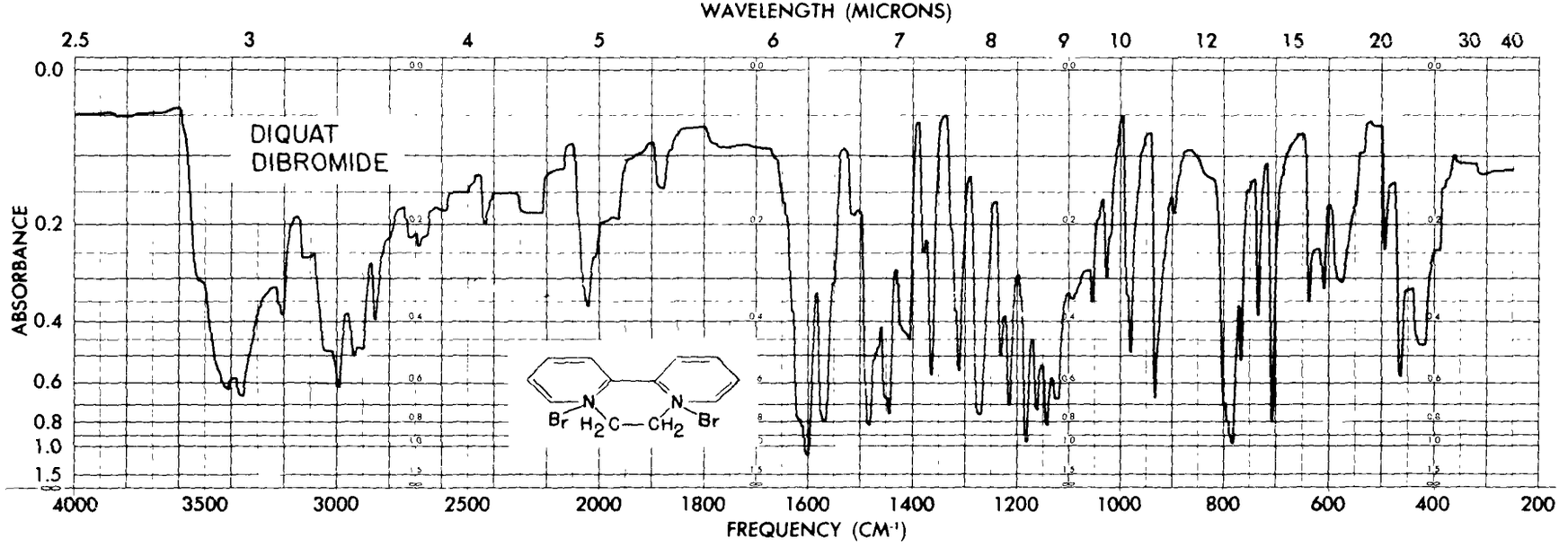

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIPHACINONE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

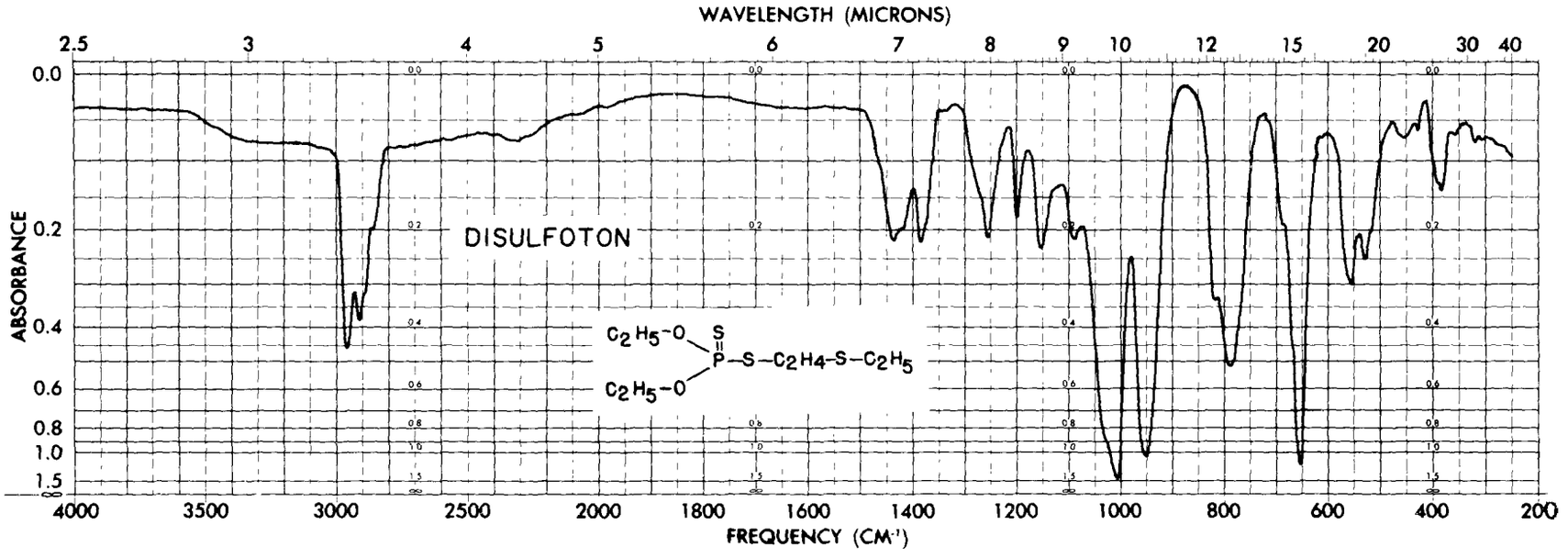

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIPHENAMID
O=C—N(CH3)2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

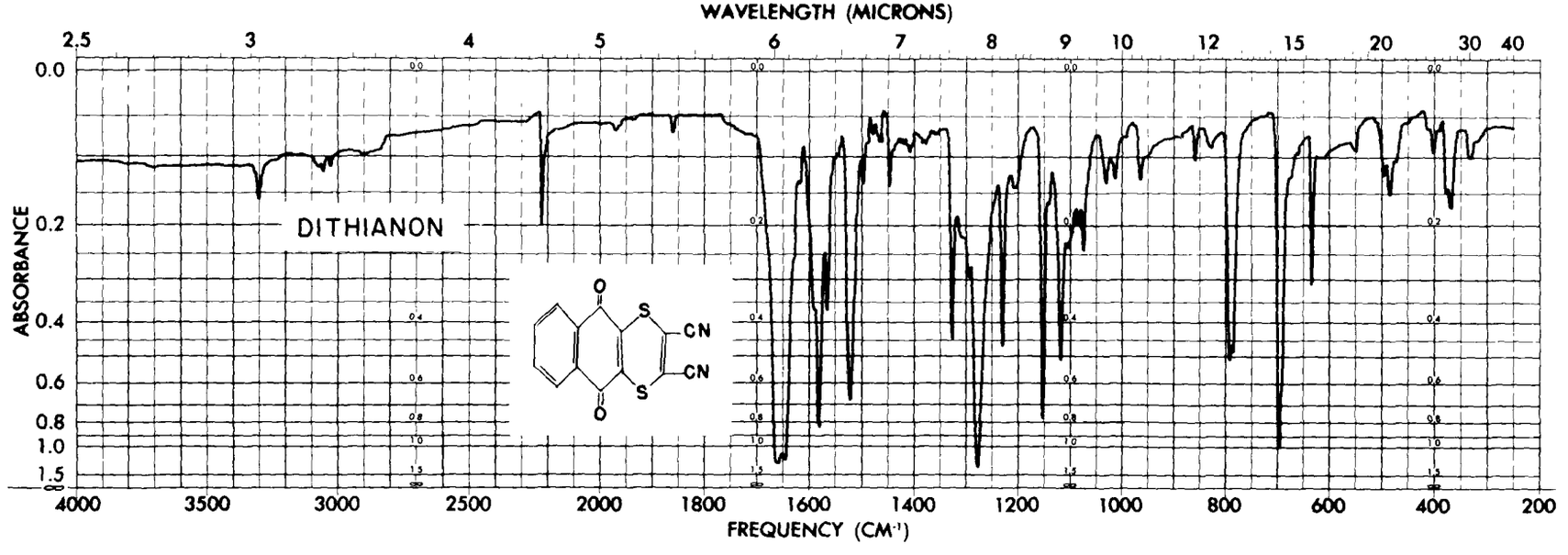

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIPHENYL
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

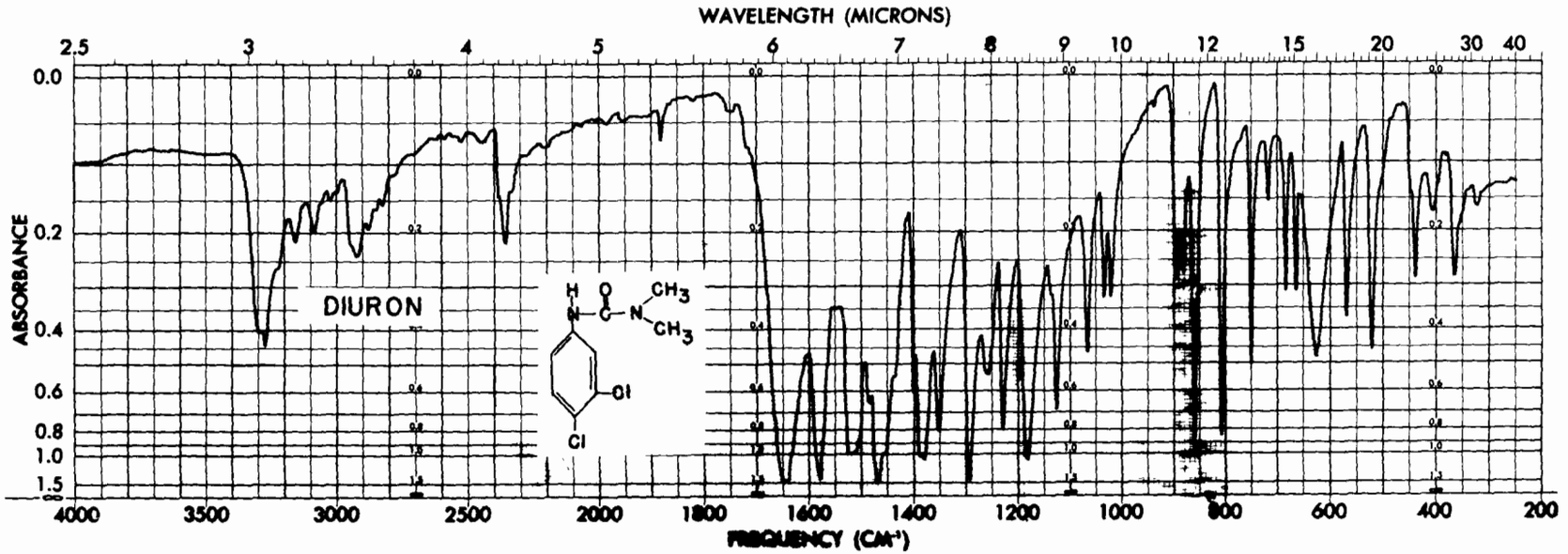

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIPHENYLAMINE
N
H
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

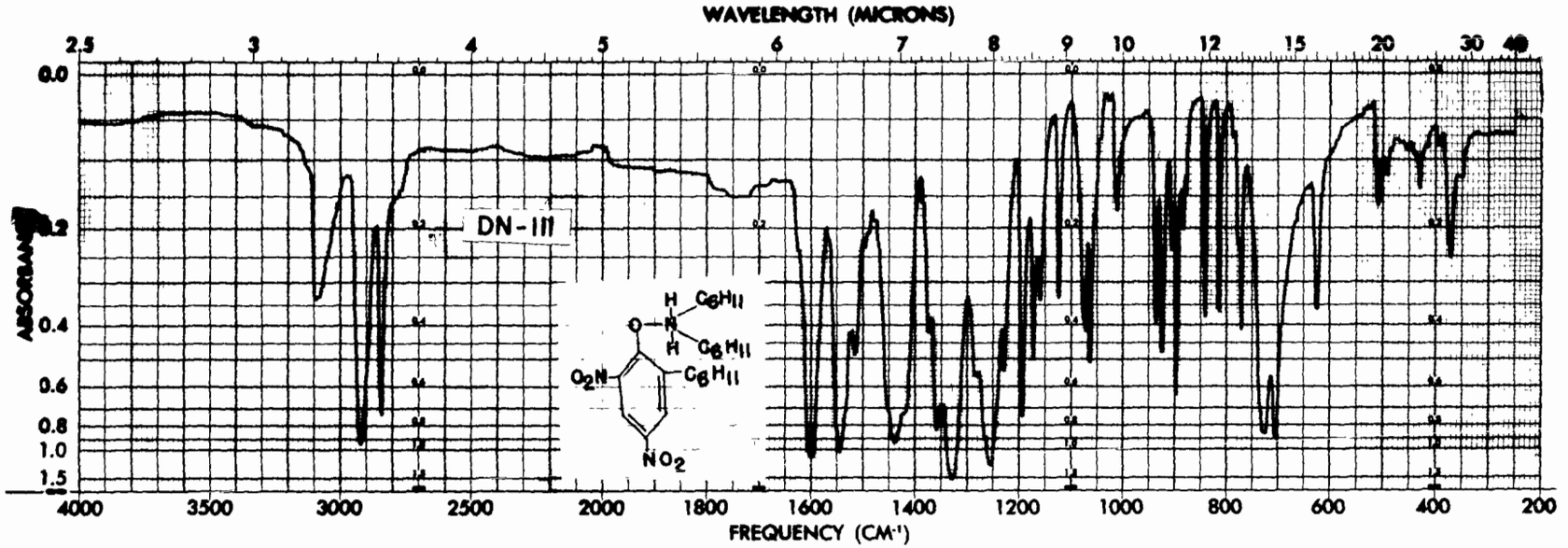

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIPROPALIN
N(C3H7)2
NO2
NO2
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

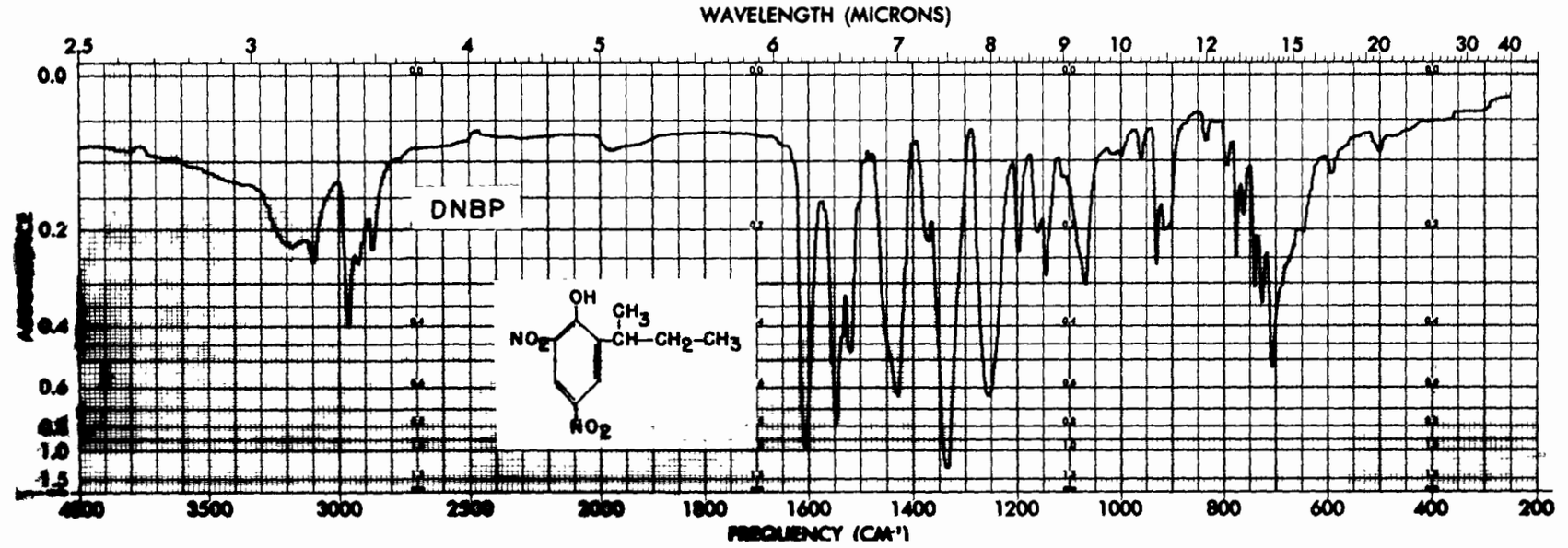

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DIQUAT
DIBROMIDE
N
N
Br
H2C
CH2
Br
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

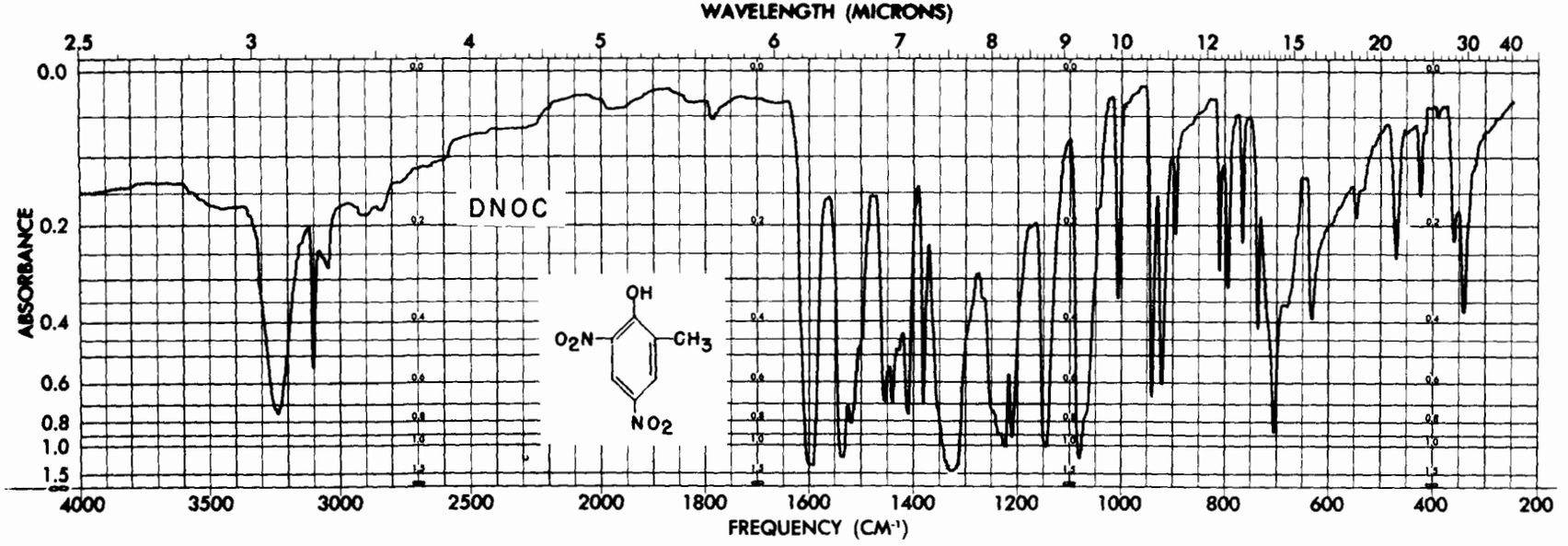

WAVELENGTH (MICRONS)
2.5 3 4 5 6 7 8 9 10 12 15 20 30 40
ABSORBANCE
0.0 0.2 0.4 0.6 0.8 1.0 1.5
DISULFOTON
C_2H_5-O S
P–S–C_2H_4–S–C_2H_5
C_2H_5-O
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 200
FREQUENCY (CM^{-1})

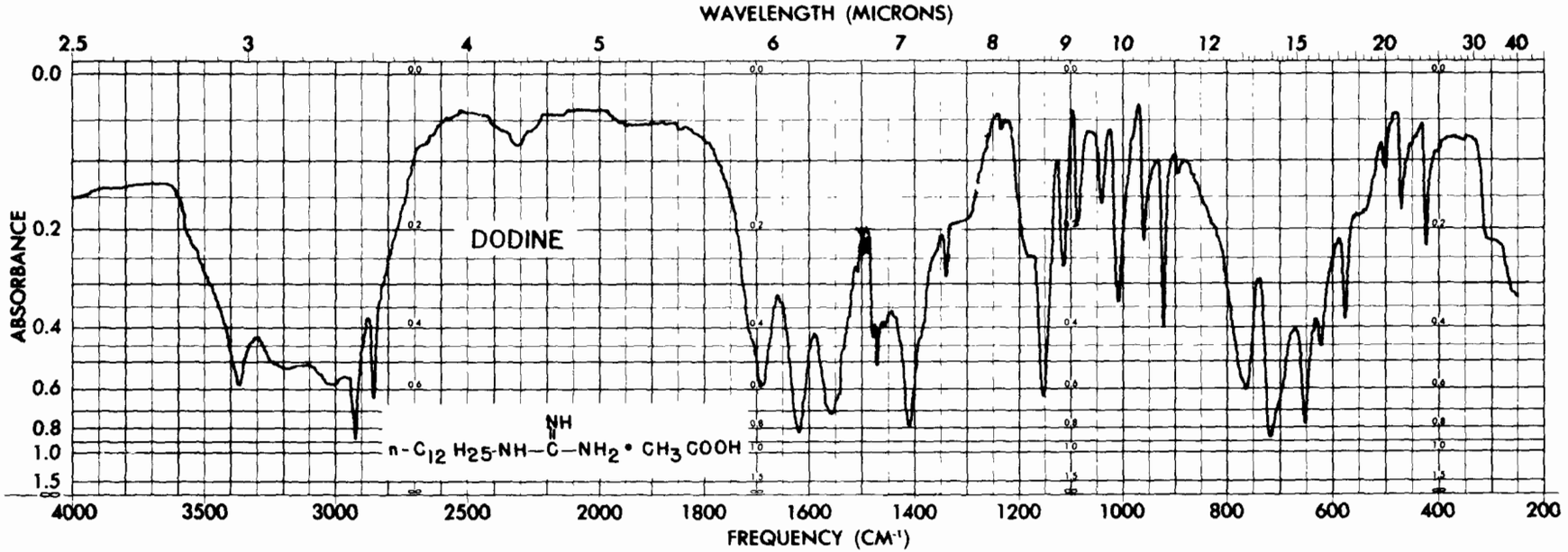

WAVELENGTH (MICRONS)
2.5 3 4 5 6 7 8 9 10 12 15 20 30 40
ABSORBANCE
0.0 0.2 0.4 0.6 0.8 1.0 1.5
DITHIANON
O
S
CN
CN
S
O
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 200
FREQUENCY (CM^{-1})

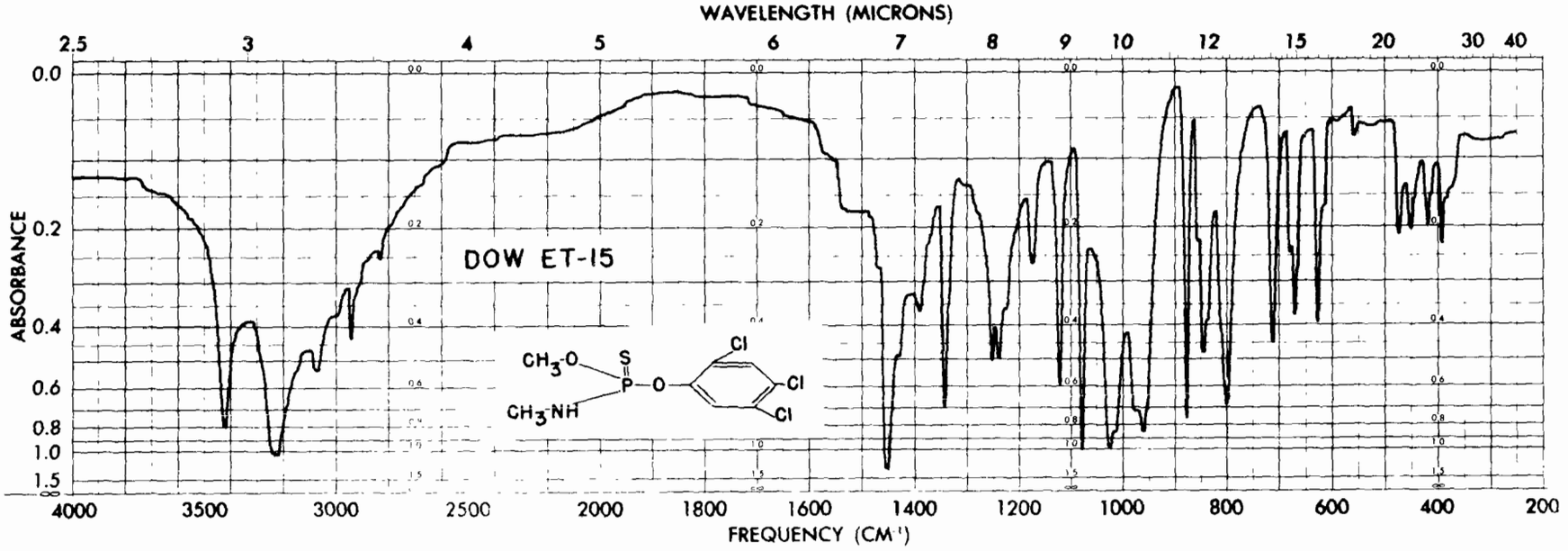

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
DIURON
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

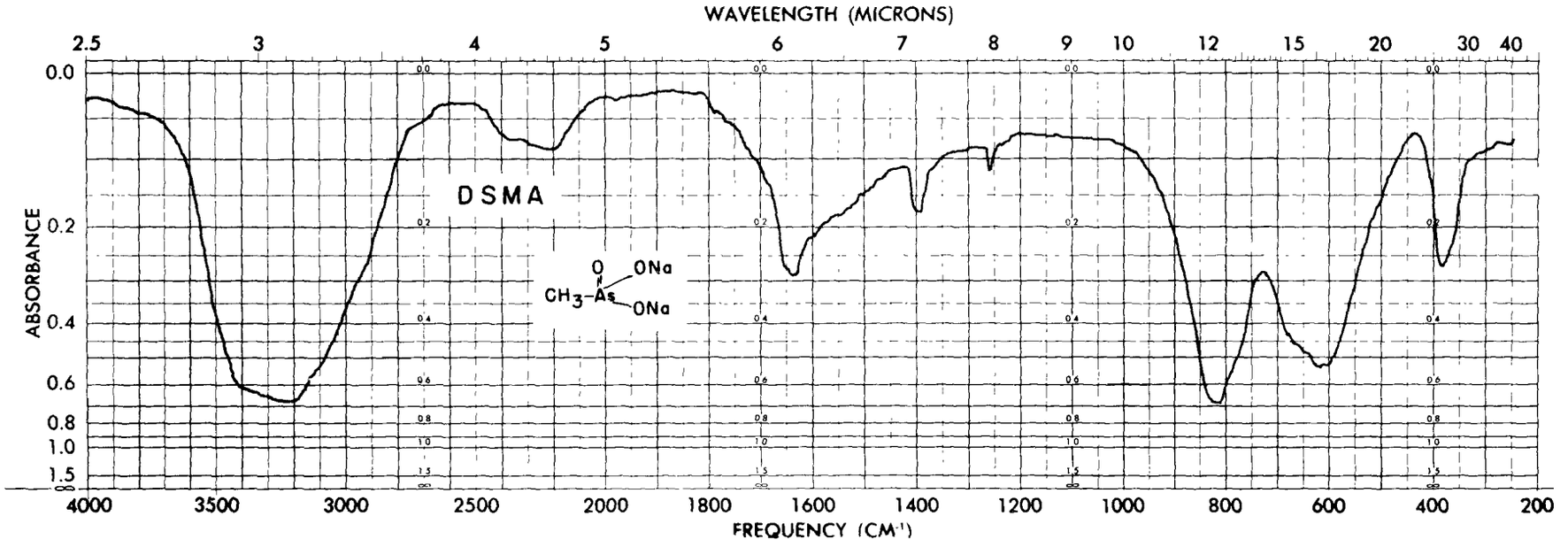

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
0.0
0.4
0.6
0.8
1.0
1.5
DN-111
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

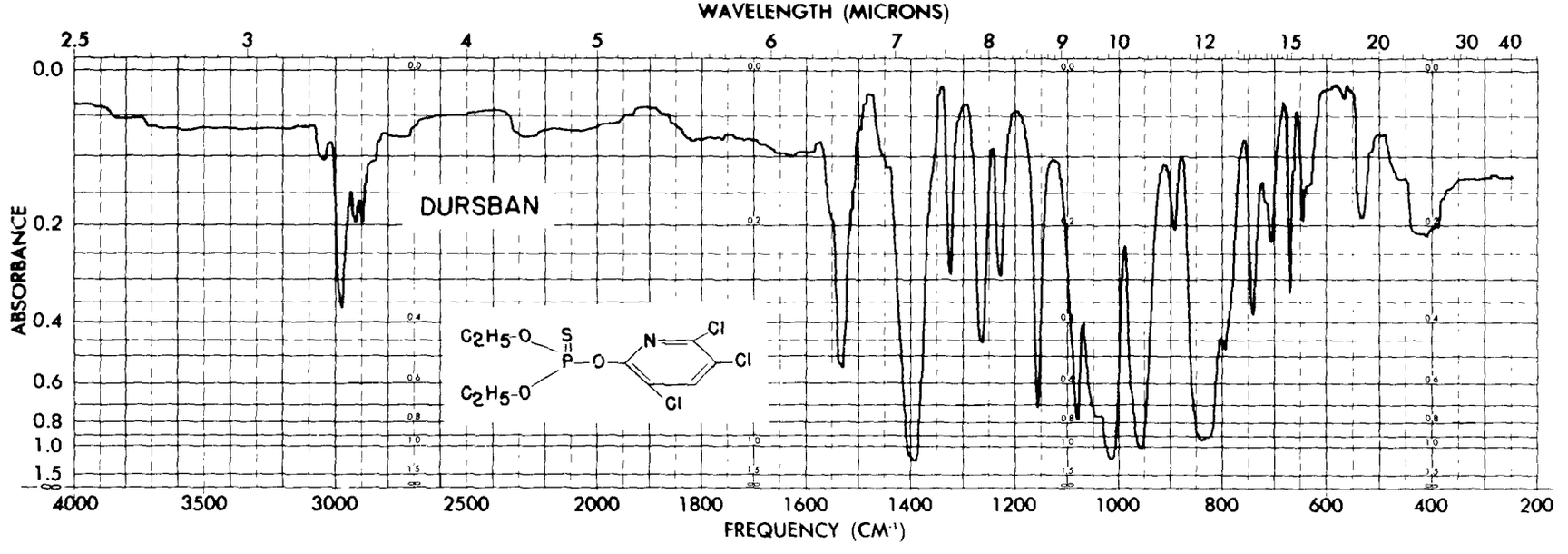

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
1.0
1.5
DNBP
OH
CH3
NO2
CH–CH2–CH3
NO2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

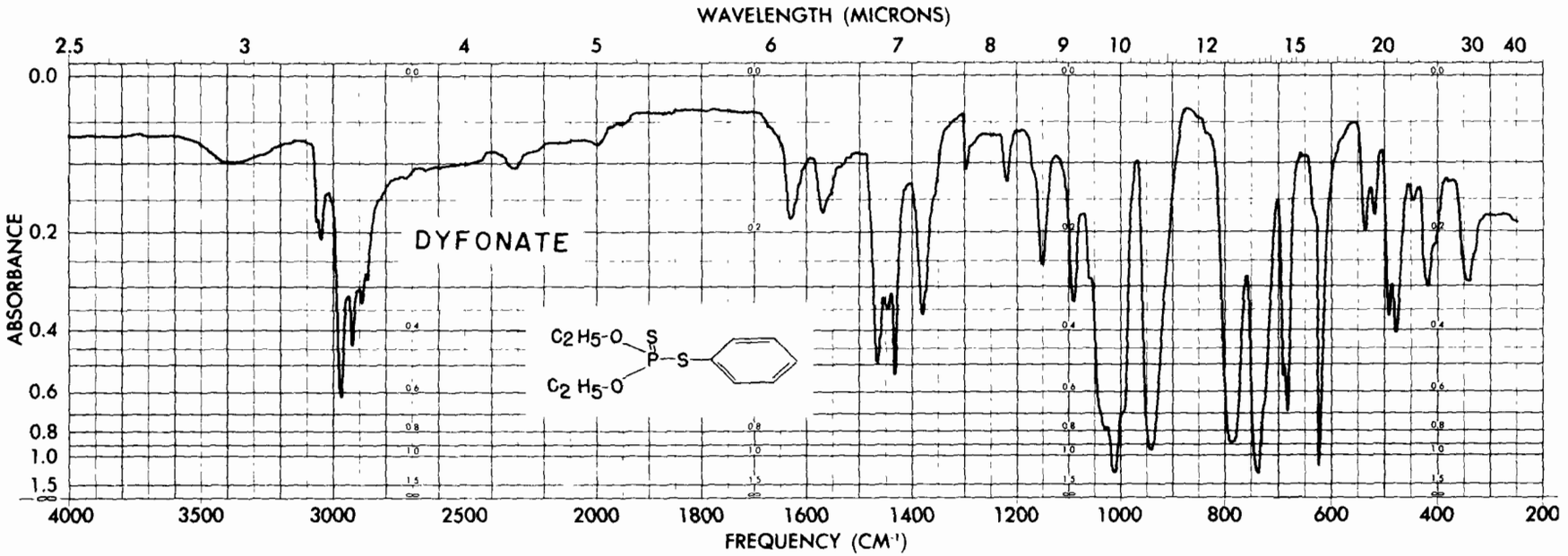

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
DNOC
OH
O2N
CH3
NO2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

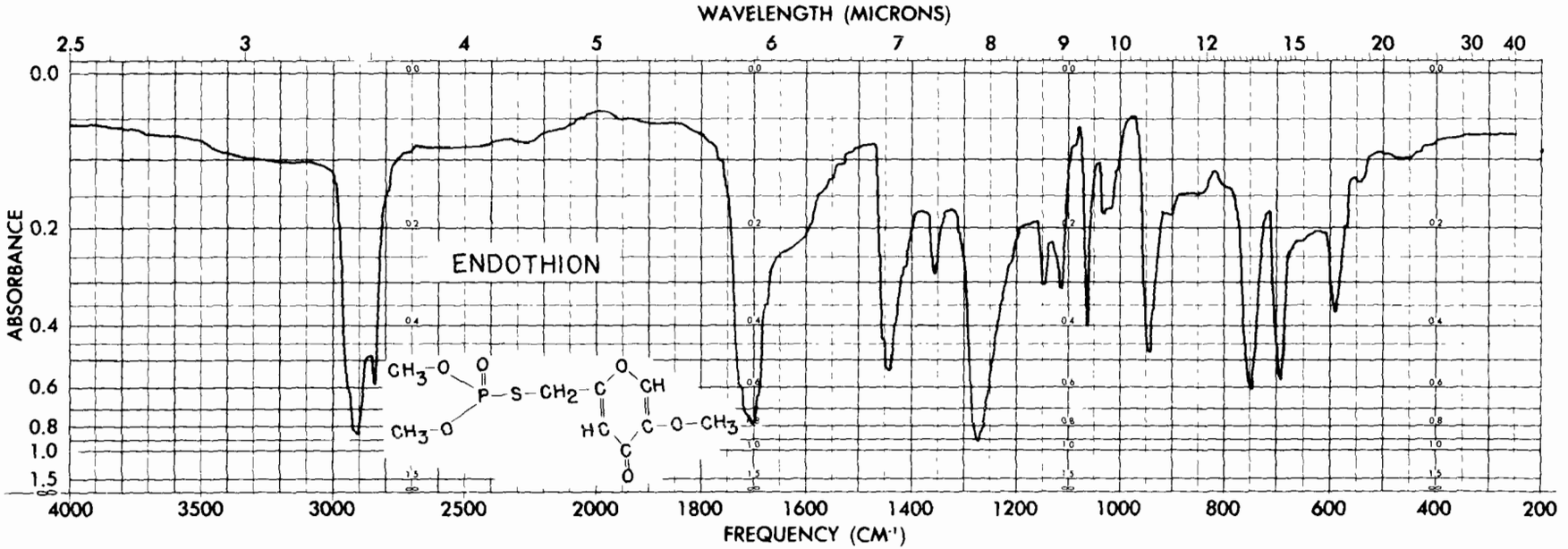

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DODINE
NH
n-C12 H25-NH-C-NH2 • CH3 COOH
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

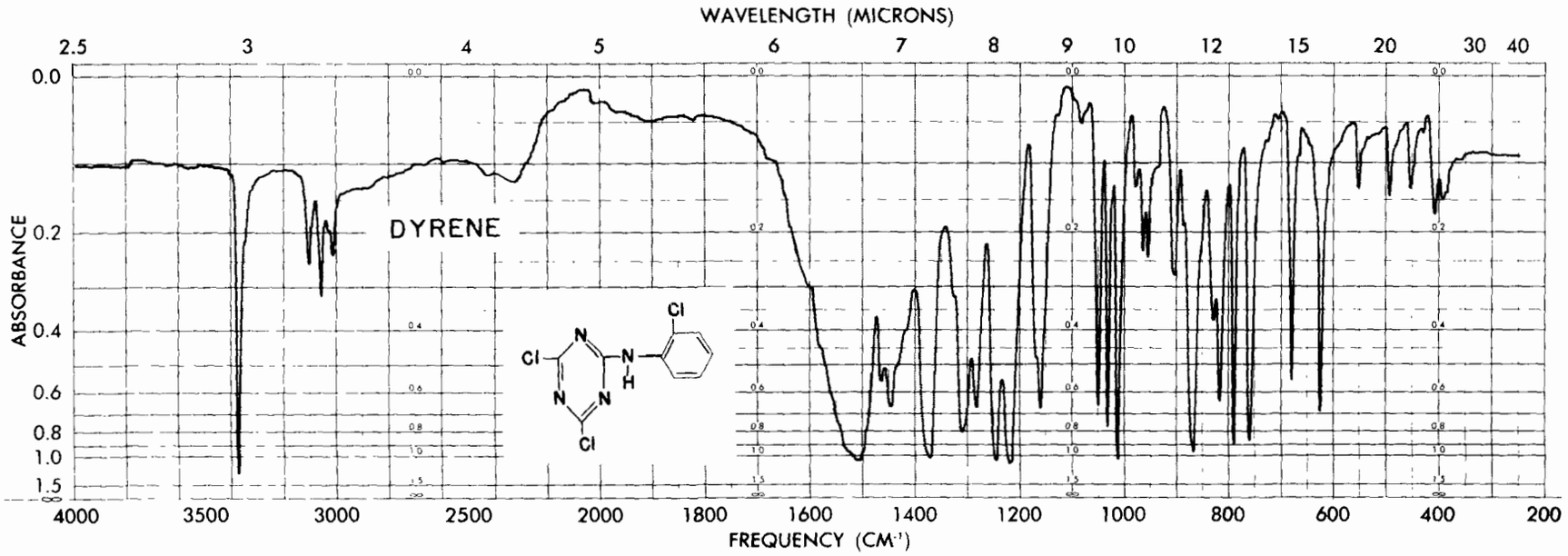

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DOW ET-15
CH3-O
S
P
O
CH3-NH
Cl
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

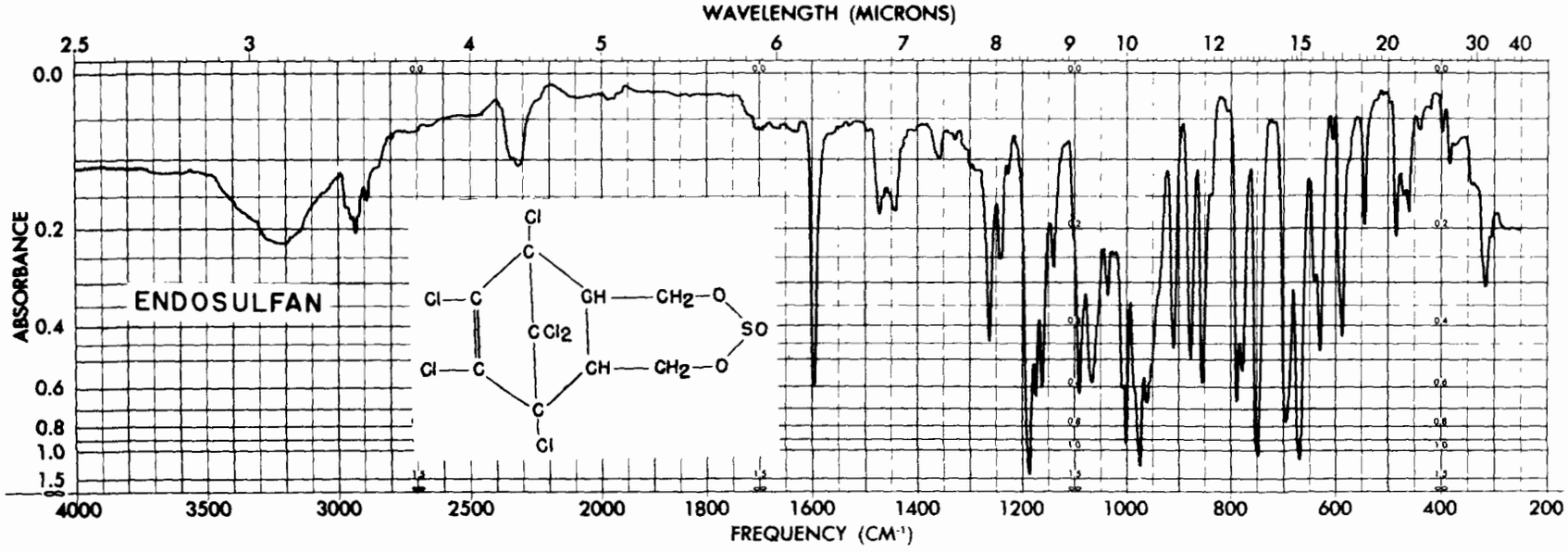

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
DSMA
O
ONa
CH3–As
ONa
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

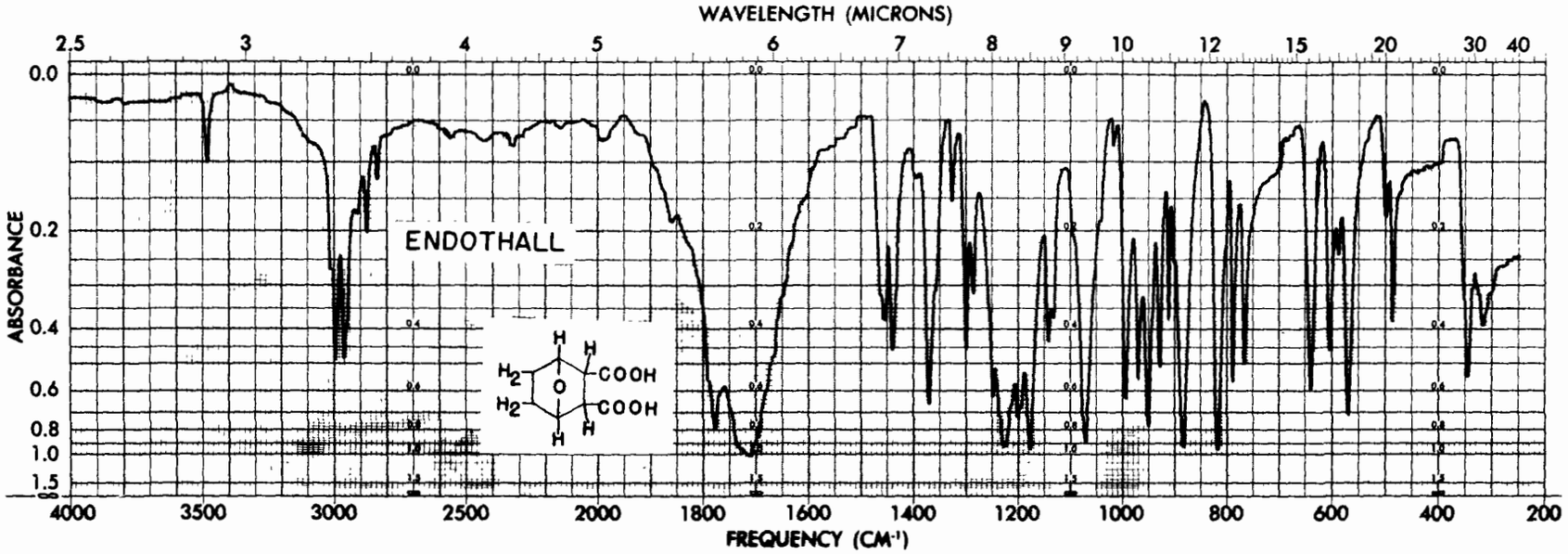

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
DURSBAN
C2H5-O
S
P
O
N
Cl
Cl
Cl
C2H5-O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

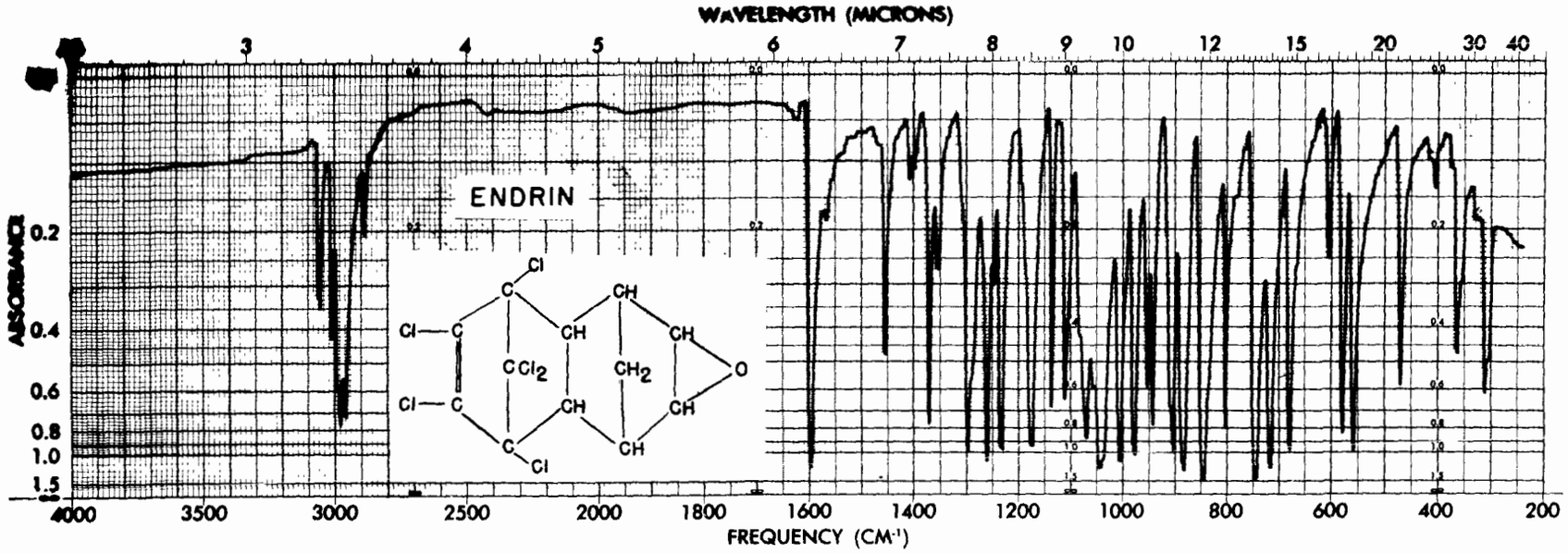

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DYFONATE
C2 H5-O
S
P
S
C2 H5-O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

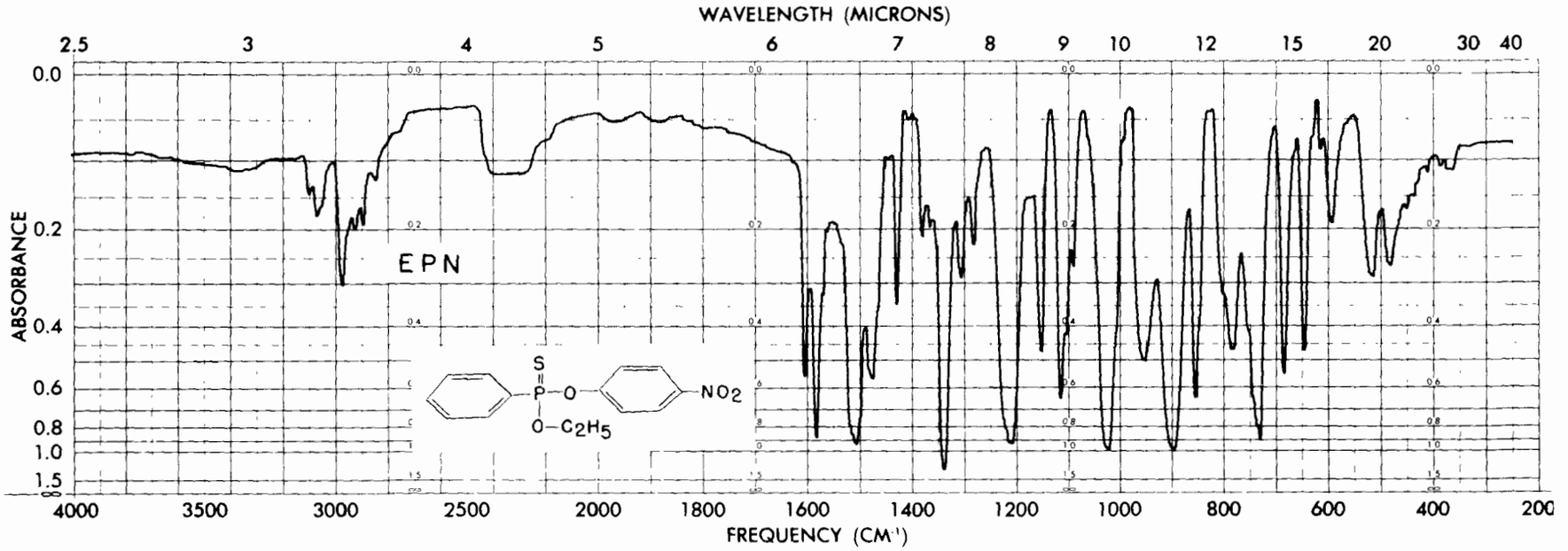

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ENDOTHION
CH3-O
O
P
S-CH2-C
O
CH
CH3-O
HC
C-O-CH3
C
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

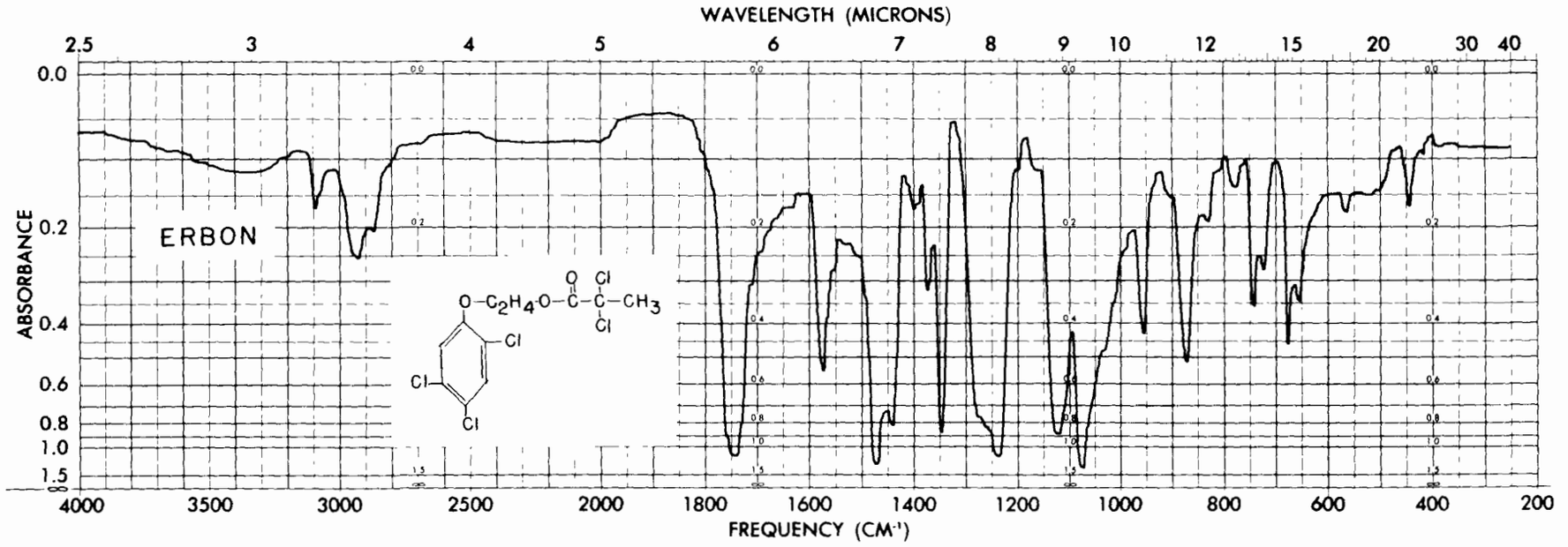

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
DYRENE
Cl
N
Cl
N
N
H
N
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

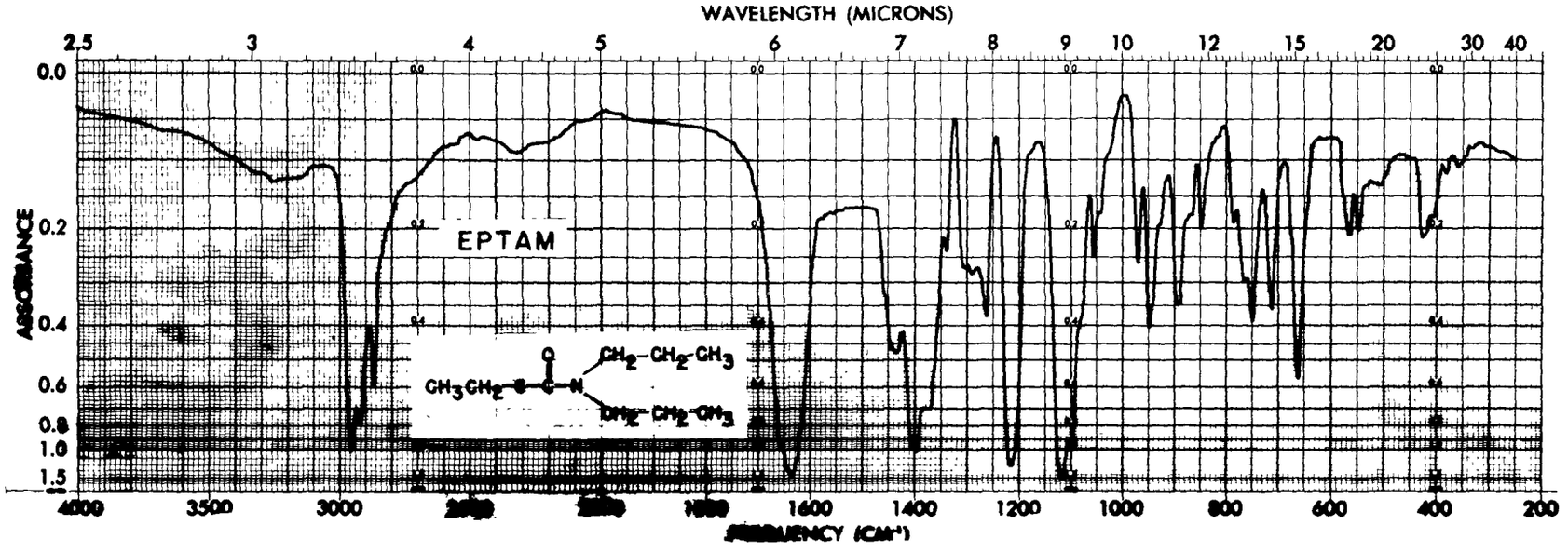

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ENDOSULFAN
Cl
C
Cl—C
CH—CH2—O
CCl2
SO
Cl—C
CH—CH2—O
C
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

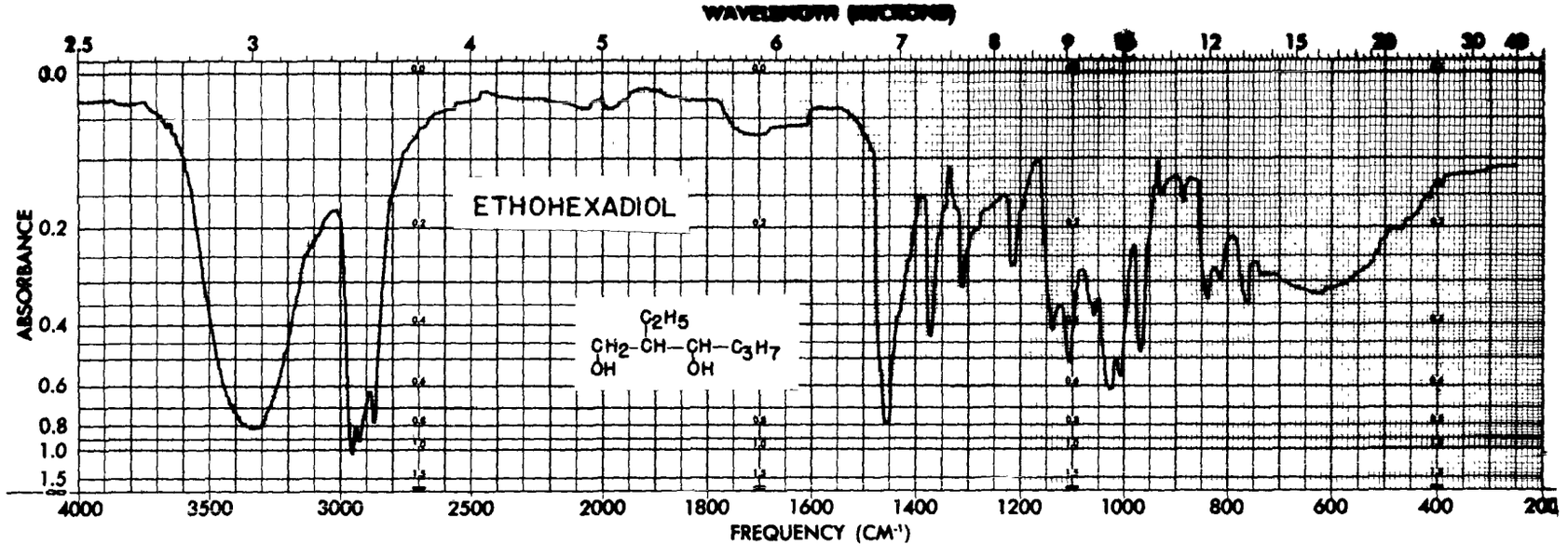

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ENDOTHALL
COOH
COOH
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

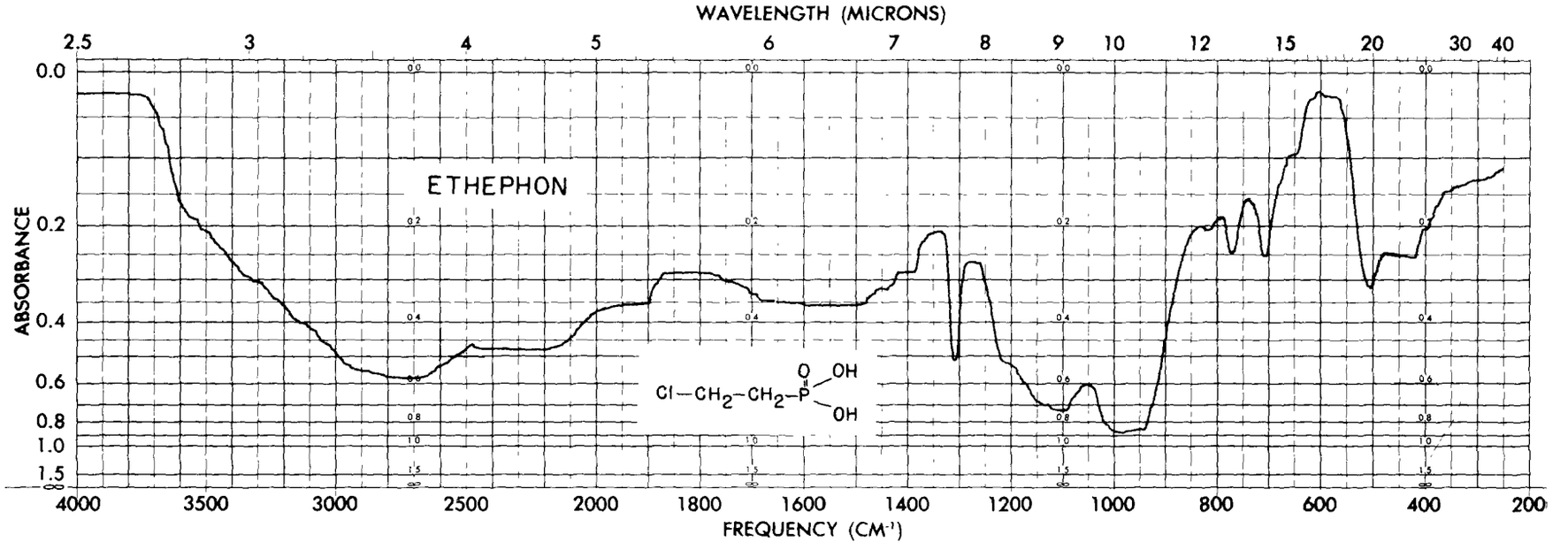

WAVELENGTH (MICRONS)
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.2
0.4
0.6
0.8
1.0
1.5
ENDRIN
Cl
CCl2
CH2
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

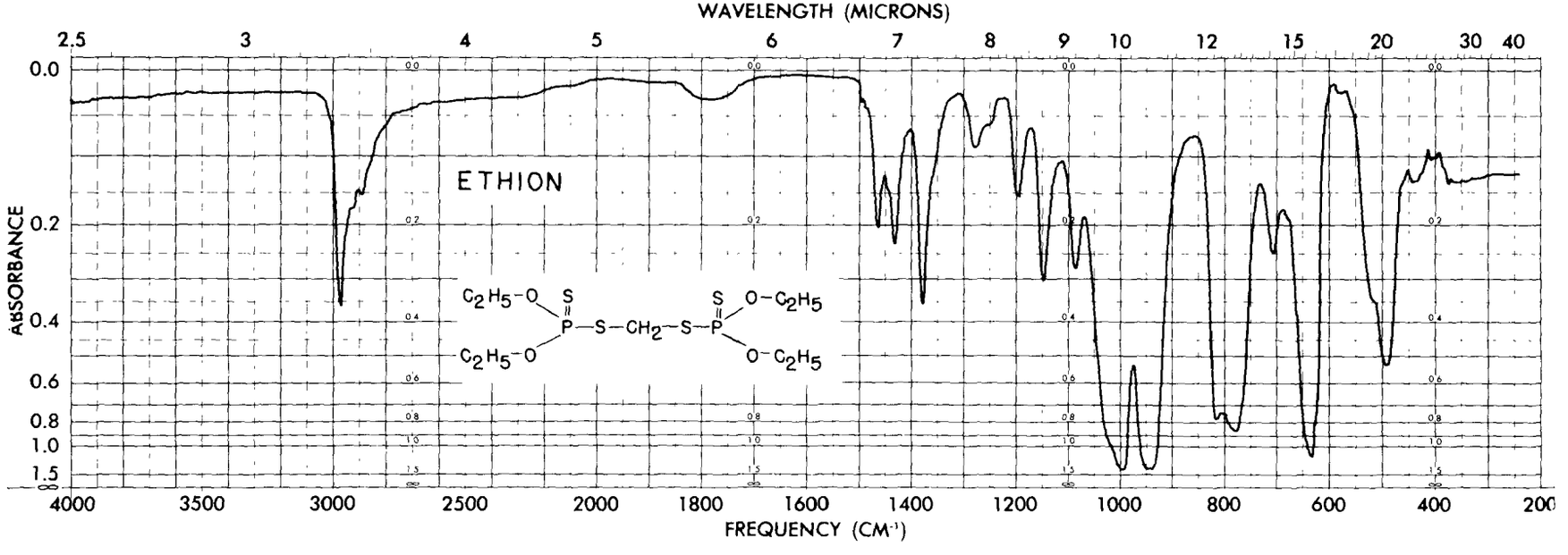

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
EPN
S
P
O
NO2
O–C2H5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

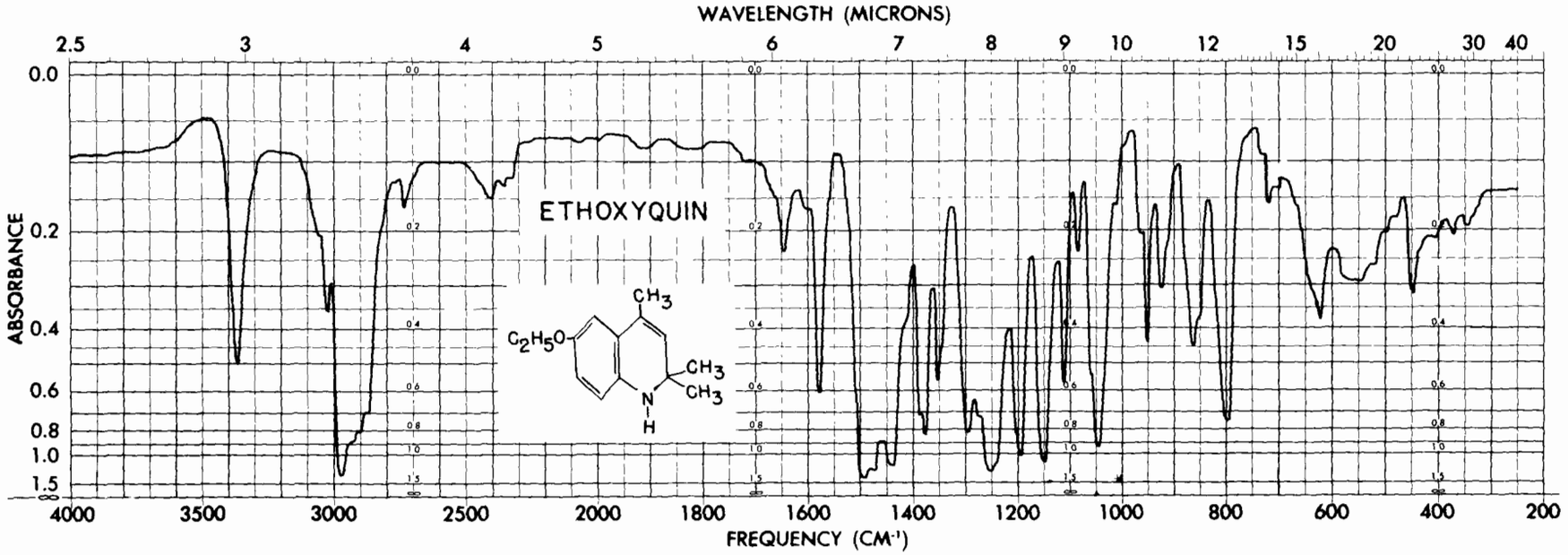

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ERBON
O–C2H4–O–C–C–CH3
O
Cl
Cl
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

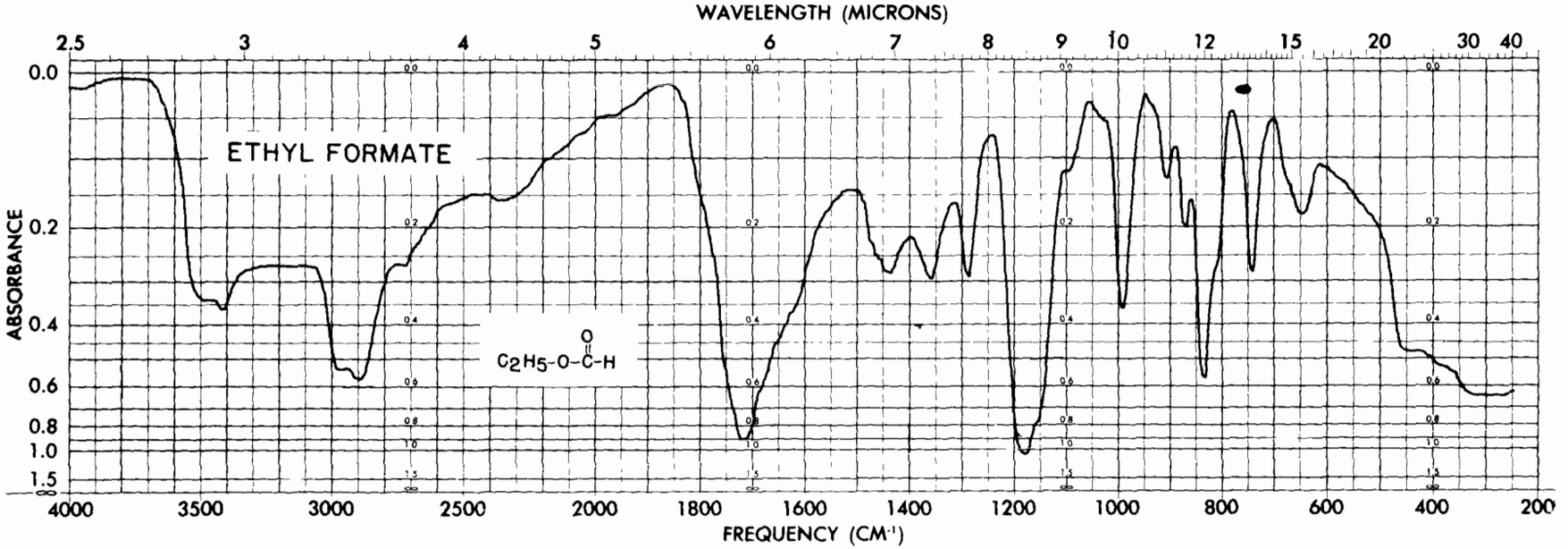

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
EPTAM
4000
3500
3000
1600
1400
1200
1000
800
600
400
200

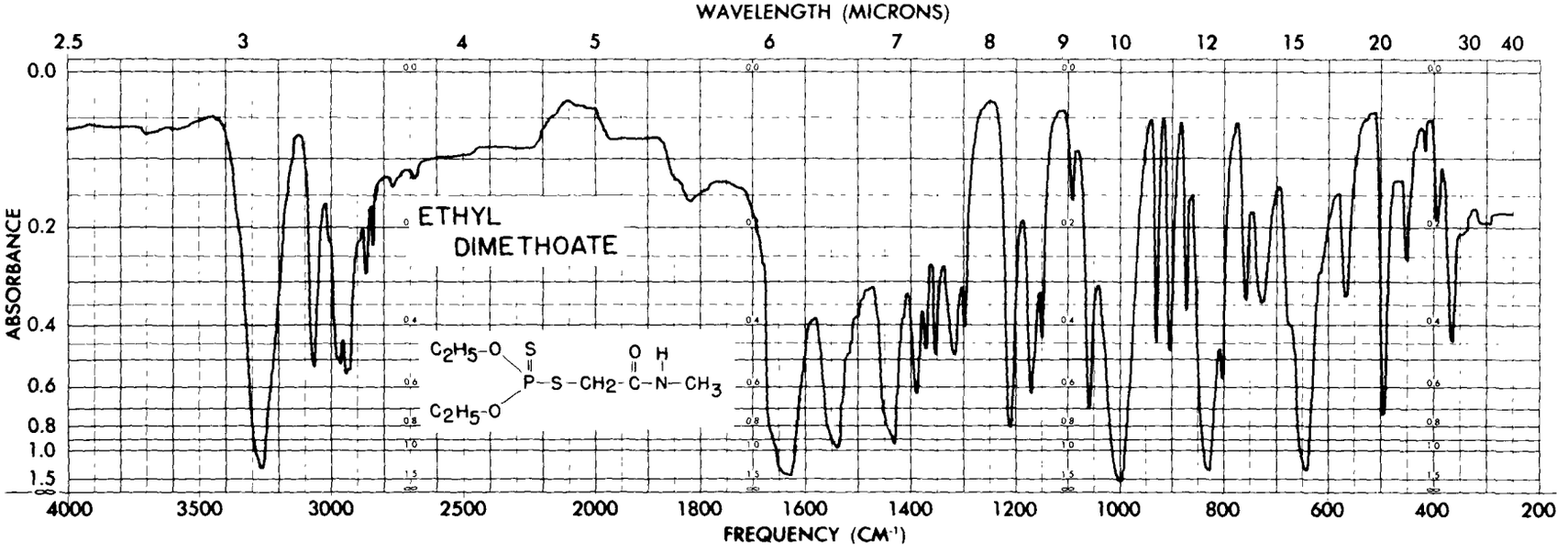

2.5
3
4
5
6
7
12
15
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
ETHOHEXADIOL
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
FREQUENCY (CM⁻¹)

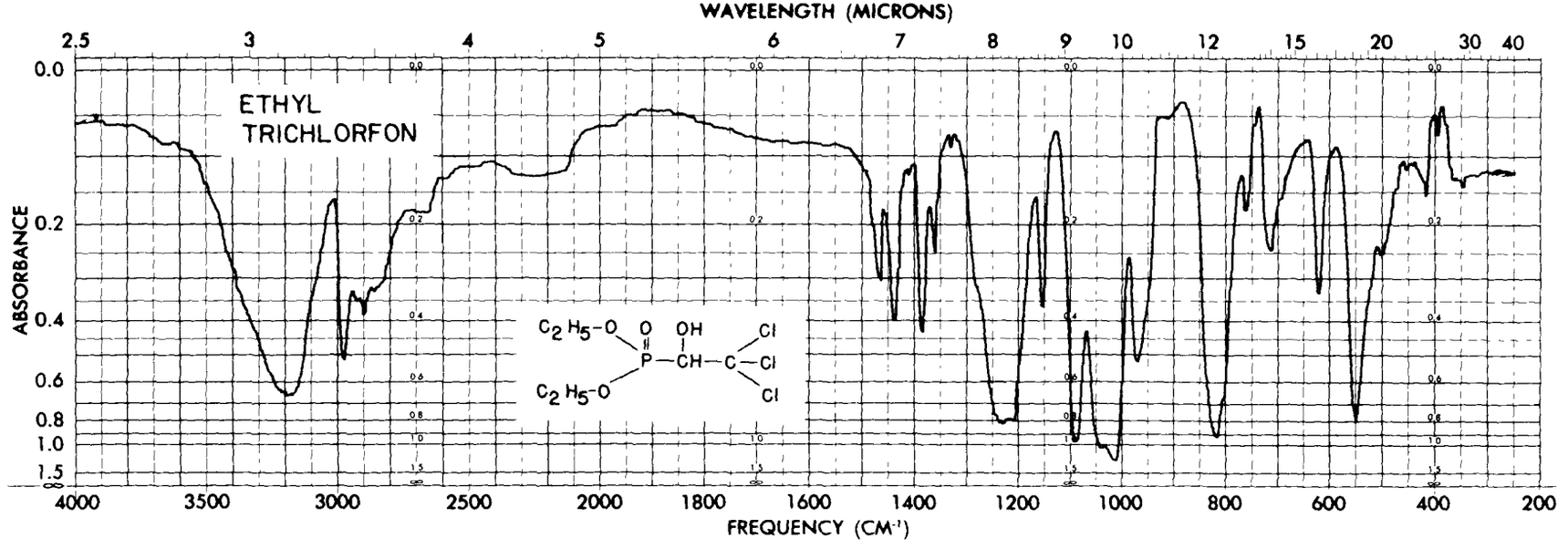

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ETHEPHON
Cl—CH2—CH2—P(=O)(OH)—OH
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

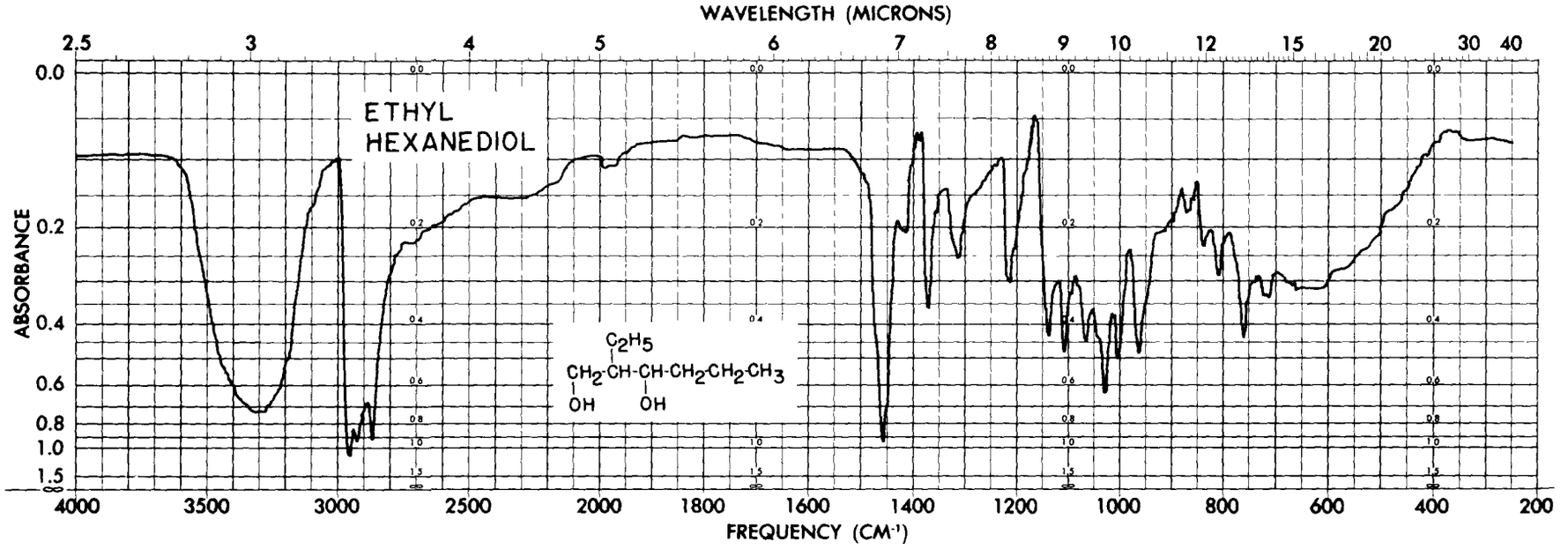

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ETHION
(C2H5-O)2P(=S)-S-CH2-S-P(=S)(O-C2H5)2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

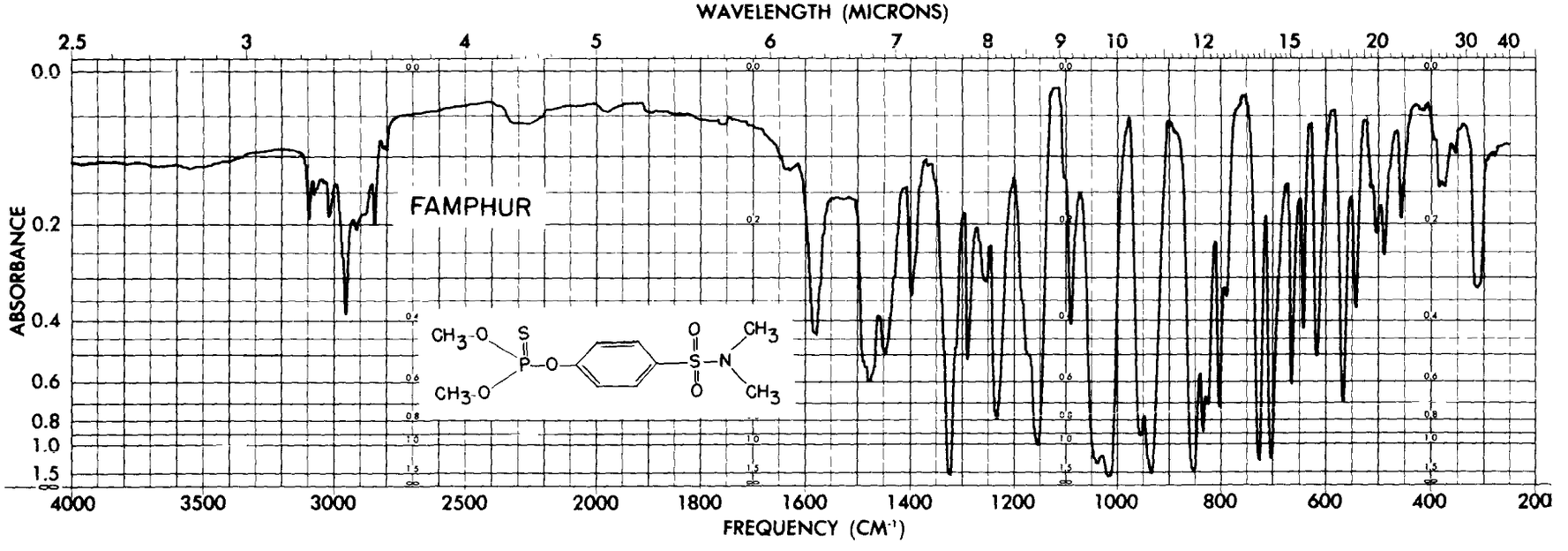

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ETHOXYQUIN
C_2H_5O
CH_3
CH_3
CH_3
N
H
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

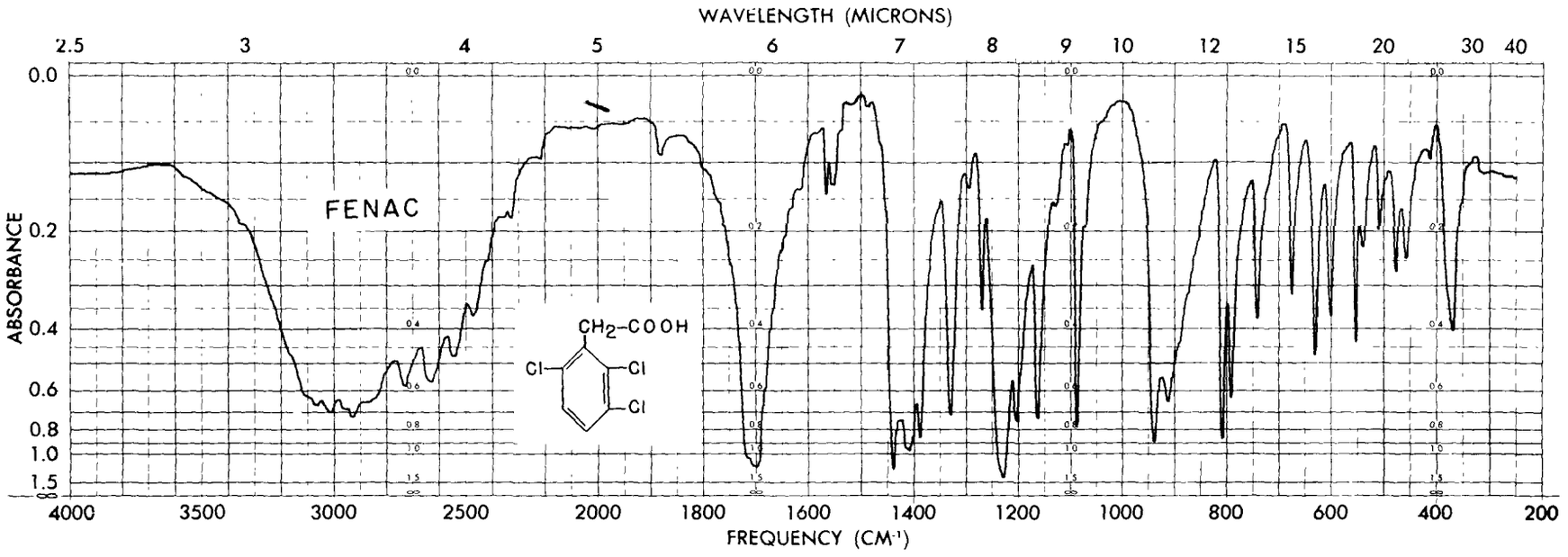

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ETHYL FORMATE
C_2H_5-O-C-H
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

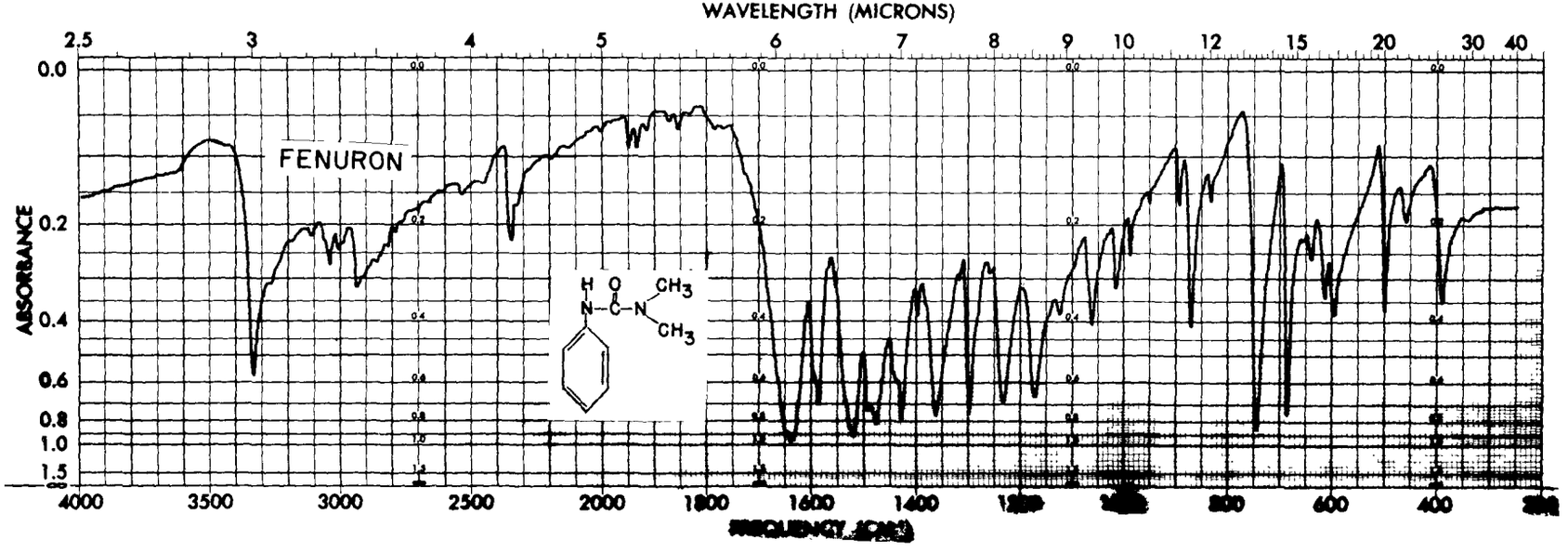

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ETHYL
DIMETHOATE
C_2H_5-O
S
P–S–CH_2–C–N–CH_3
O H
C_2H_5-O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

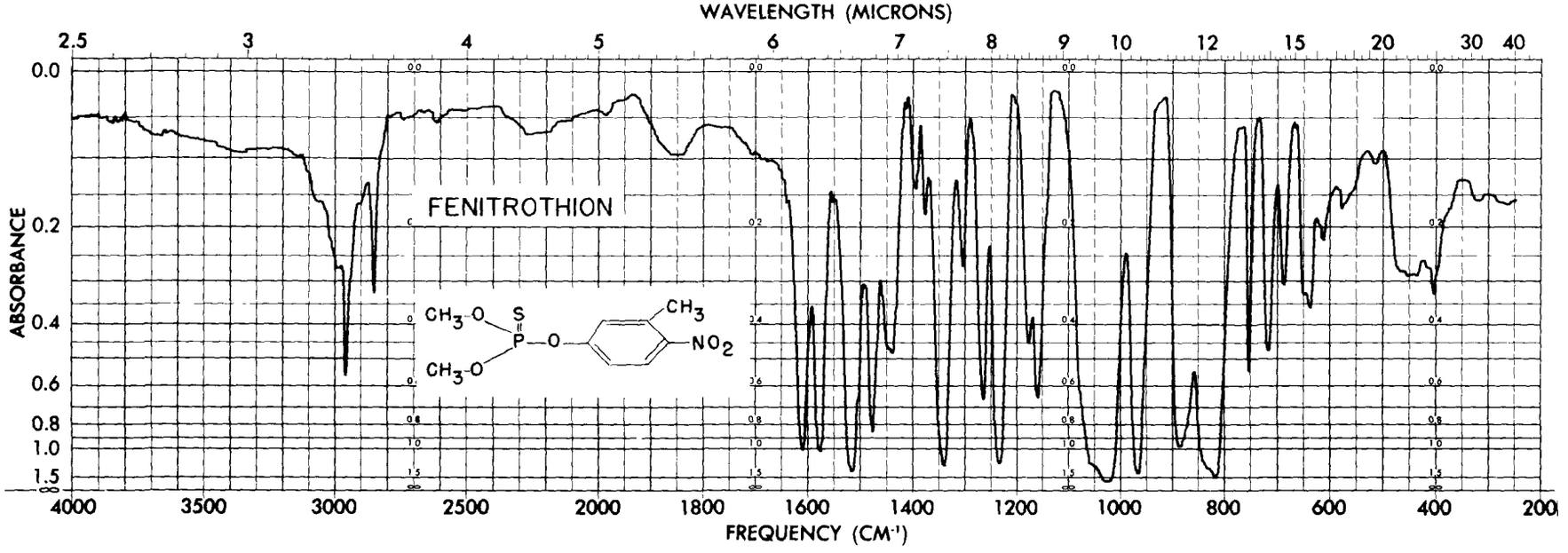

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ETHYL
TRICHLORFON
C_2H_5-O
O
OH
P–CH–C
Cl
Cl
Cl
C_2H_5-O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

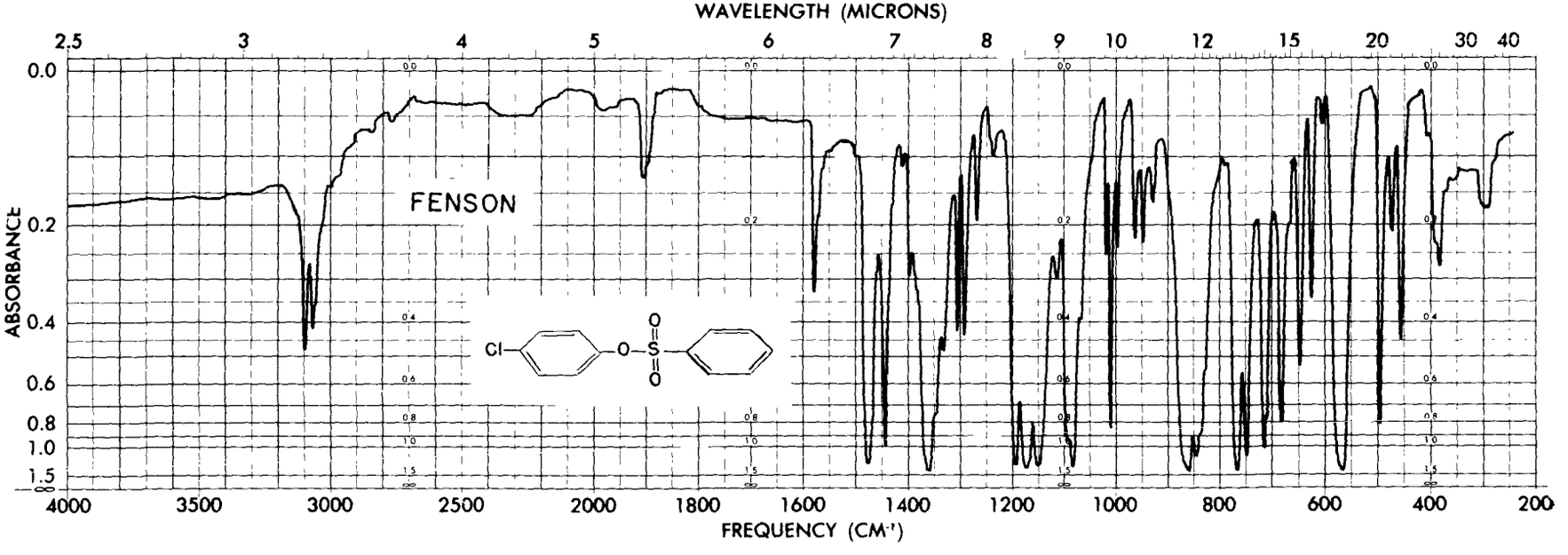

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ETHYL
HEXANEDIOL
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

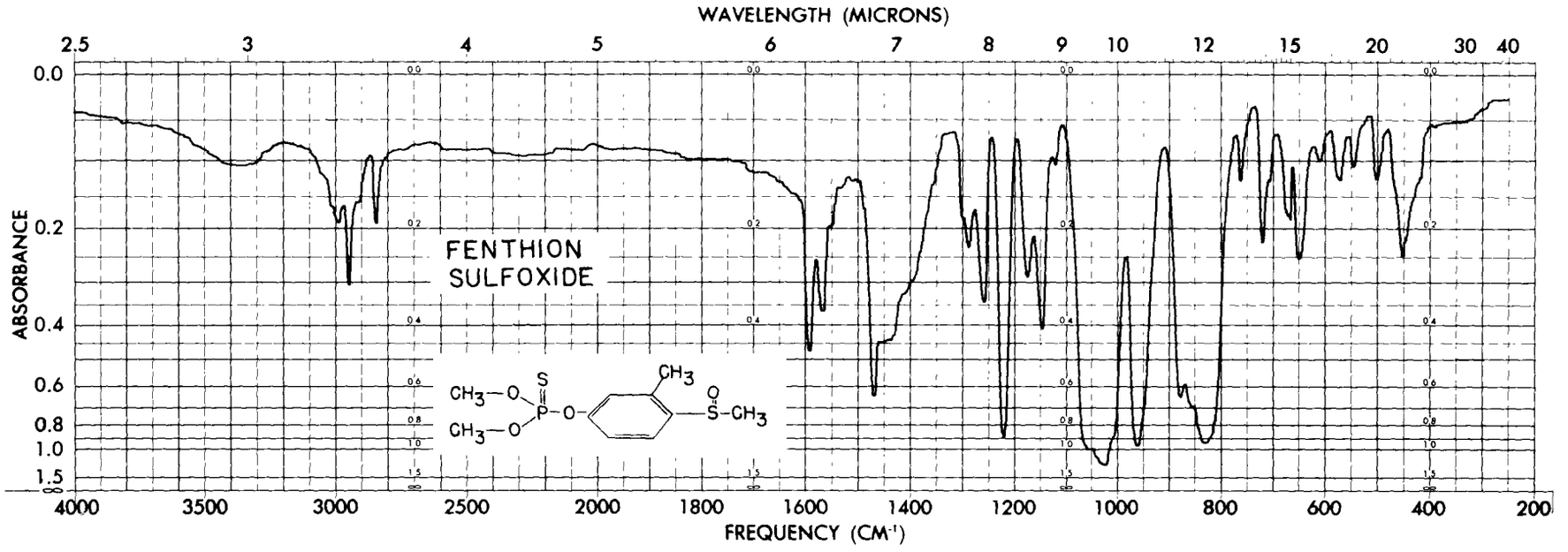

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
FAMPHUR
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

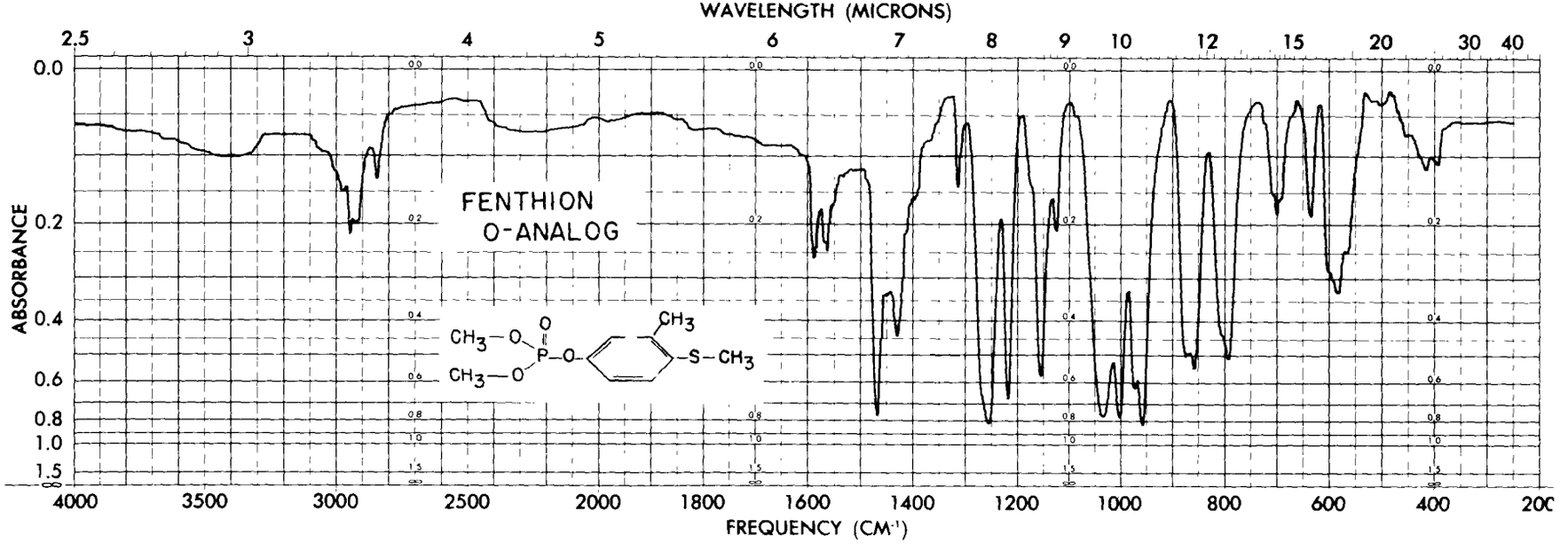

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
FENAC
CH2-COOH
Cl
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

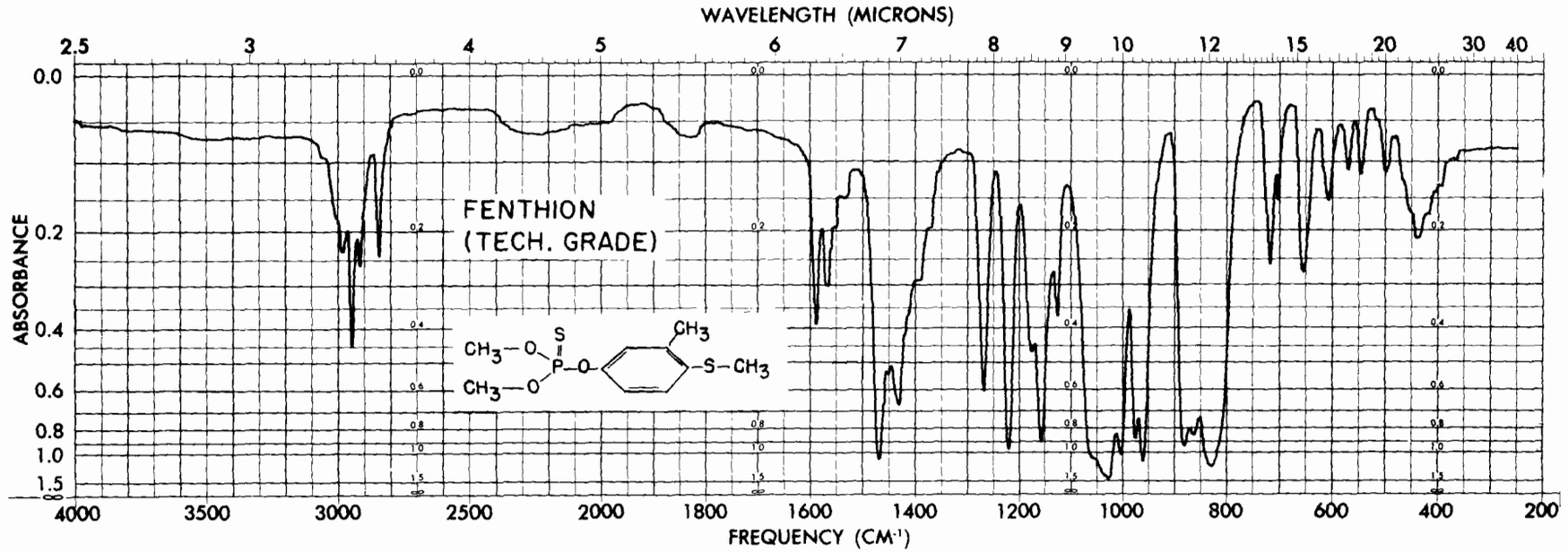

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
FENURON
H
O
CH3
N-C-N
CH3
4000
3500
3000
2500
2000
1800
1600
1400
600
400

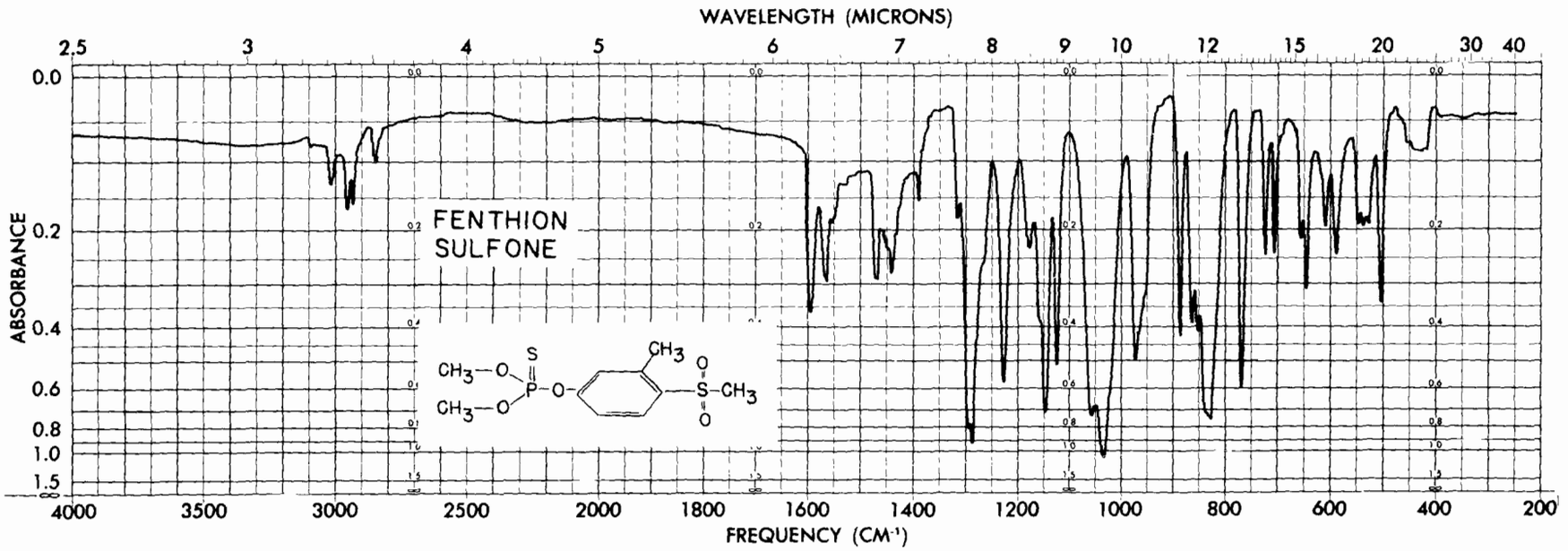

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
FENITROTHION
CH3-O
S
P
O
CH3-O
CH3
NO2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

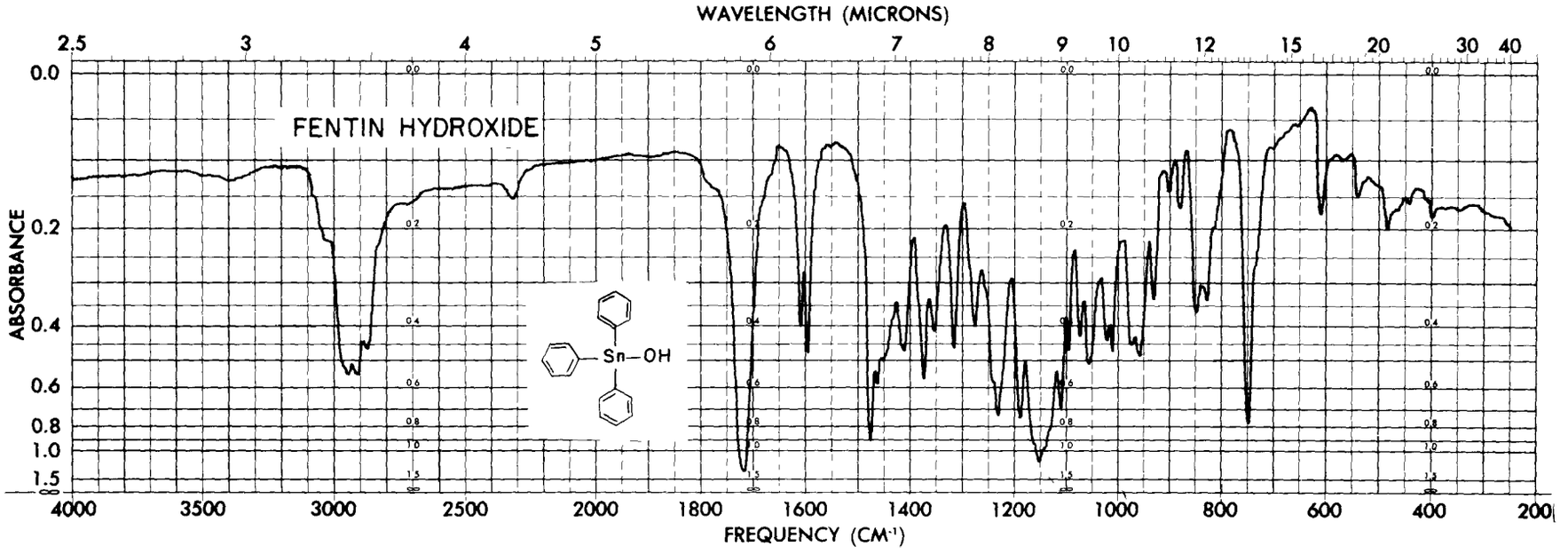

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
FENSON
Cl
O
S
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

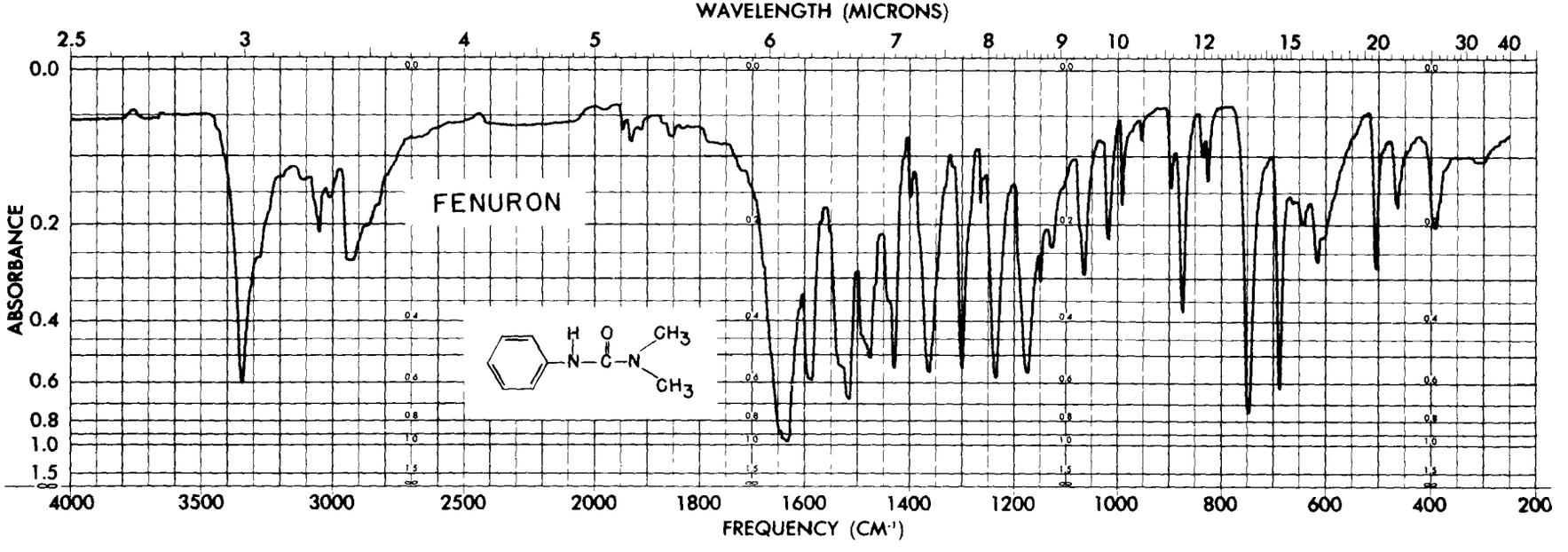

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
FENTHION
SULFOXIDE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

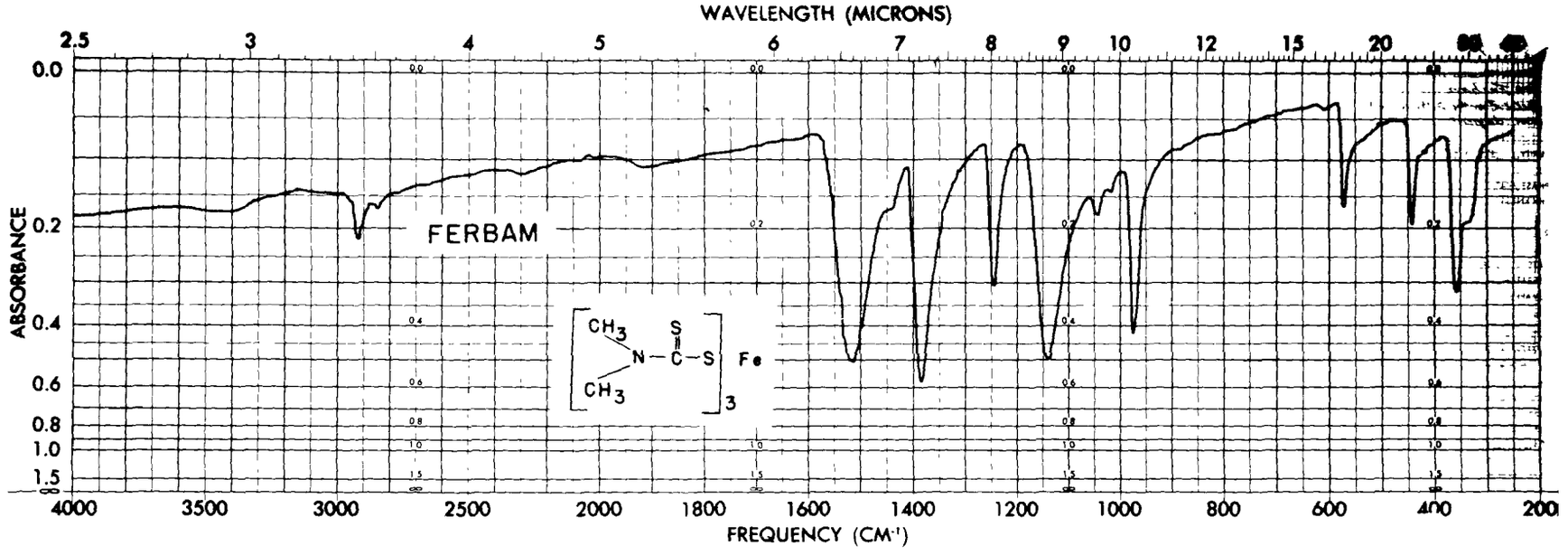

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
FENTHION
O-ANALOG
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
FREQUENCY (CM-1)

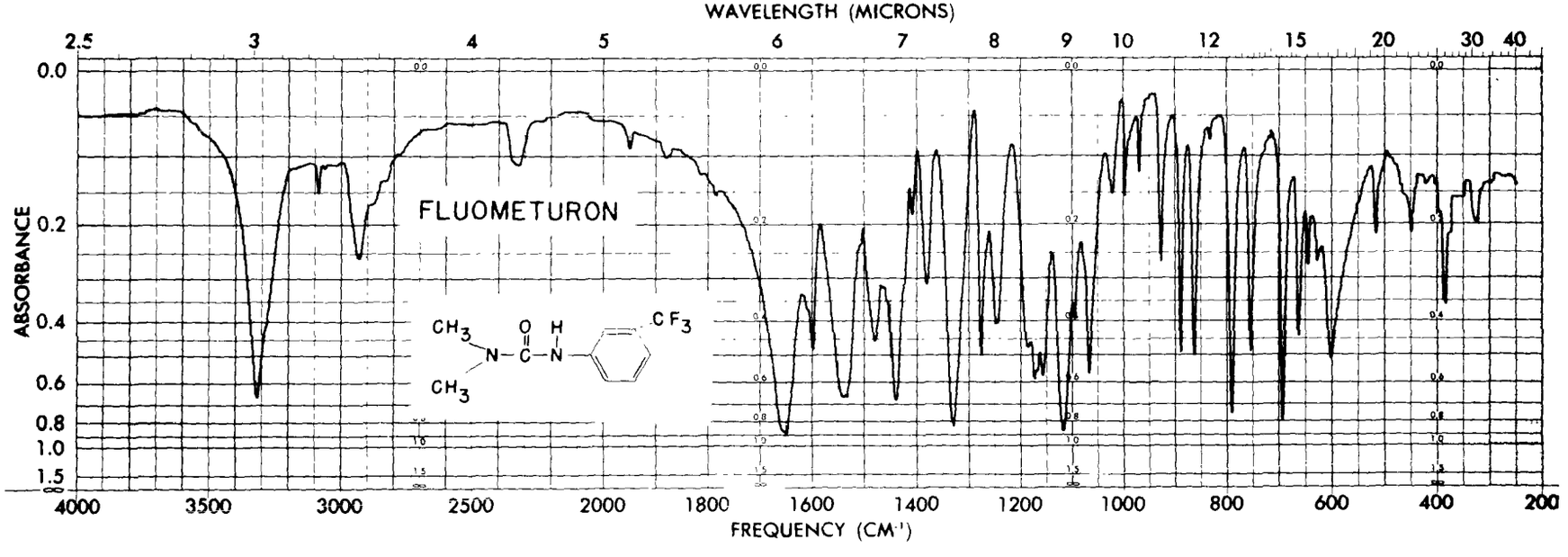

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
FENTHION
(TECH. GRADE)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

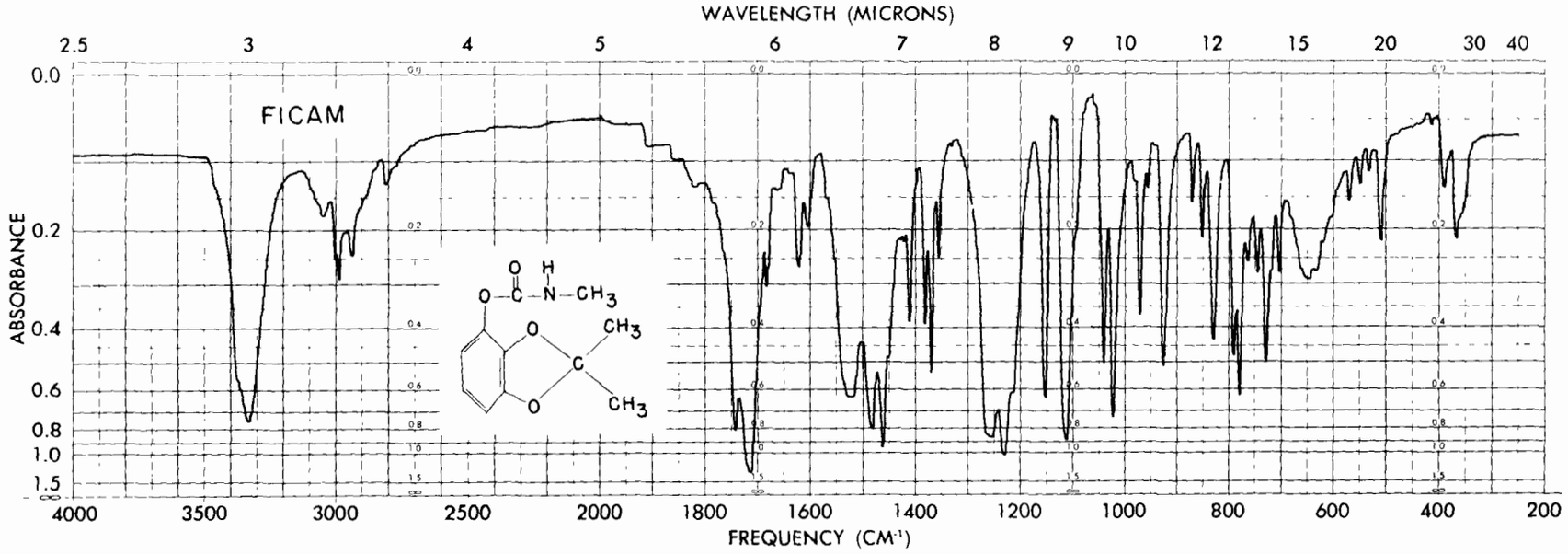

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
FENTHION
SULFONE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

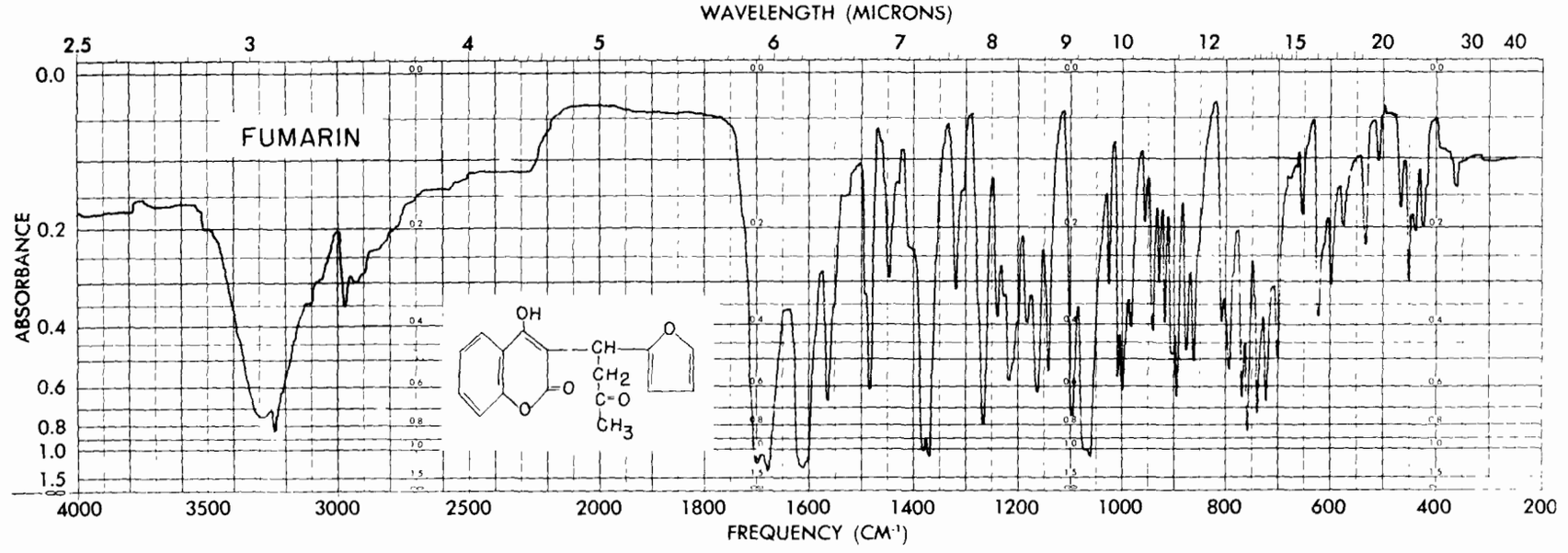

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
FENTIN HYDROXIDE
Sn—OH
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

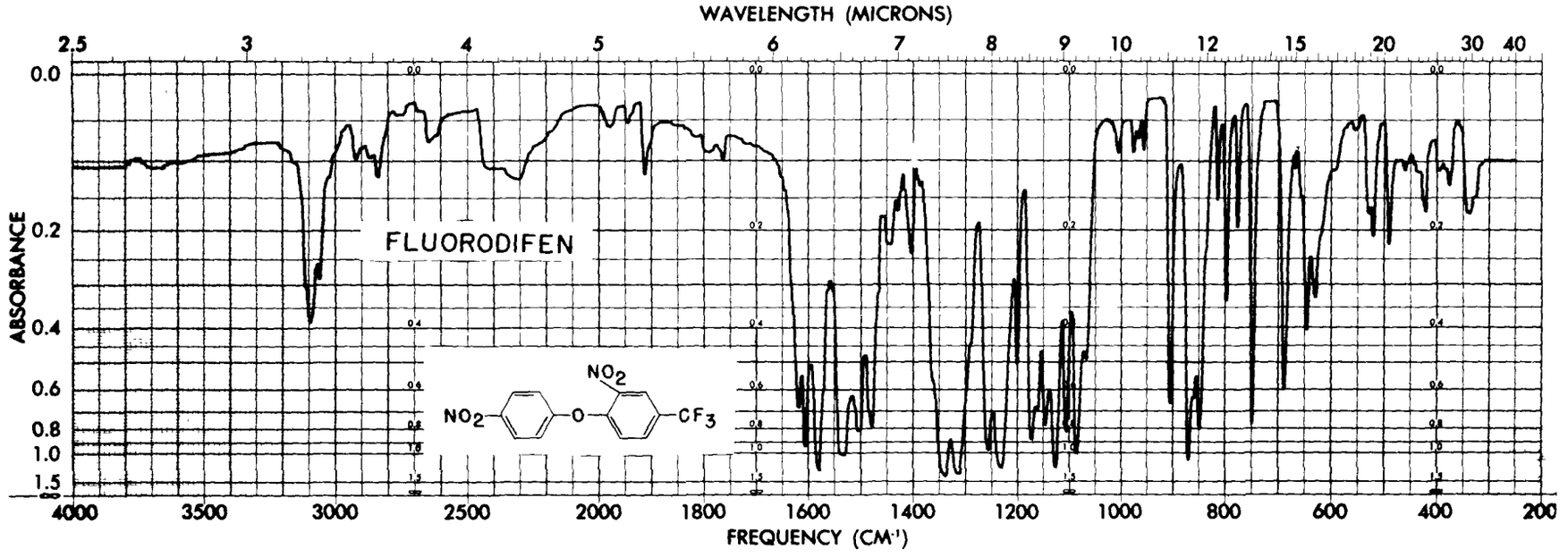

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
FENURON
H
O
N—C—N
CH3
CH3
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

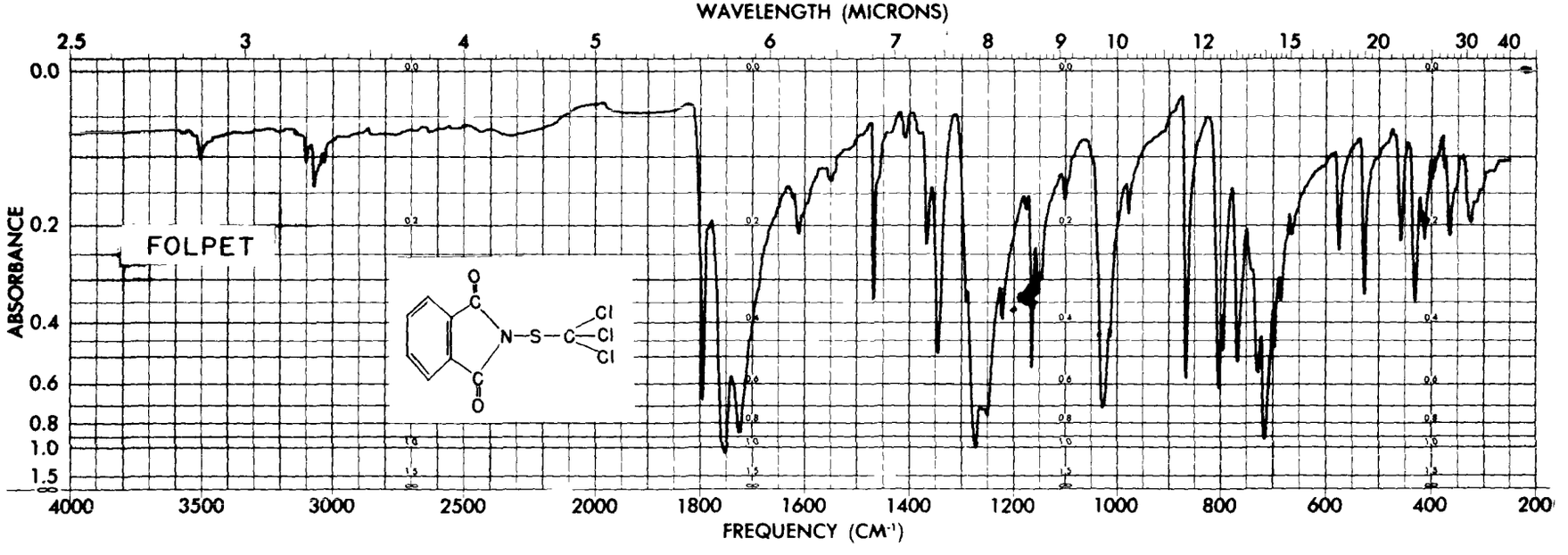

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
FERBAM
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
FLUOMETURON
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
FICAM
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
FUMARIN
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
FLUORODIFEN
NO2
NO2
O
CF3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
FOLPET
O
C
N
S
C
Cl
Cl
Cl
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
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800
600
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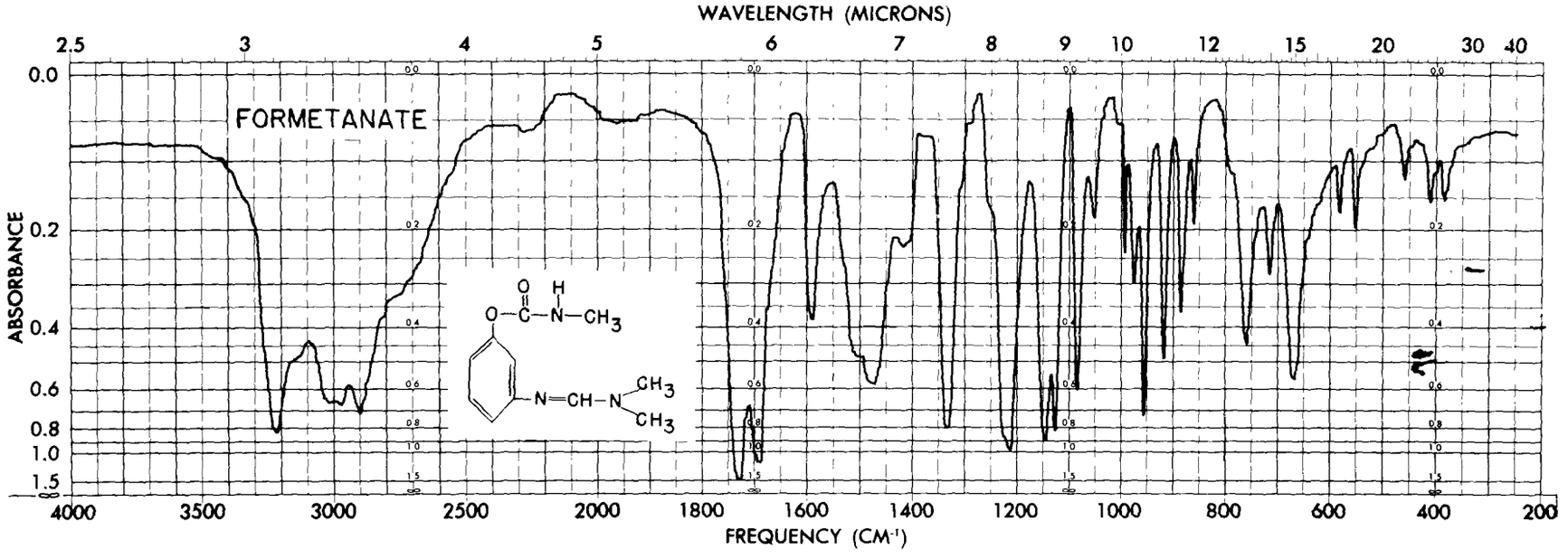
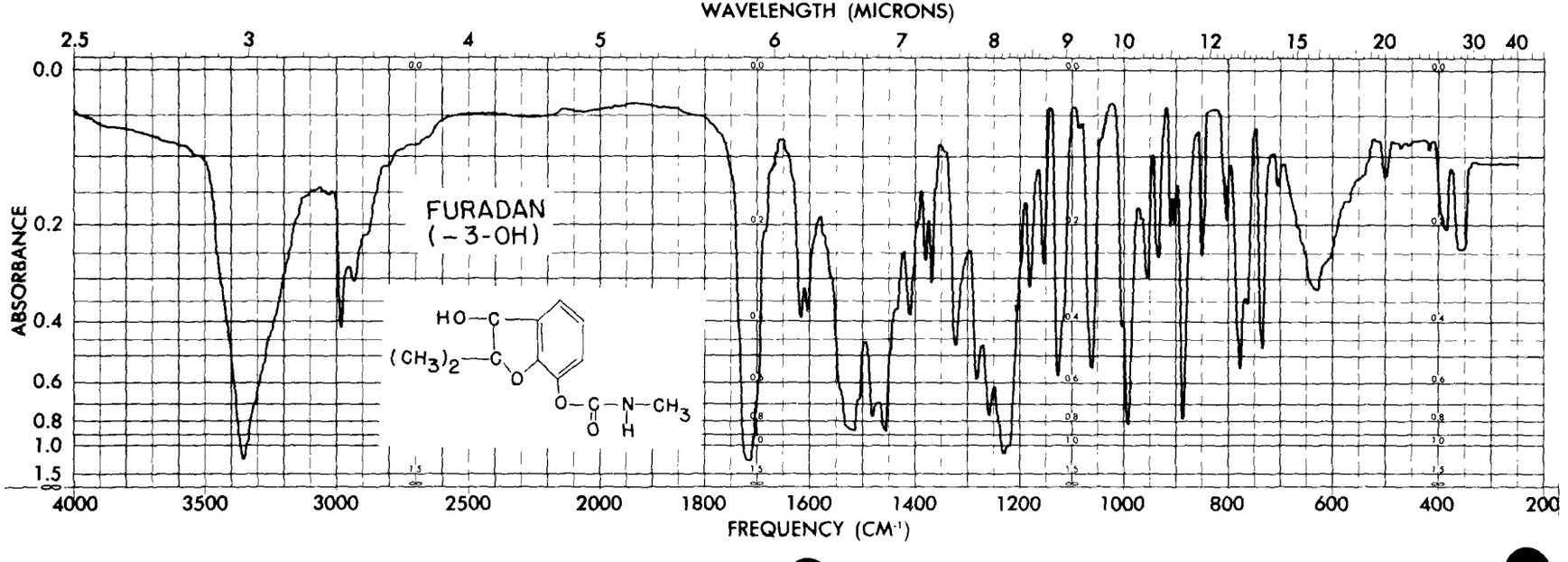
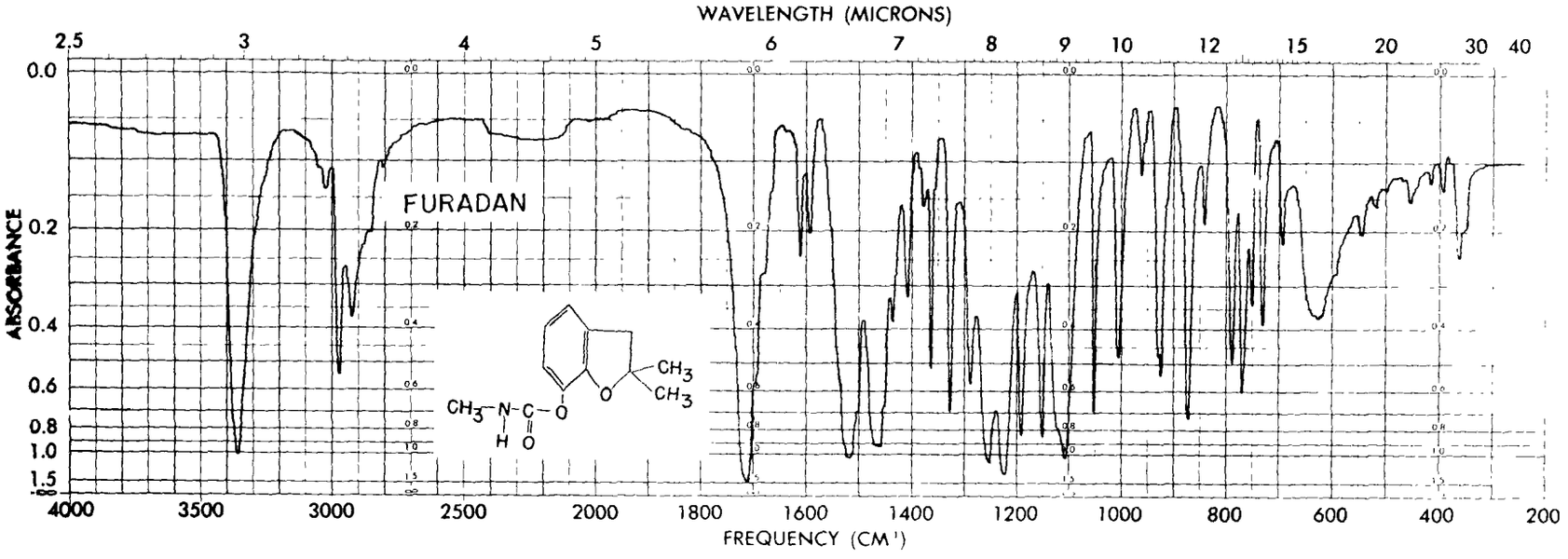
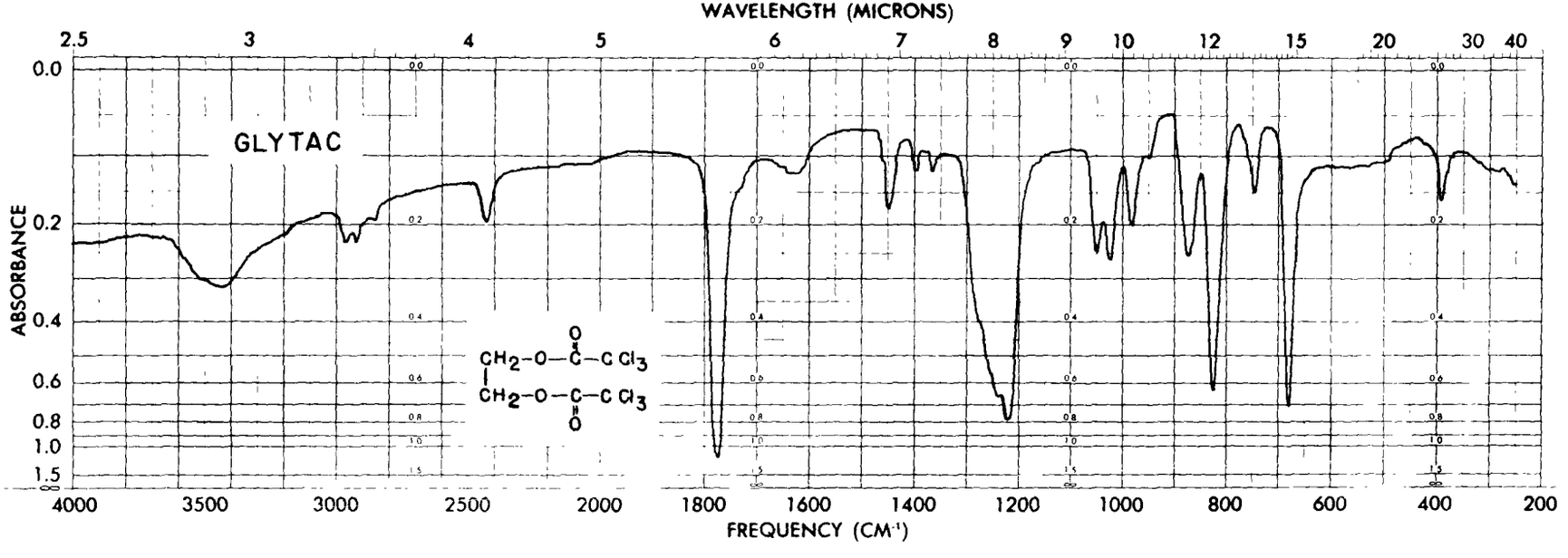
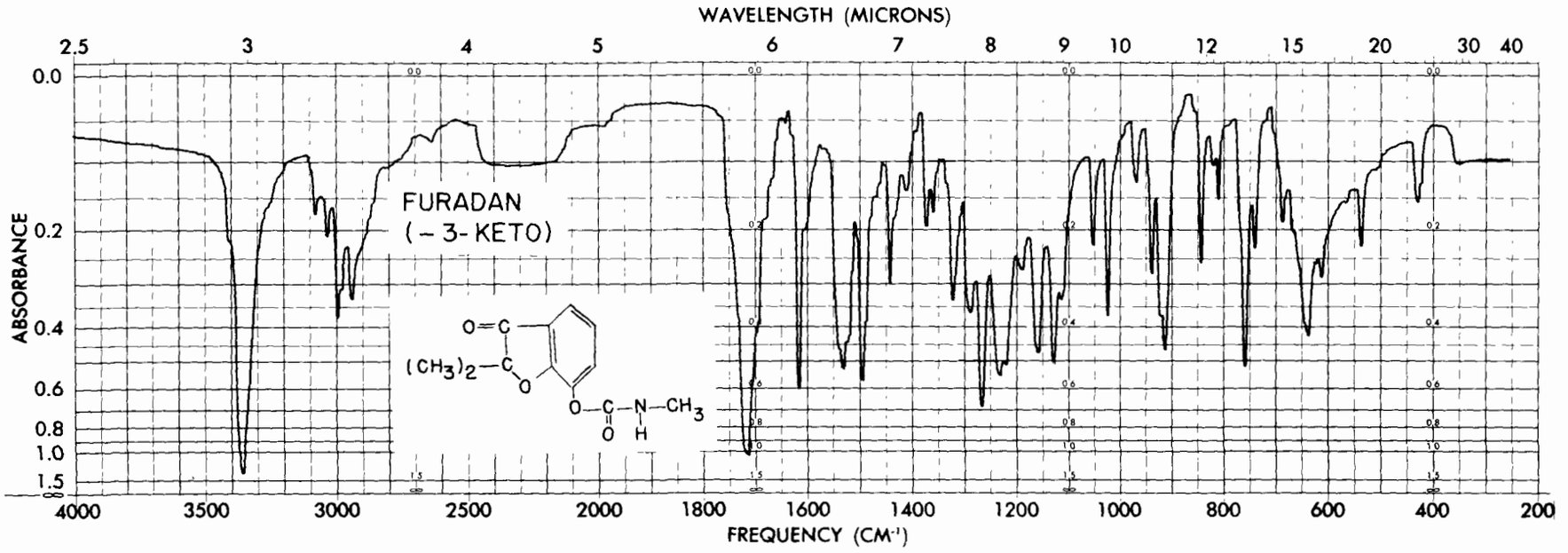
200
FREQUENCY (CM-1)

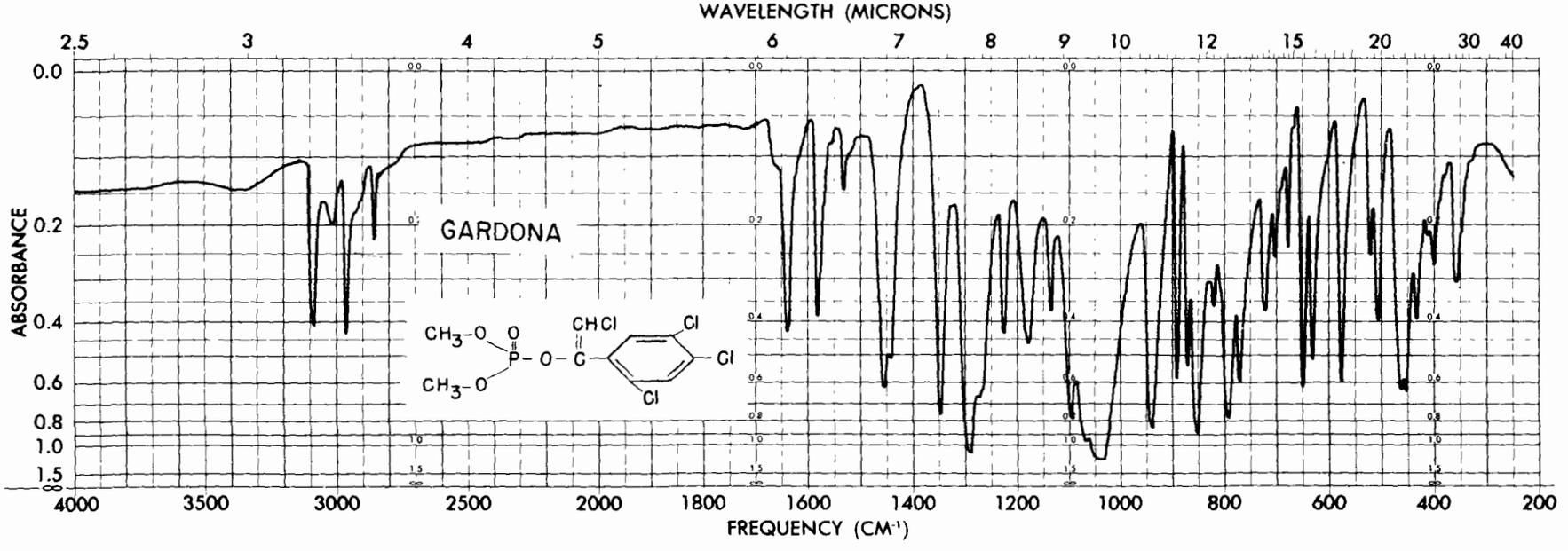

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
FORMETANATE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

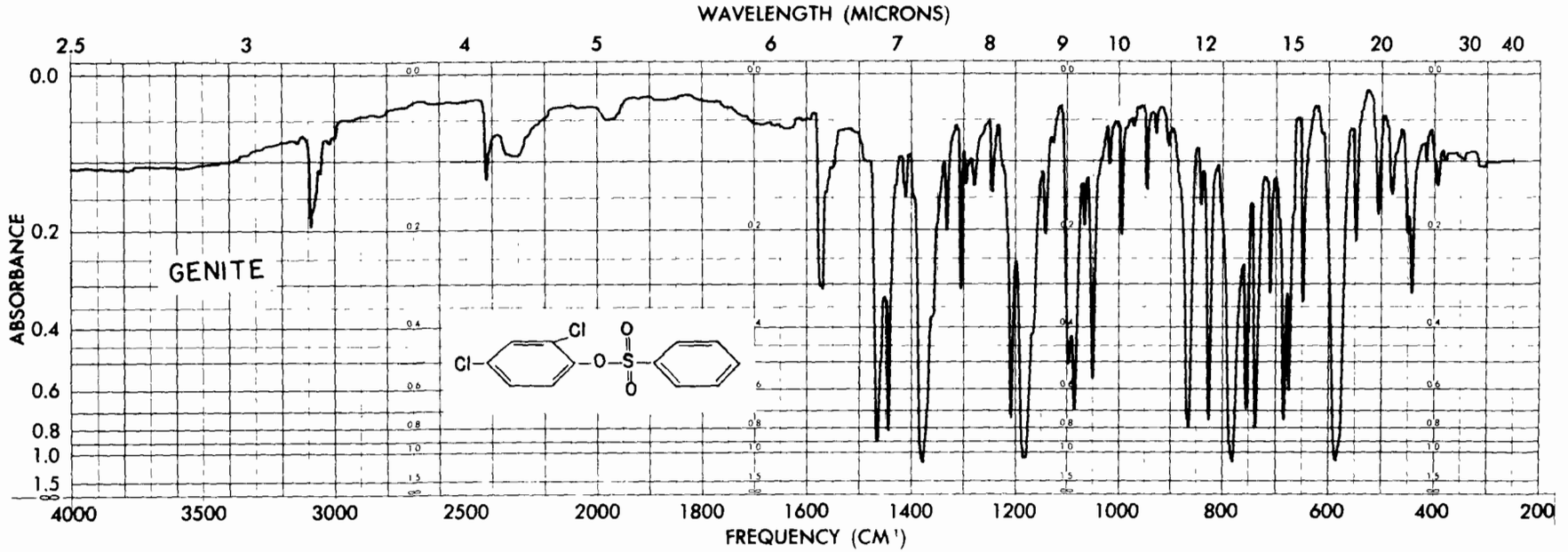

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
FURADAN
(-3-OH)
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

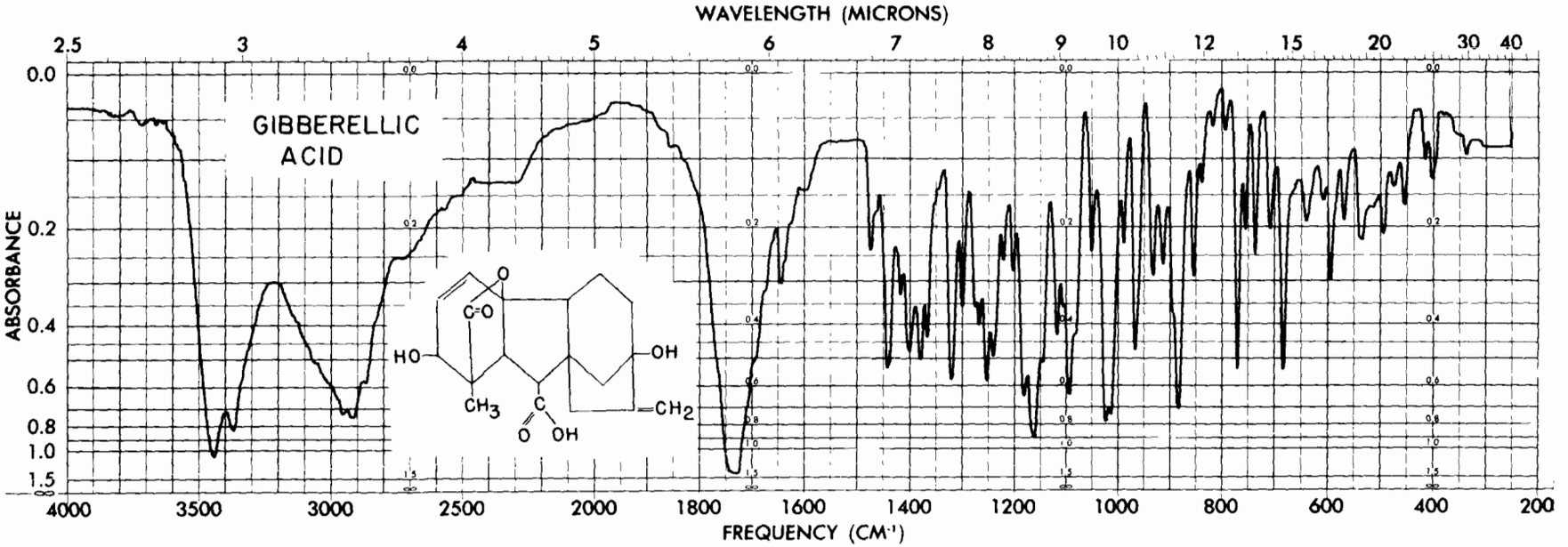

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
FURADAN
CH3
CH3
CH3—N—C—O
H O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

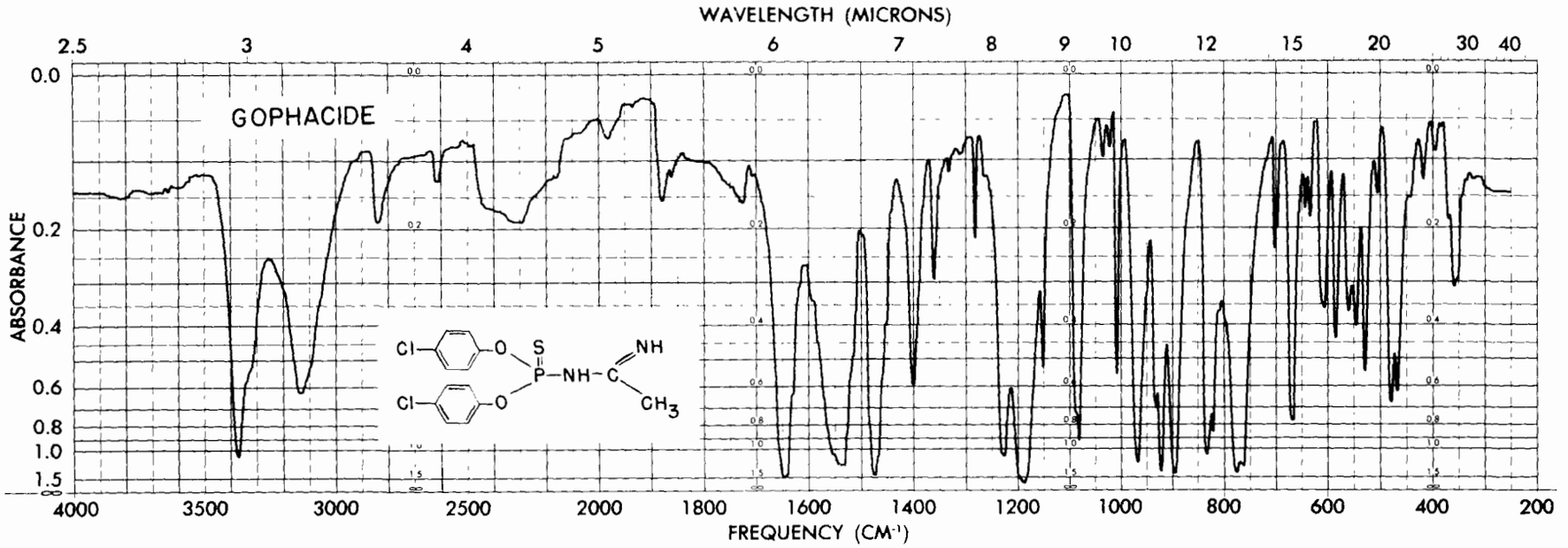

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
GLYTAC
CH2—O—C—CCl3
CH2—O—C—CCl3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

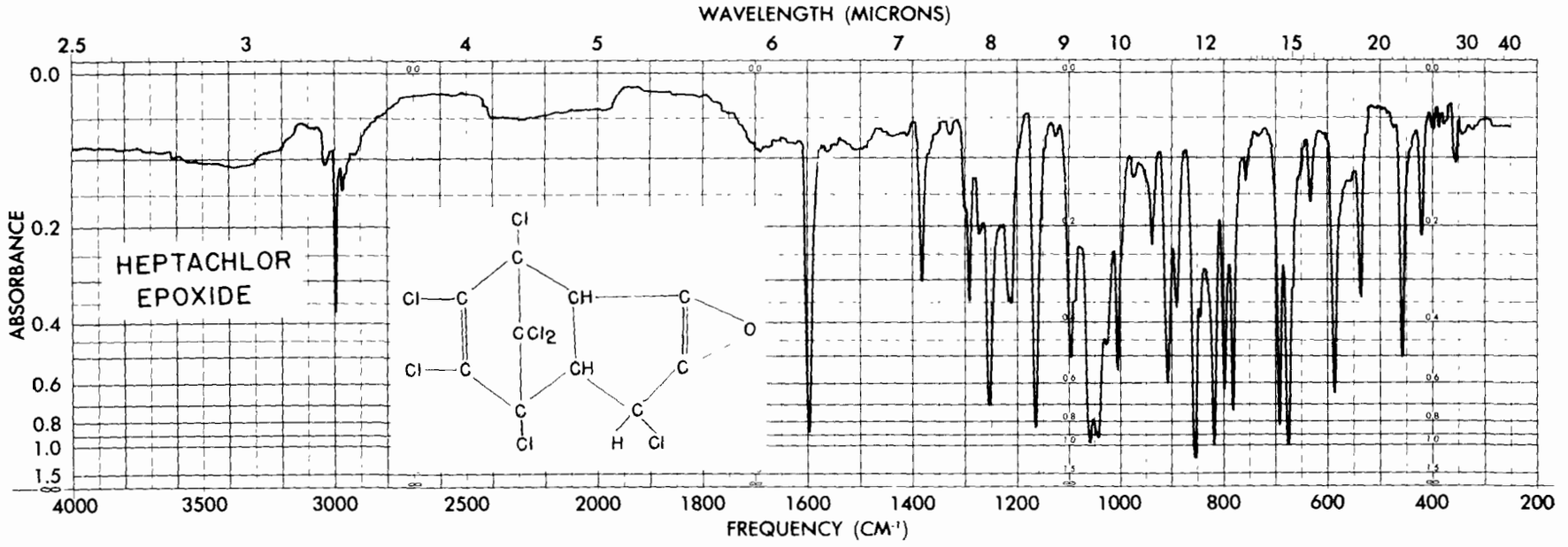

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
FURADAN
(-3-KETO)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

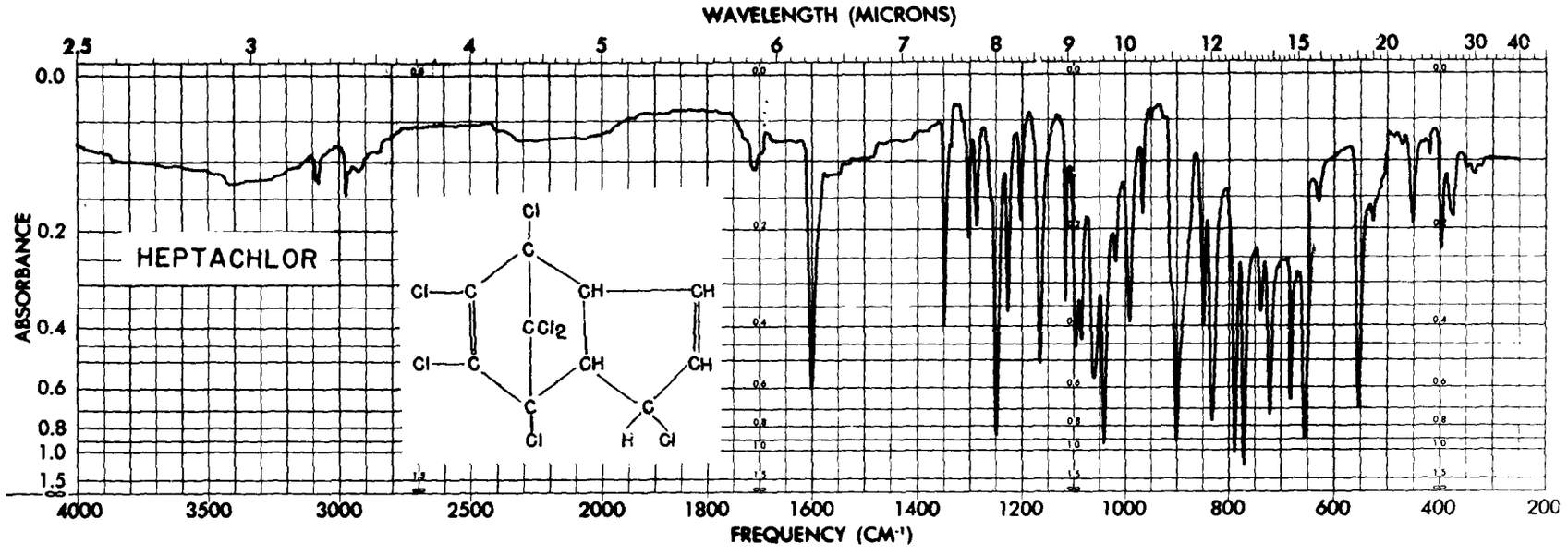

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
GARDONA
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

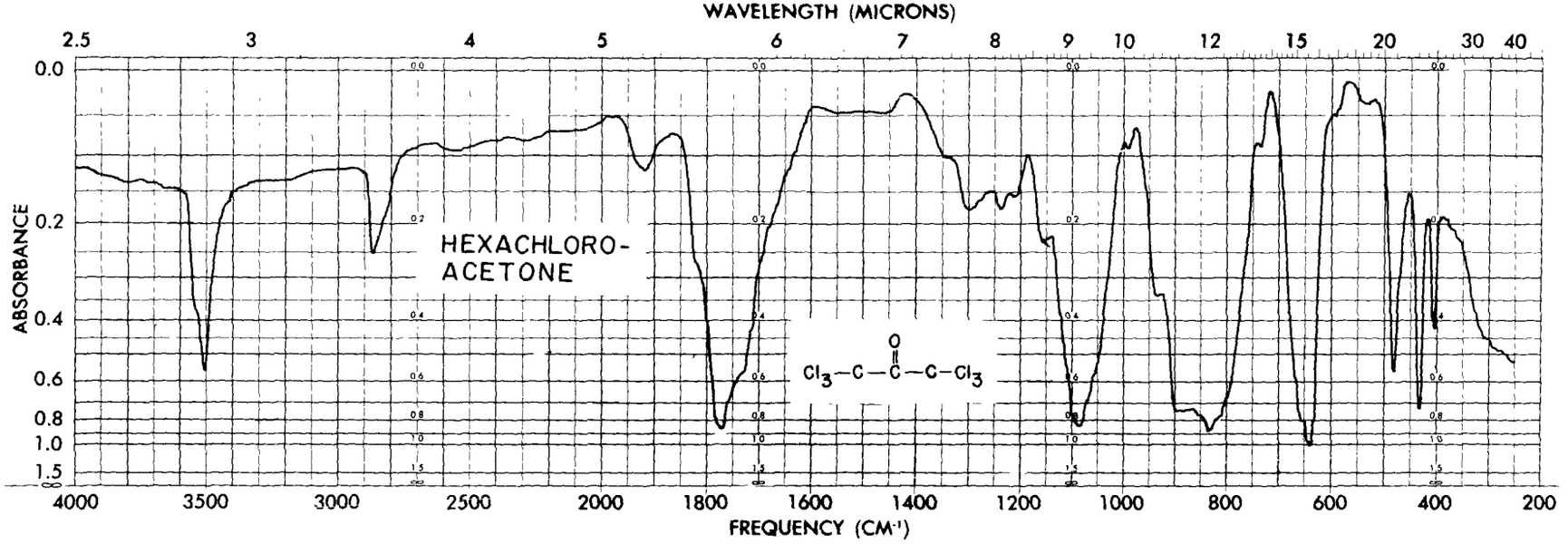

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
GENITE
Cl
Cl
O
O
S
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

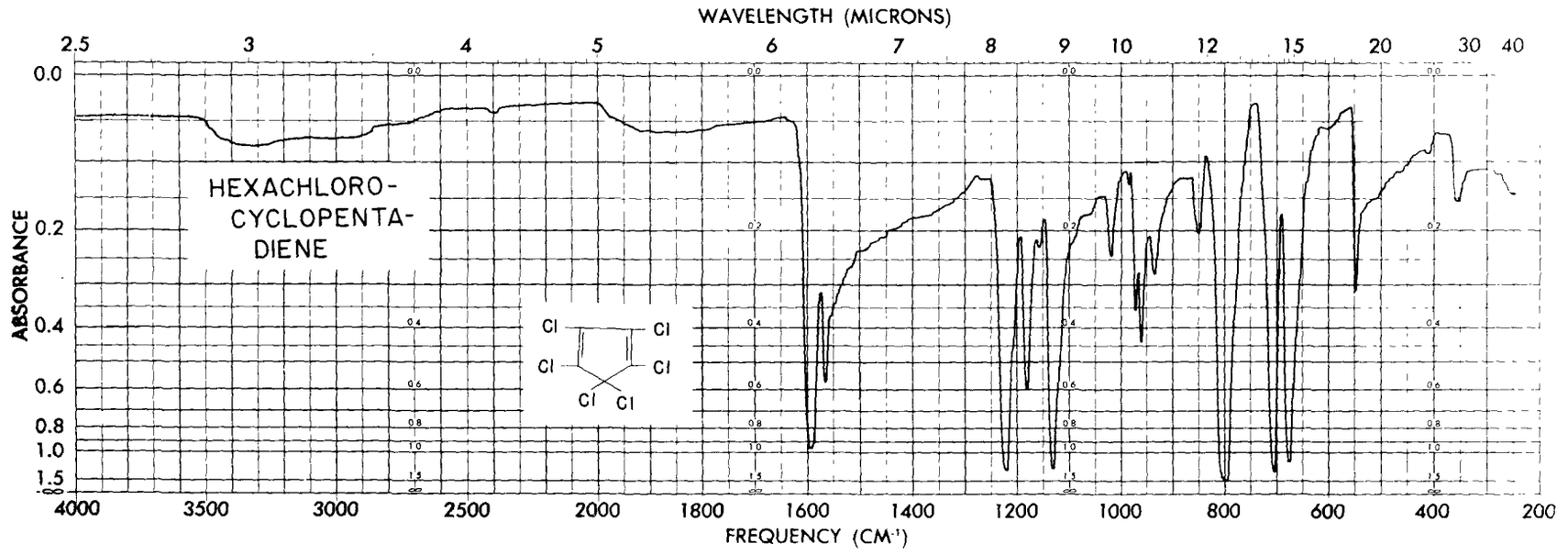

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
GIBBERELLIC
ACID
O
C=O
HO
OH
CH3
C
O
OH
=CH2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

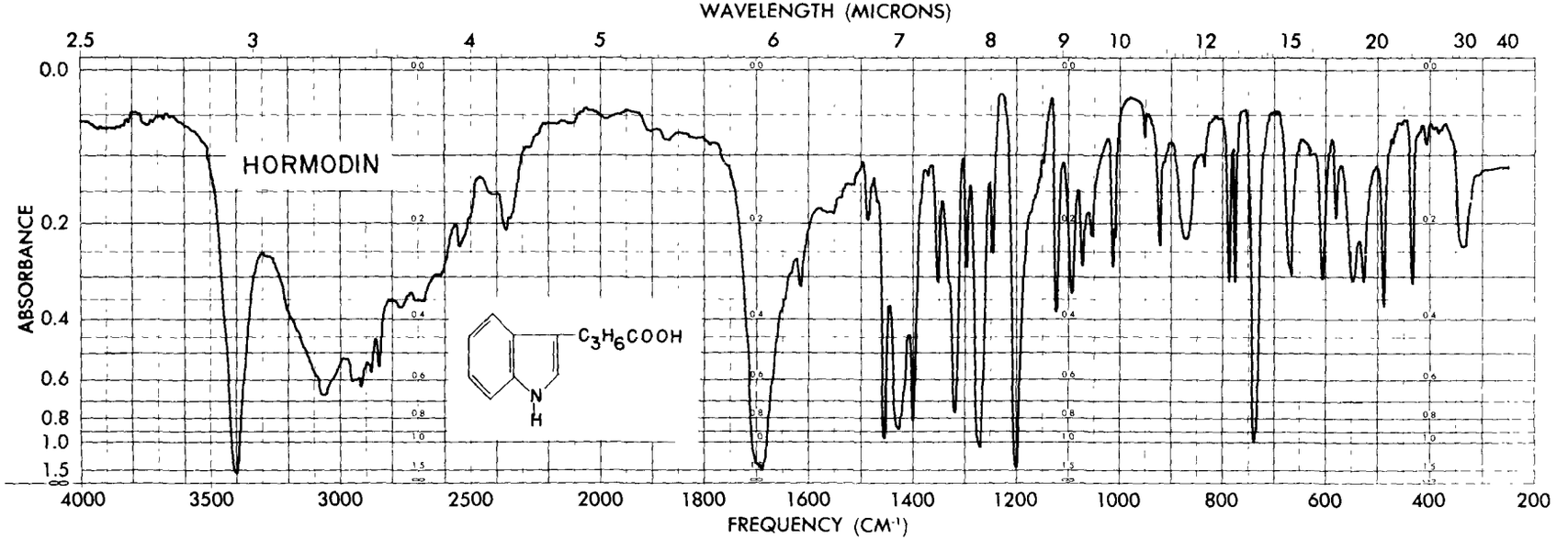

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
GOPHACIDE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
Cl
O
S
P
NH
C
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

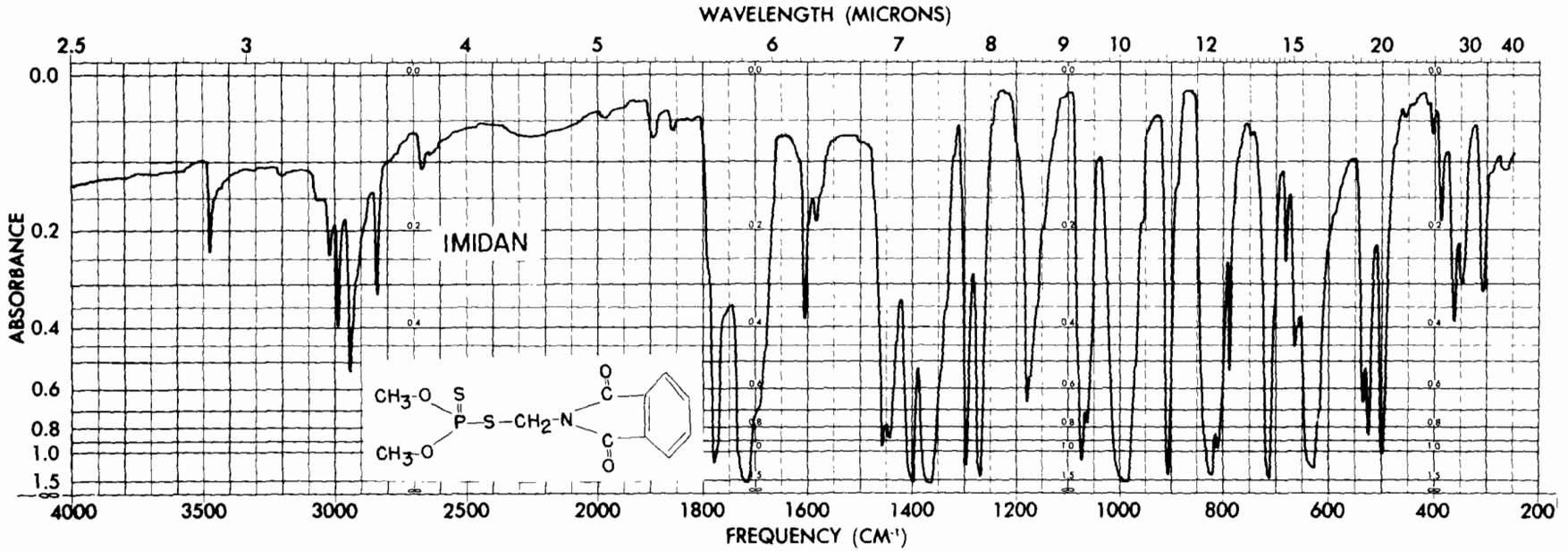

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
HEPTACHLOR
EPOXIDE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
Cl
C
CH
CCl2
O
H
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

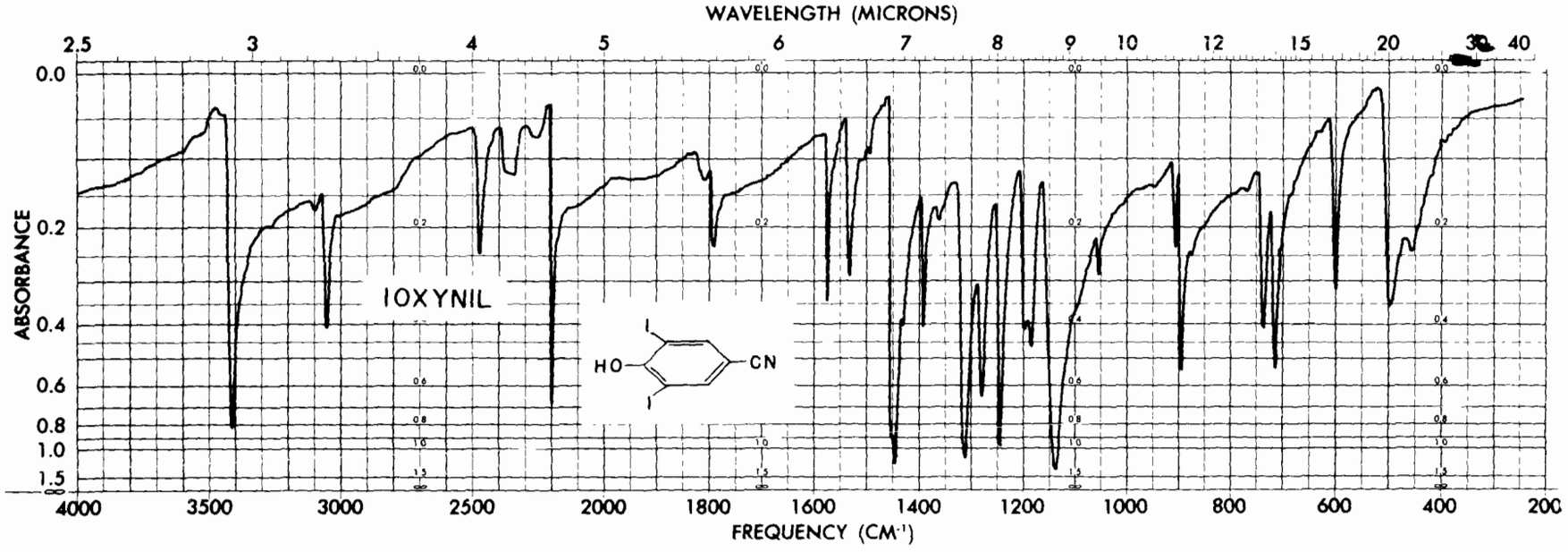

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
HEPTACHLOR
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

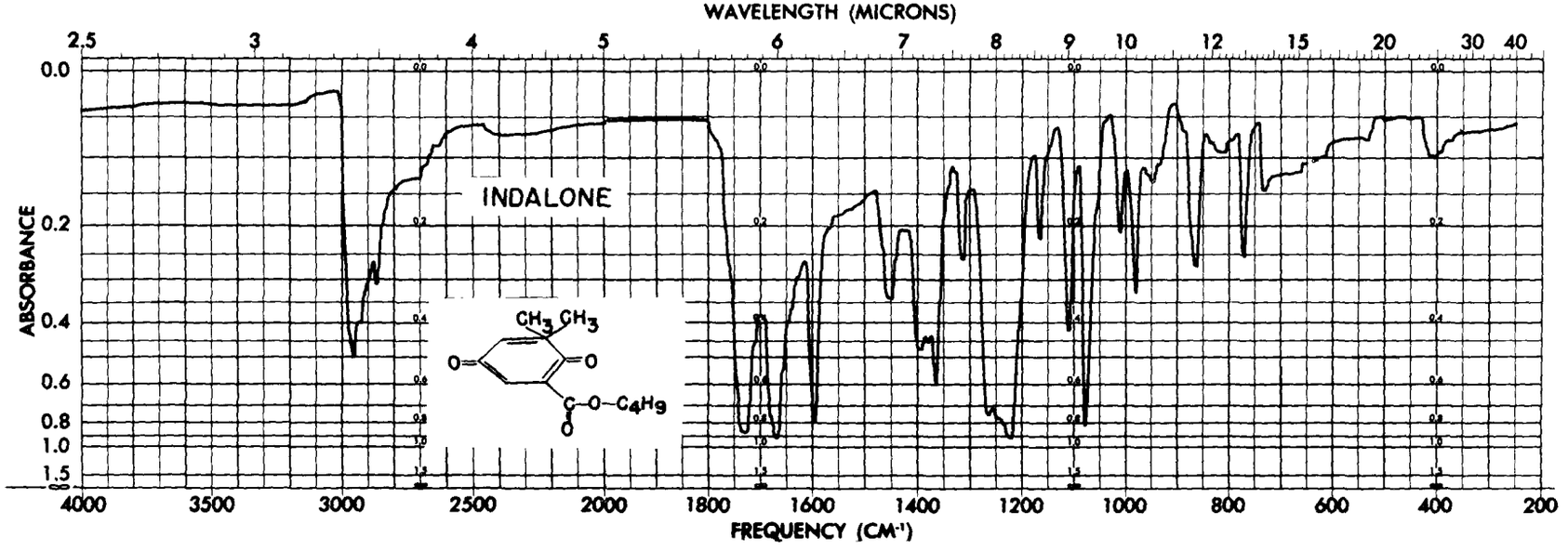

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
HEXACHLORO-
ACETONE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

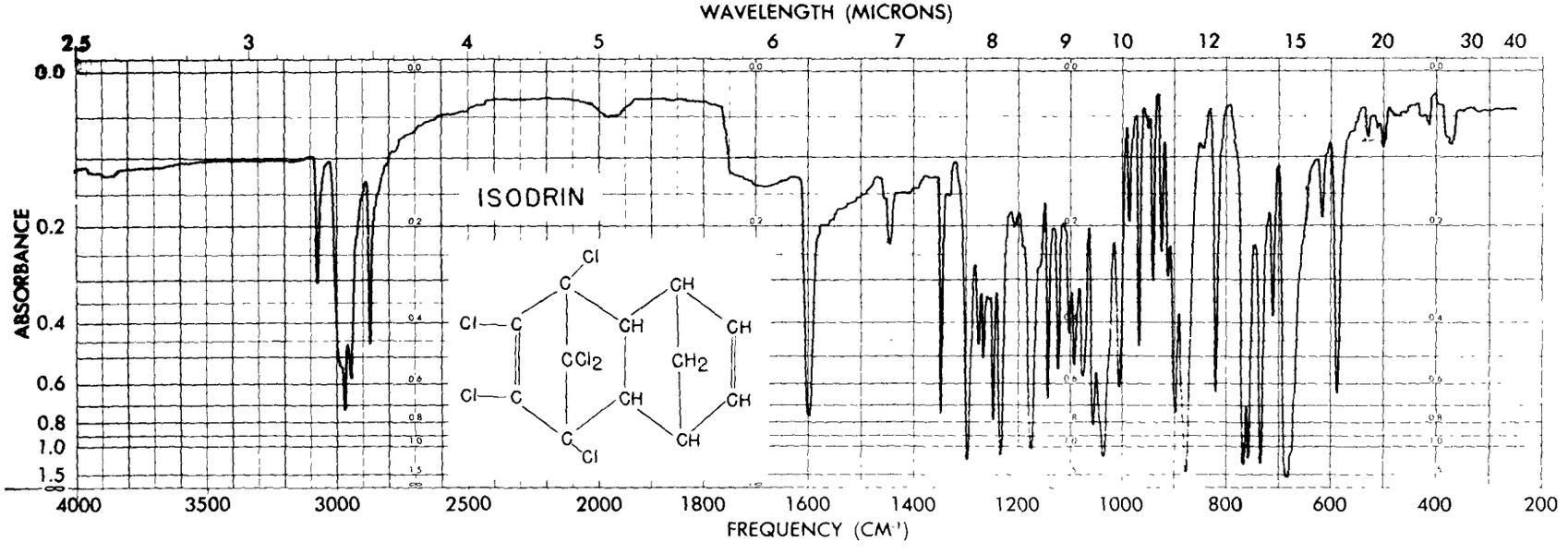

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
HEXACHLORO-
CYCLOPENTA-
DIENE
Cl
Cl
Cl
Cl
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

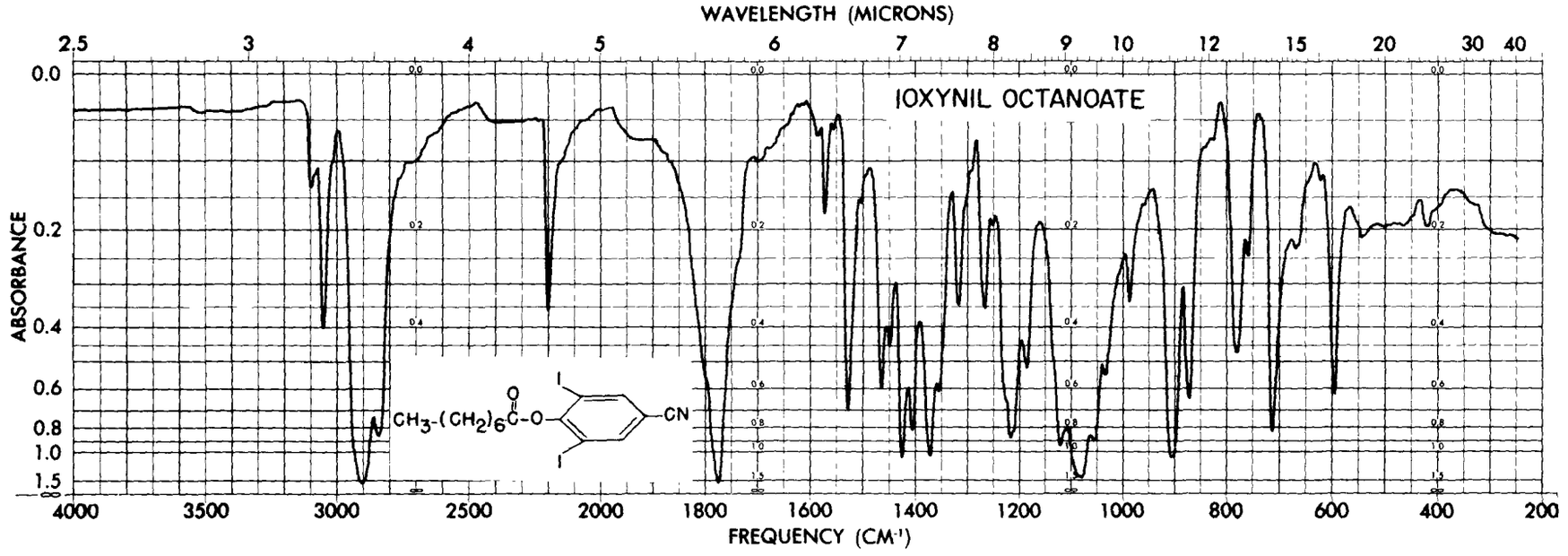

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
HORMODIN
C3H6COOH
N
H
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

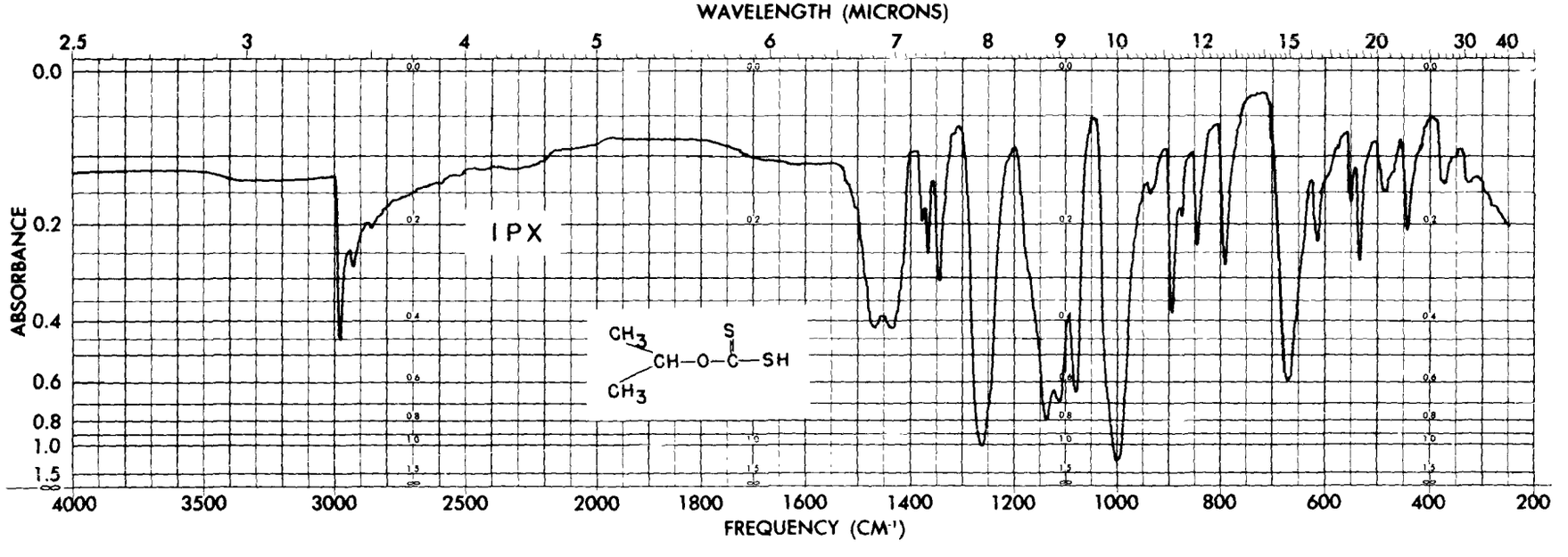

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
IMIDAN
CH3-O
S
P
S
CH2
N
CH3-O
O
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

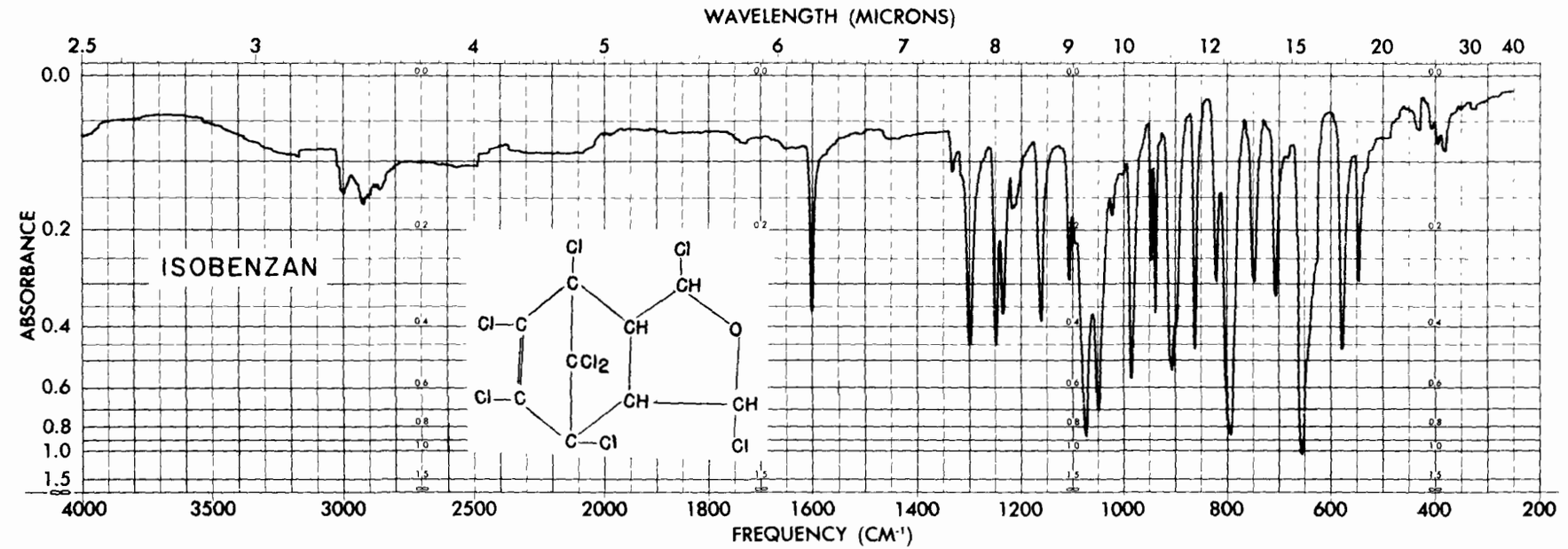

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
IOXYNIL
I
HO
CN
I
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

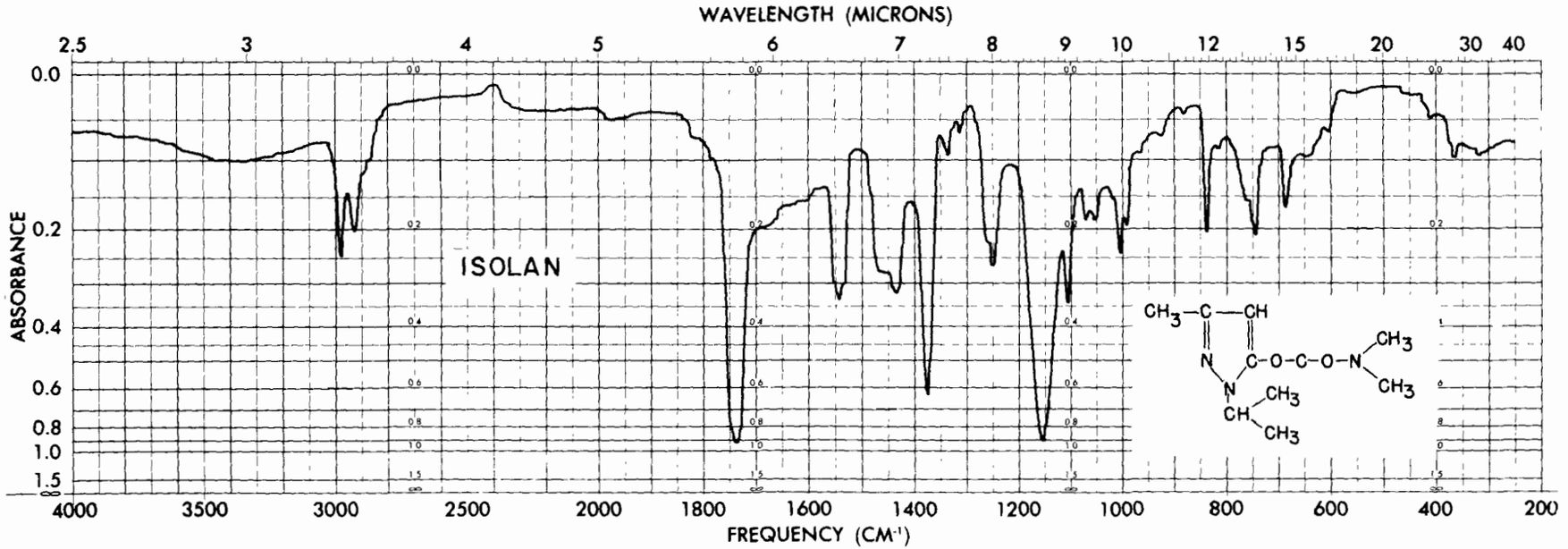

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
INDALONE
CH3 CH3
O
O
C–O–C4H9
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

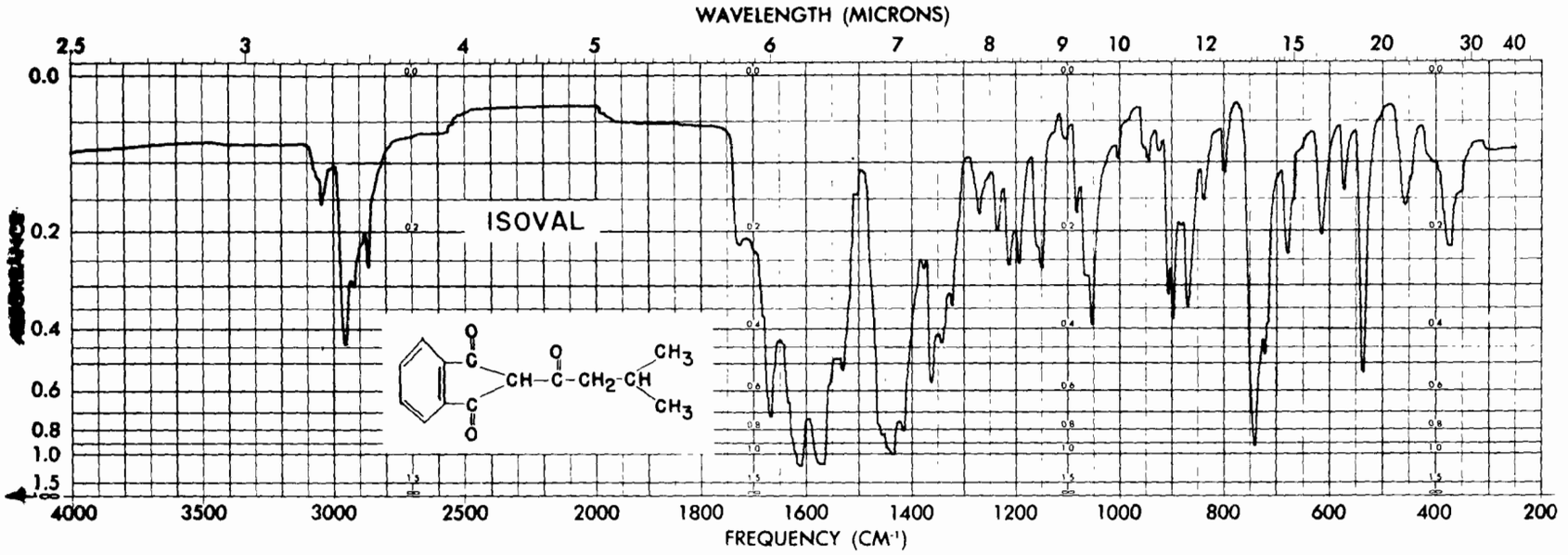

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ISODRIN
Cl
C
CH
Cl–C
CH
CH
CCl2
CH2
Cl–C
CH
CH
C
CH
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

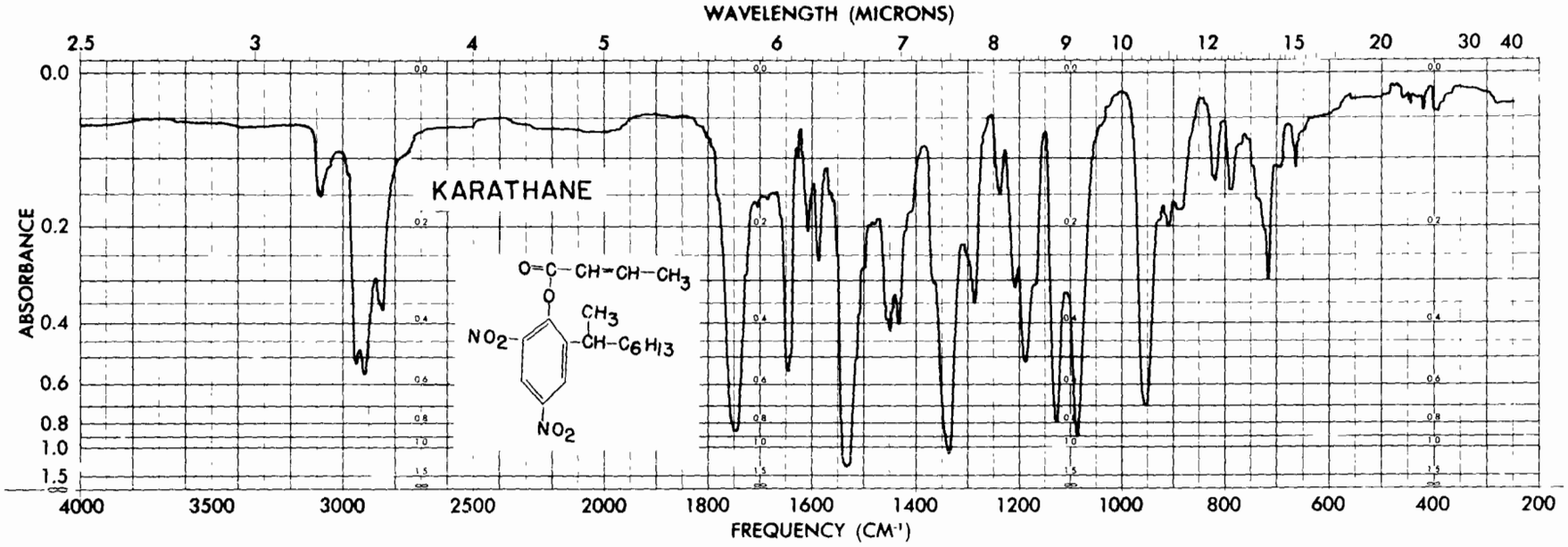

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
IOXYNIL OCTANOATE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

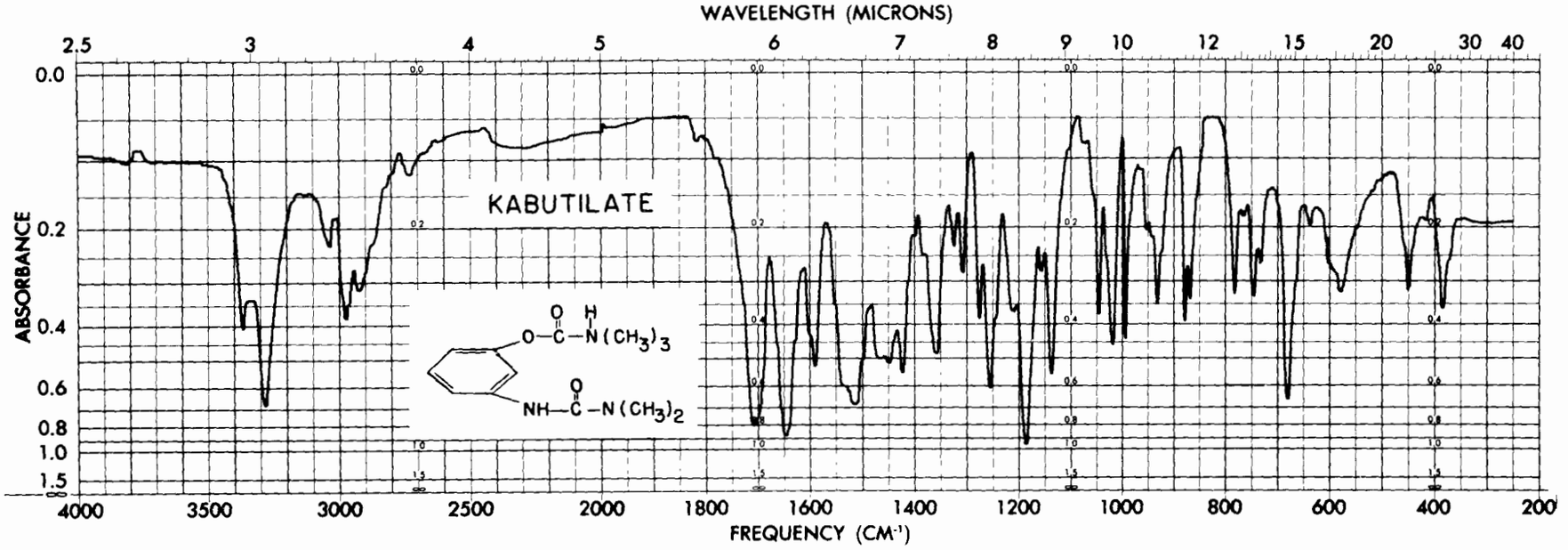

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
IPX
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

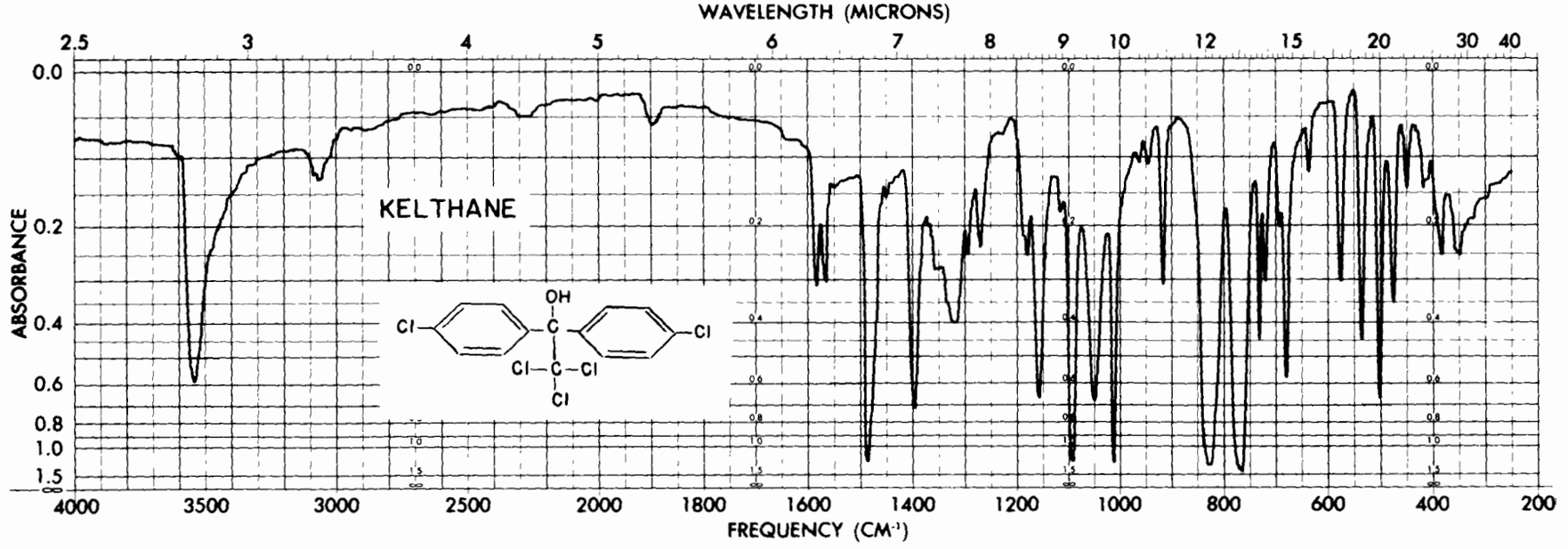

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ISOBENZAN
Cl
Cl
C
CH
Cl—C
CH
O
CCl2
Cl—C
CH
CH
C—Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

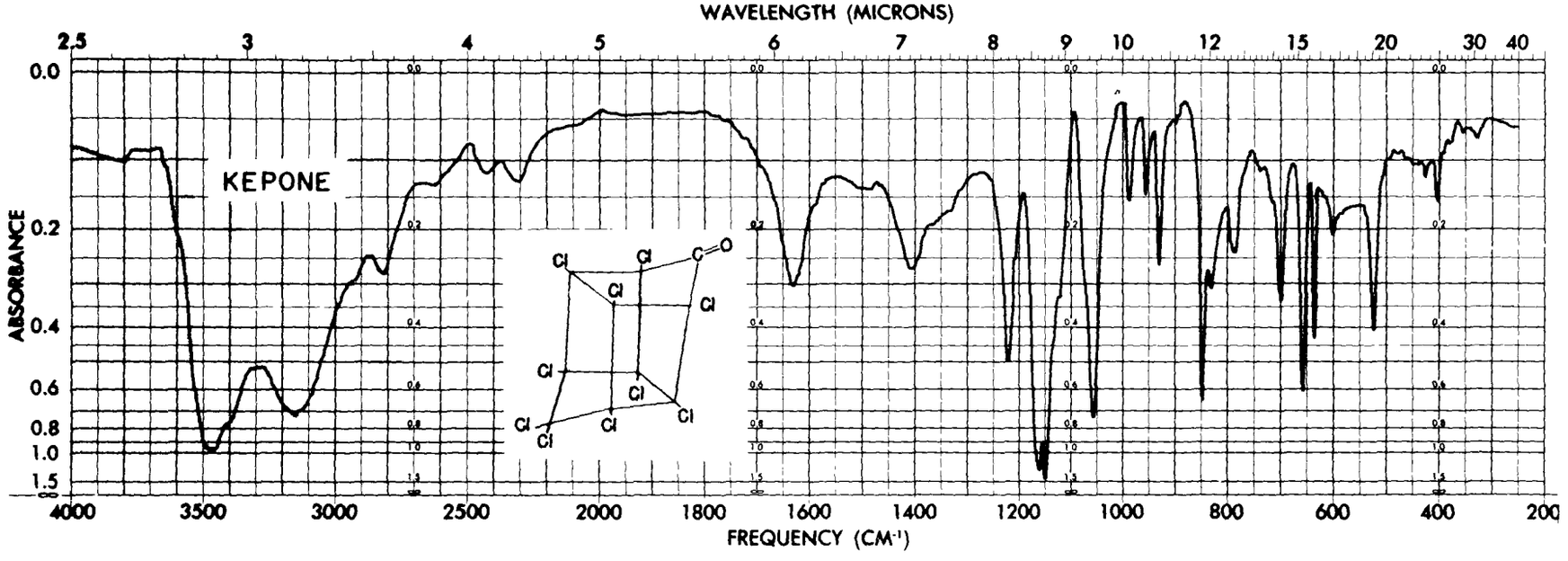

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ISOLAN
CH3—C—CH
N
C-O-C-O-N
CH3
CH3
N
CH3
CH
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

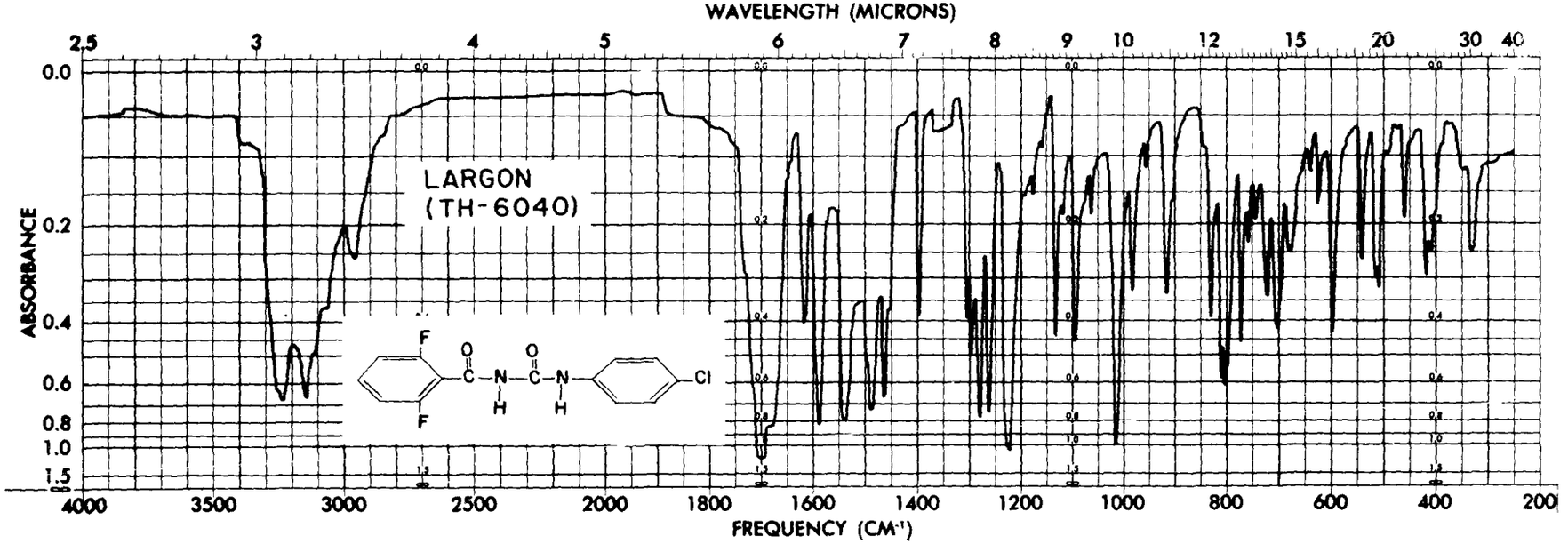

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ISOVAL
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

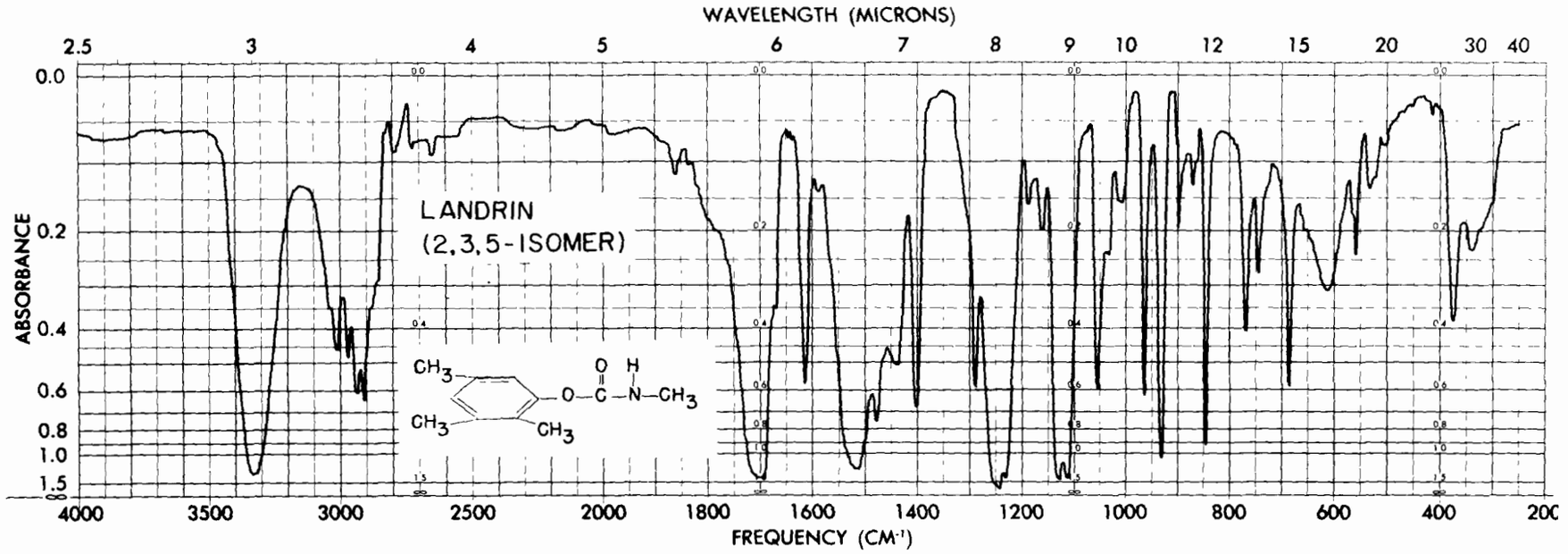

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
KARATHANE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

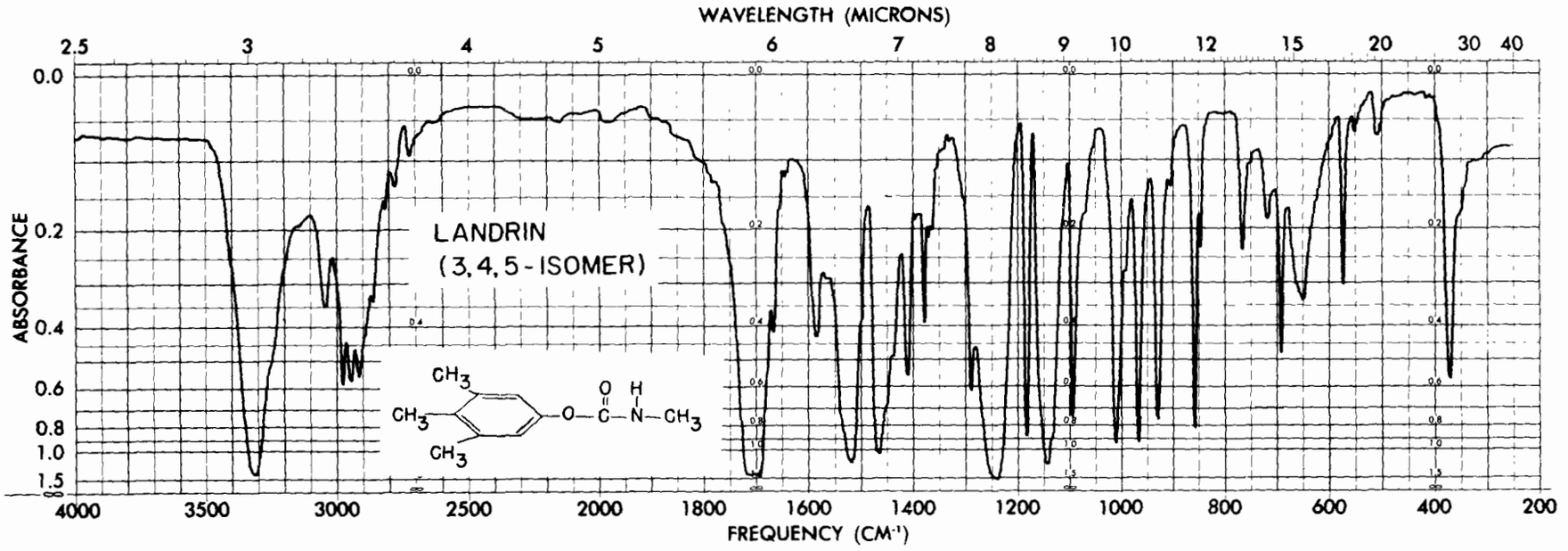

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
KABUTILATE
O H
O—C—N(CH3)3
O
NH—C—N(CH3)2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

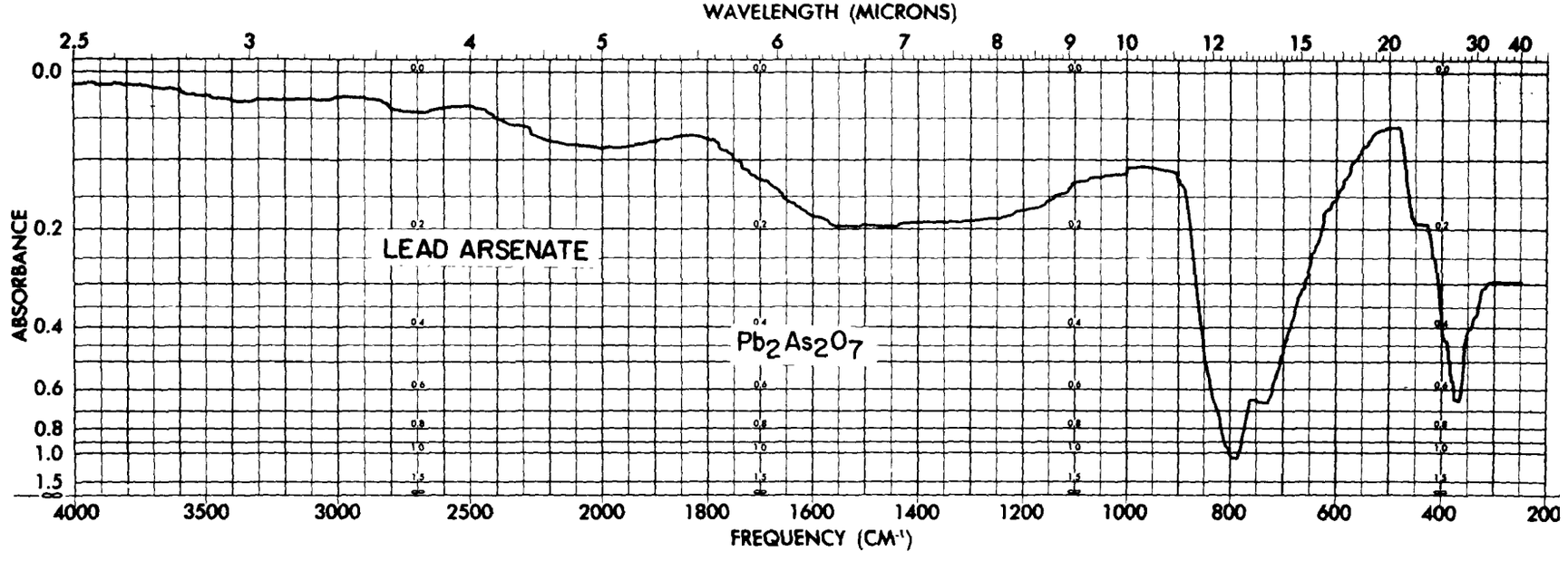

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
KELTHANE
OH
Cl
C
Cl
Cl—C—Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

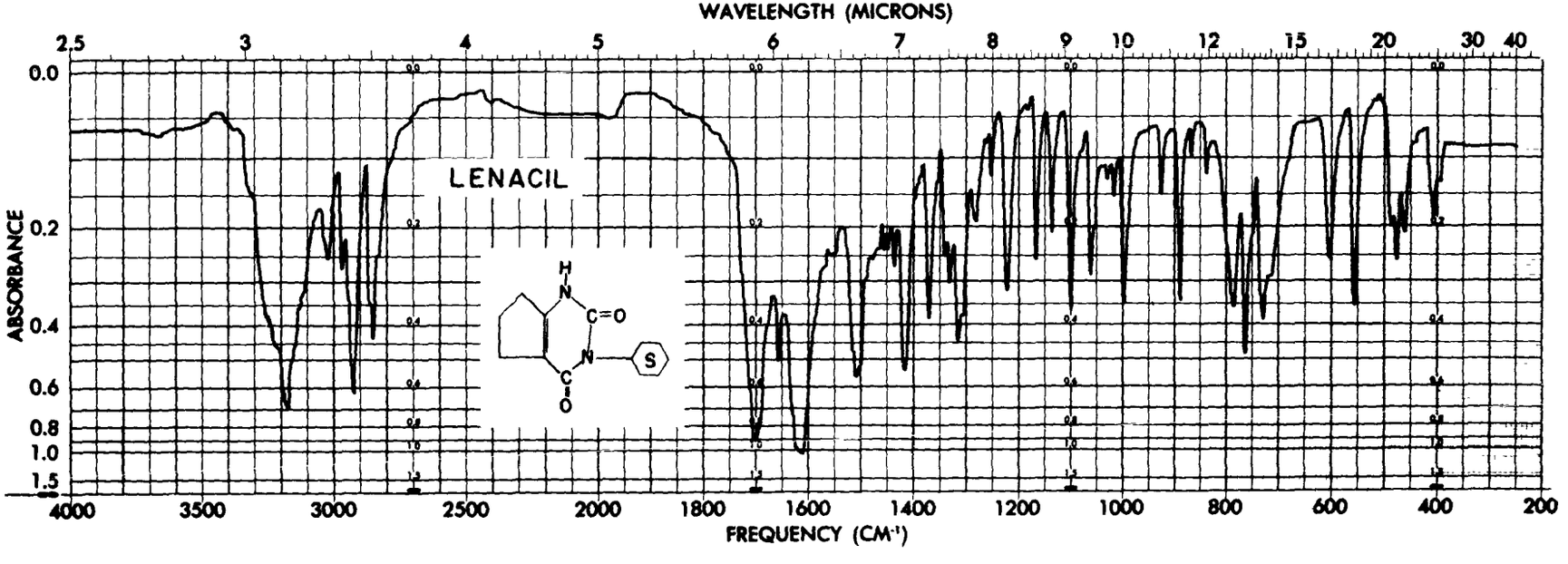

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
KEPONE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

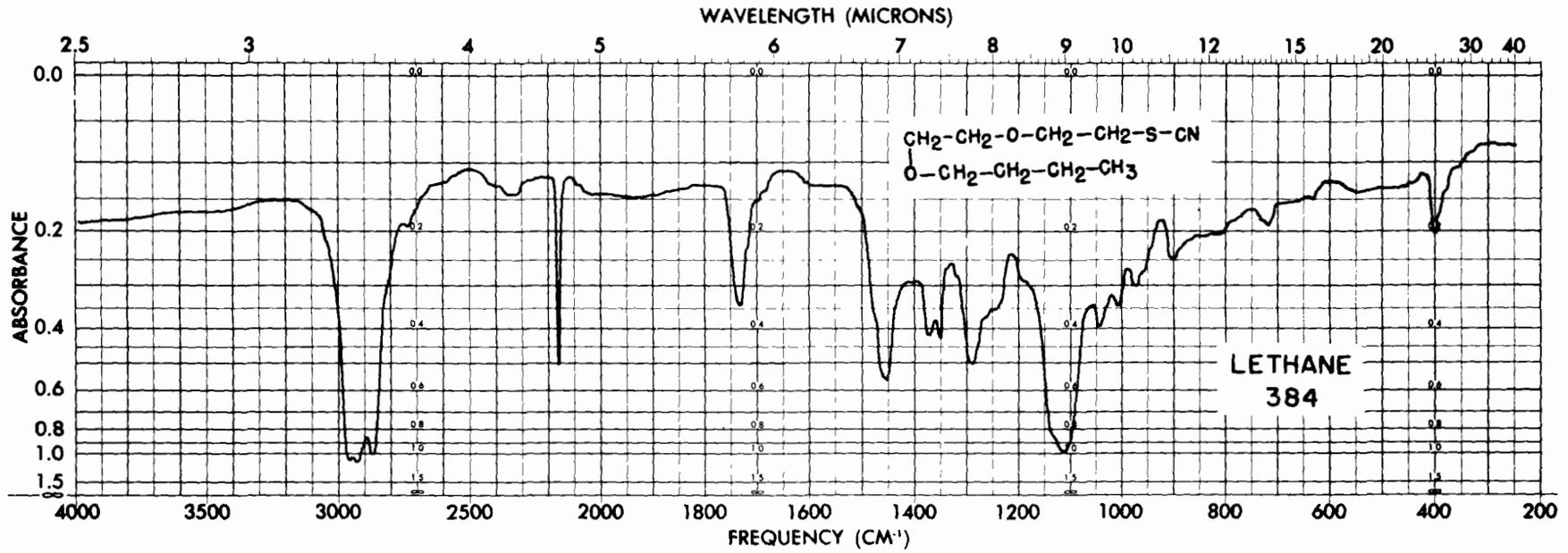

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
LARGON
(TH-6040)
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

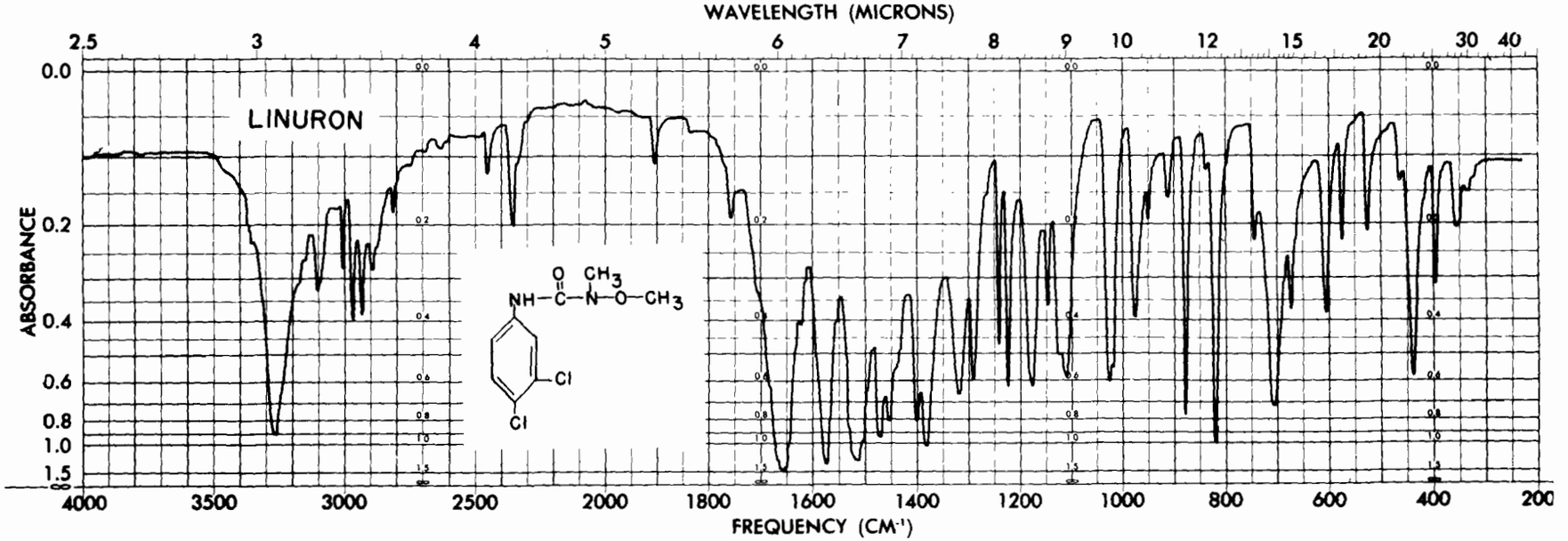

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
LANDRIN
(2,3,5-ISOMER)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

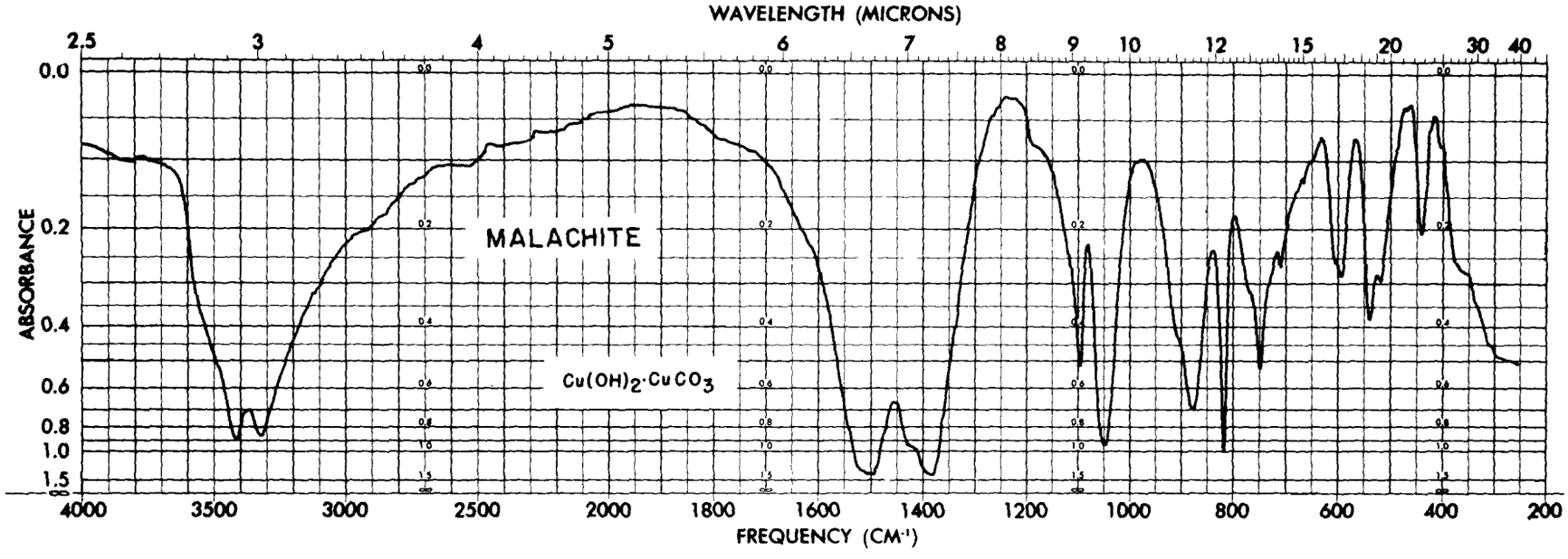

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
LANDRIN
(3,4,5-ISOMER)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

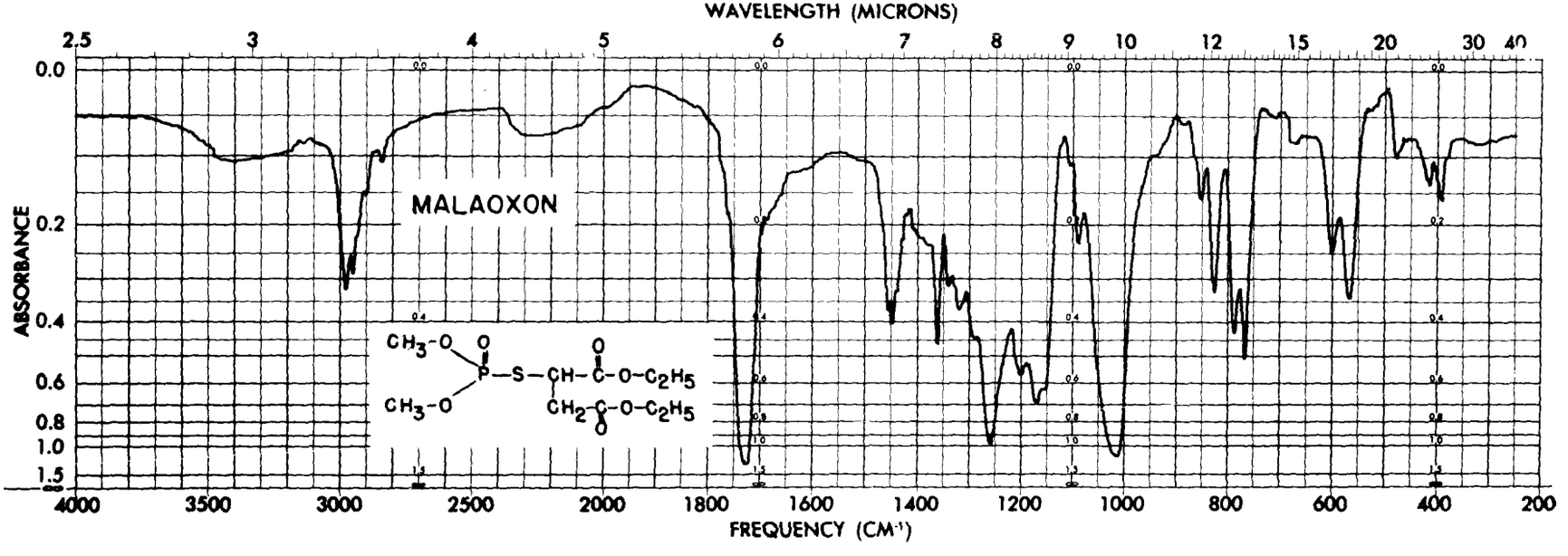

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
LEAD ARSENATE
$Pb_2As_2O_7$
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

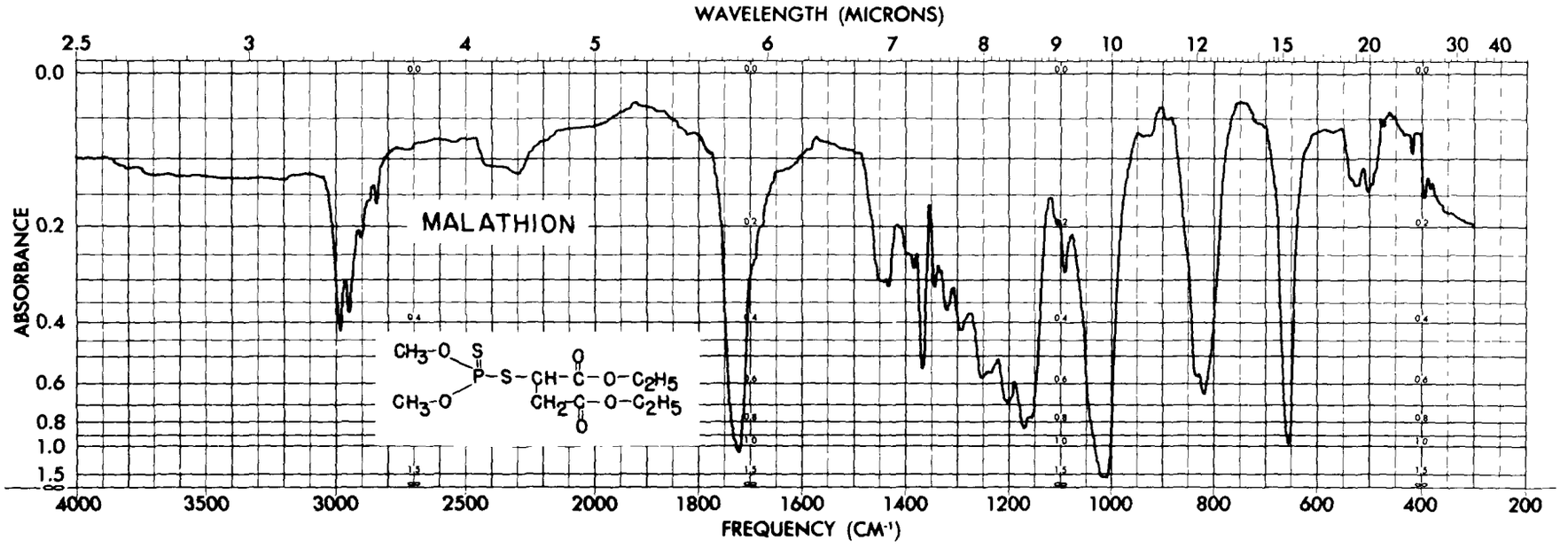

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
LENACIL
H
N
C=O
N
S
C
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

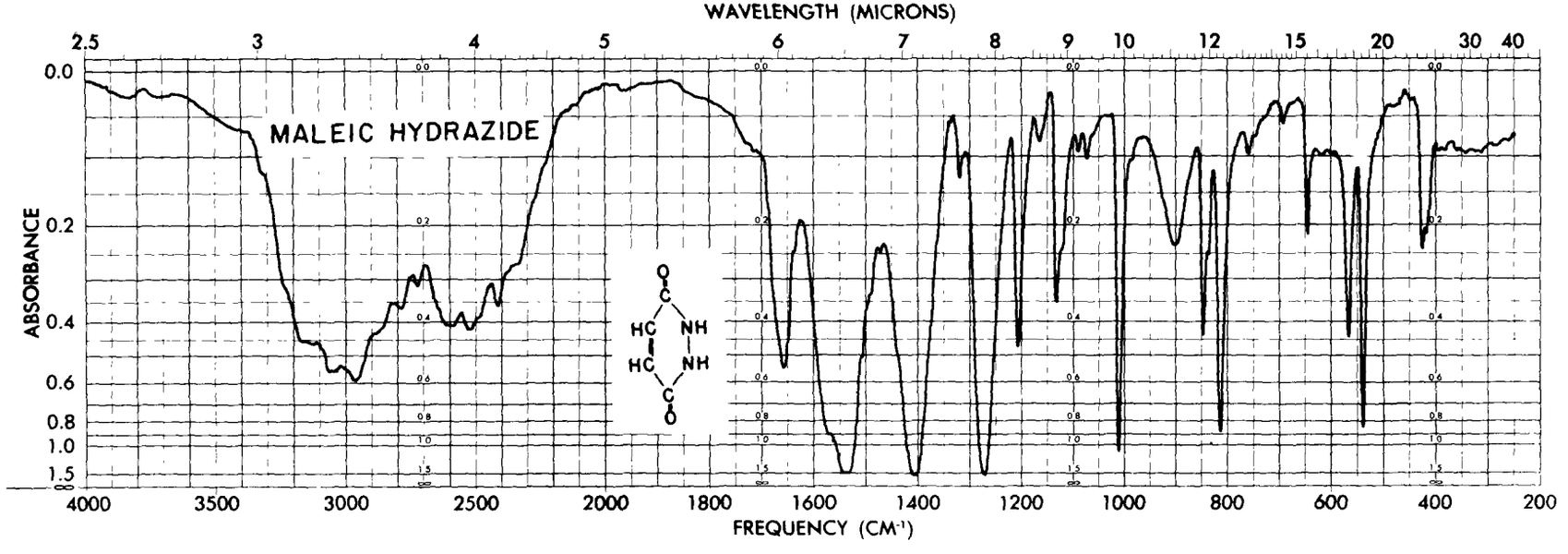

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
CH2-CH2-O-CH2-CH2-S-CN
O-CH2-CH2-CH2-CH3
LETHANE
384
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

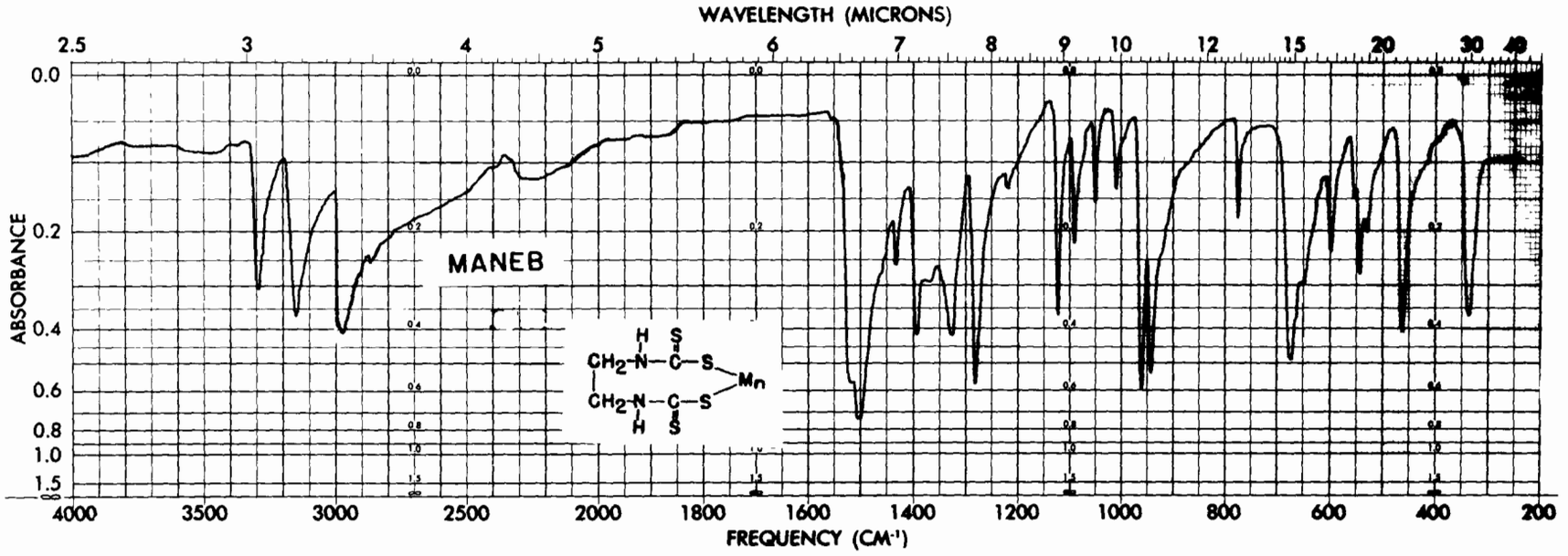

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
LINURON
NH-C-N-O-CH3
CH3
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

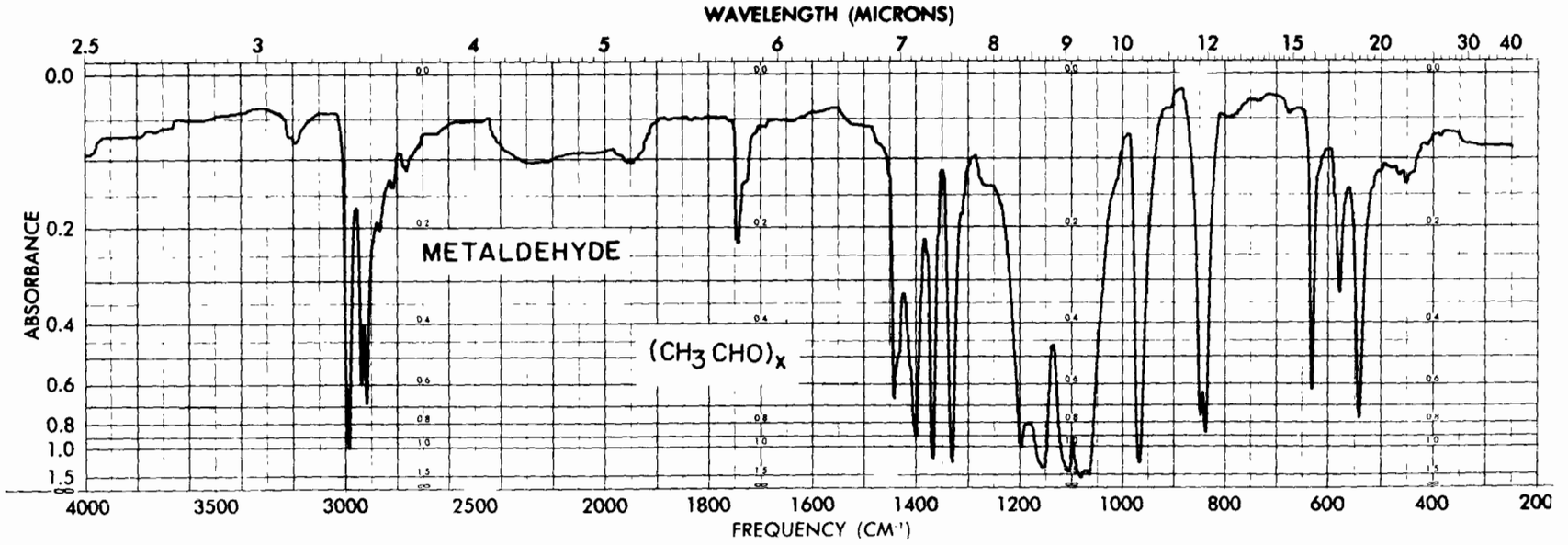

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
MALACHITE
$Cu(OH)_2 \cdot CuCO_3$
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

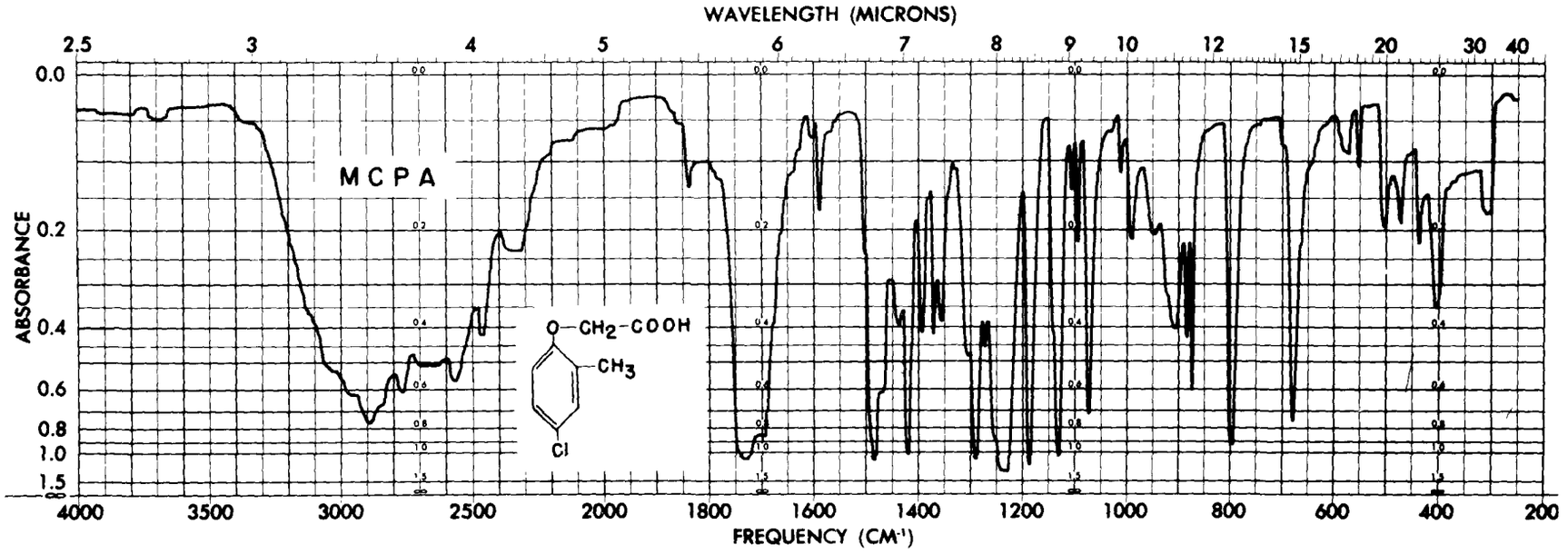

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
MALAOXON
CH_3-O
CH_3-O
P
S
CH
C
O
C_2H_5
CH_2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

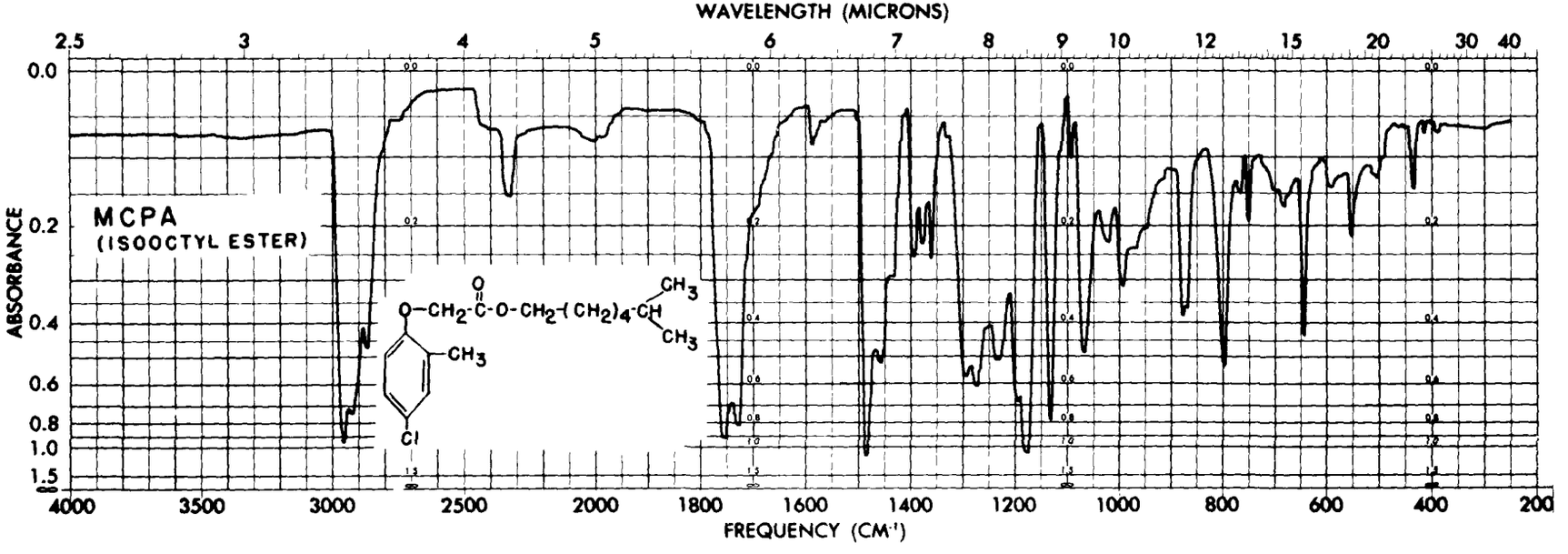

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
MALATHION
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

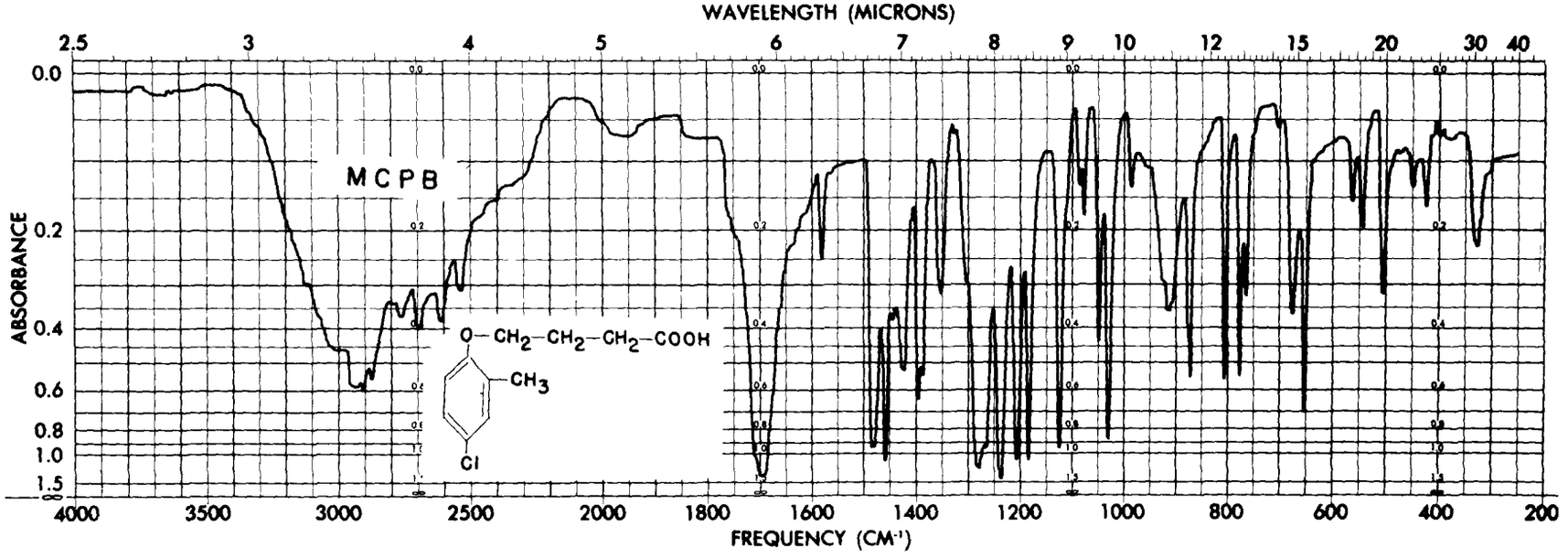

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
MALEIC HYDRAZIDE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

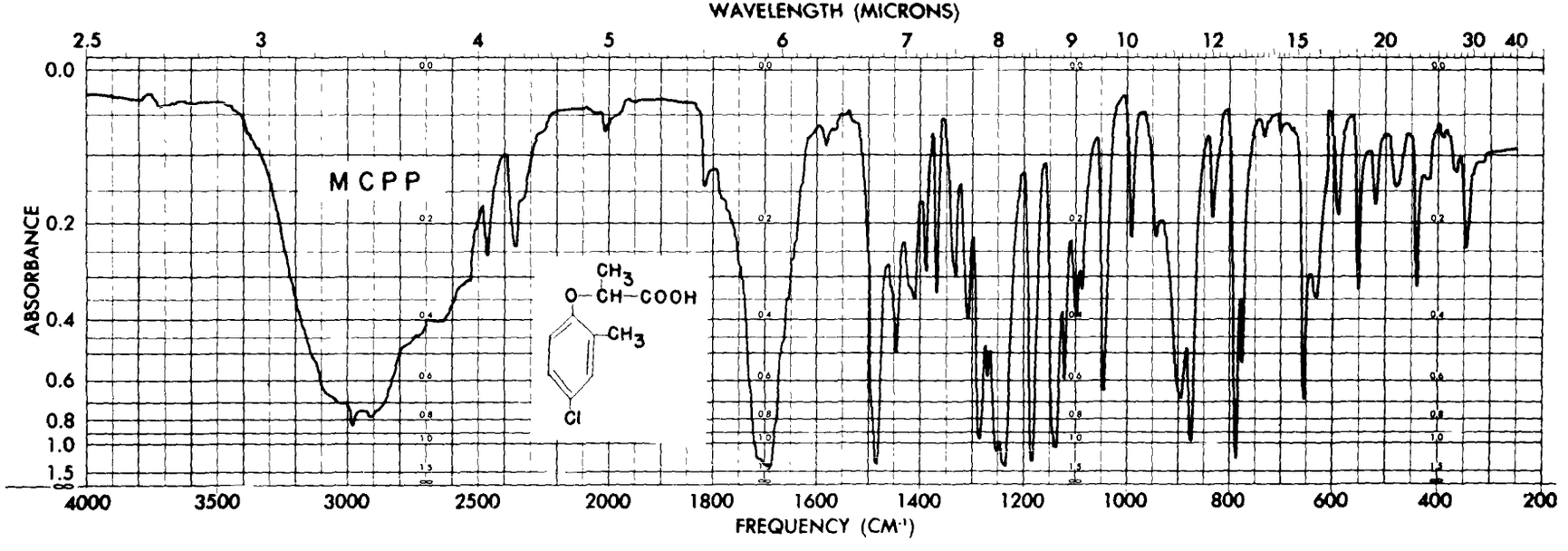

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
MANEB
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

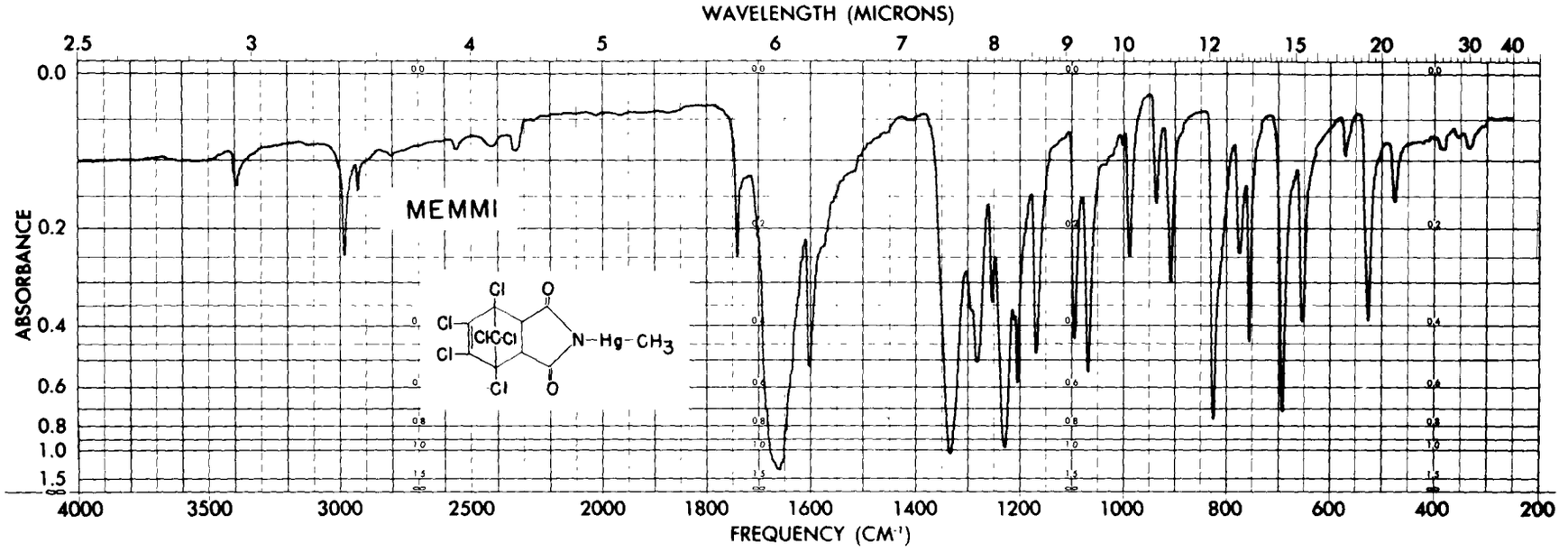

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
METALDEHYDE
(CH3 CHO)x
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

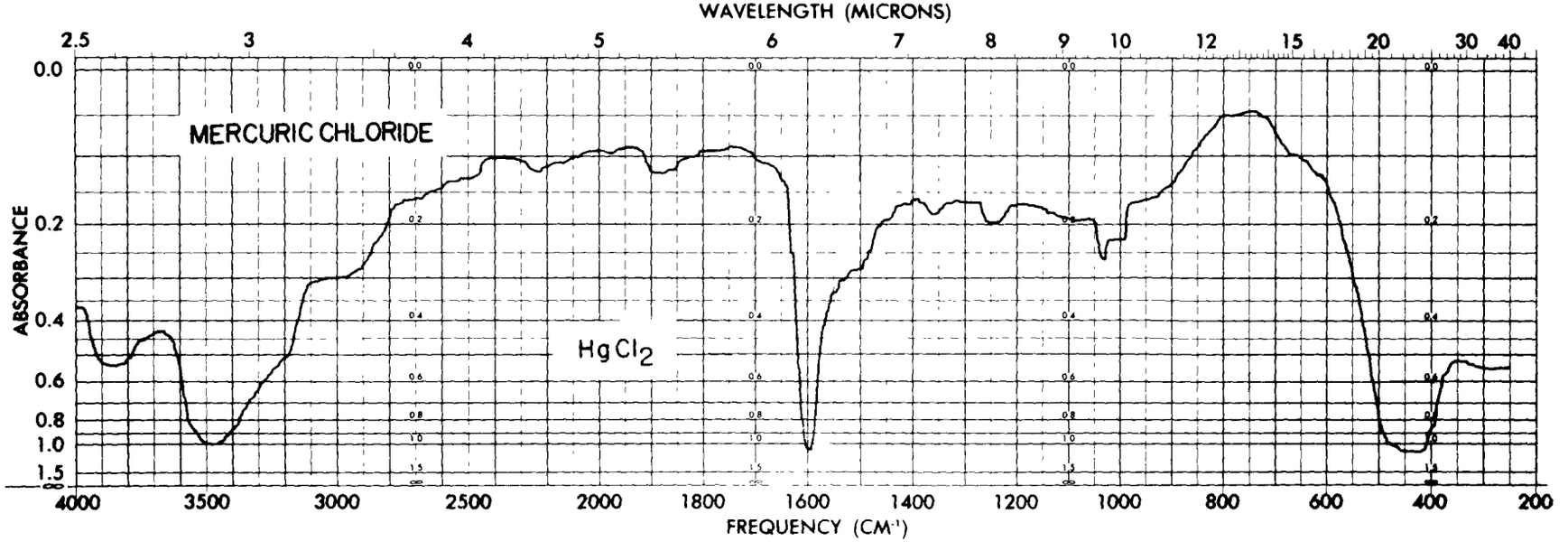

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
MCPA
O-CH2-COOH
CH3
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

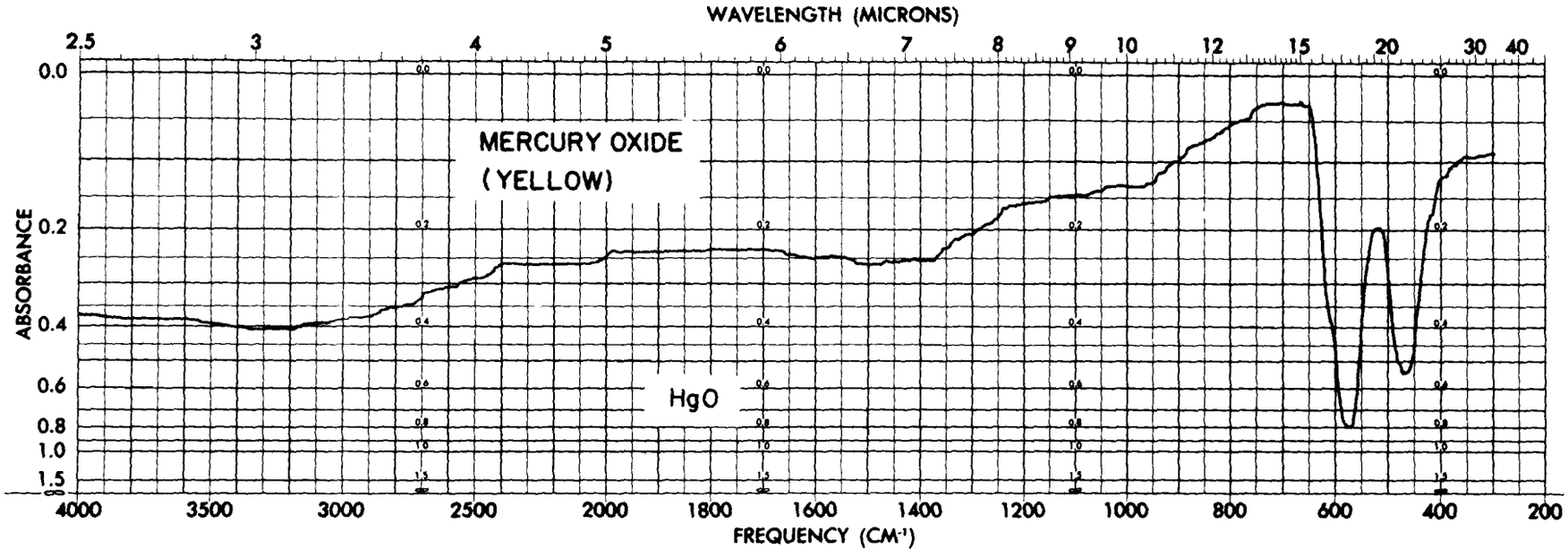

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
MCPA
(ISOOCTYL ESTER)
O
O-CH2-C-O-CH2-(CH2)4-CH
CH3
CH3
CH3
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

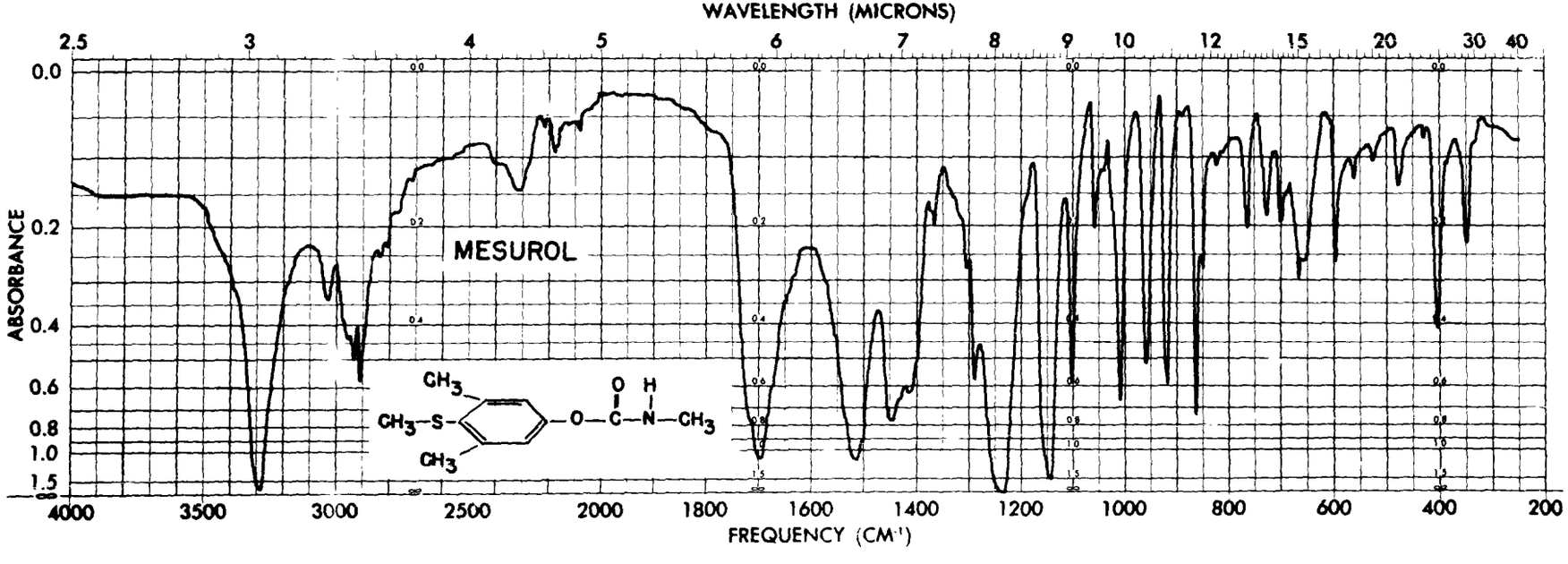

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
MCPB
O–CH2–CH2–CH2–COOH
CH3
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

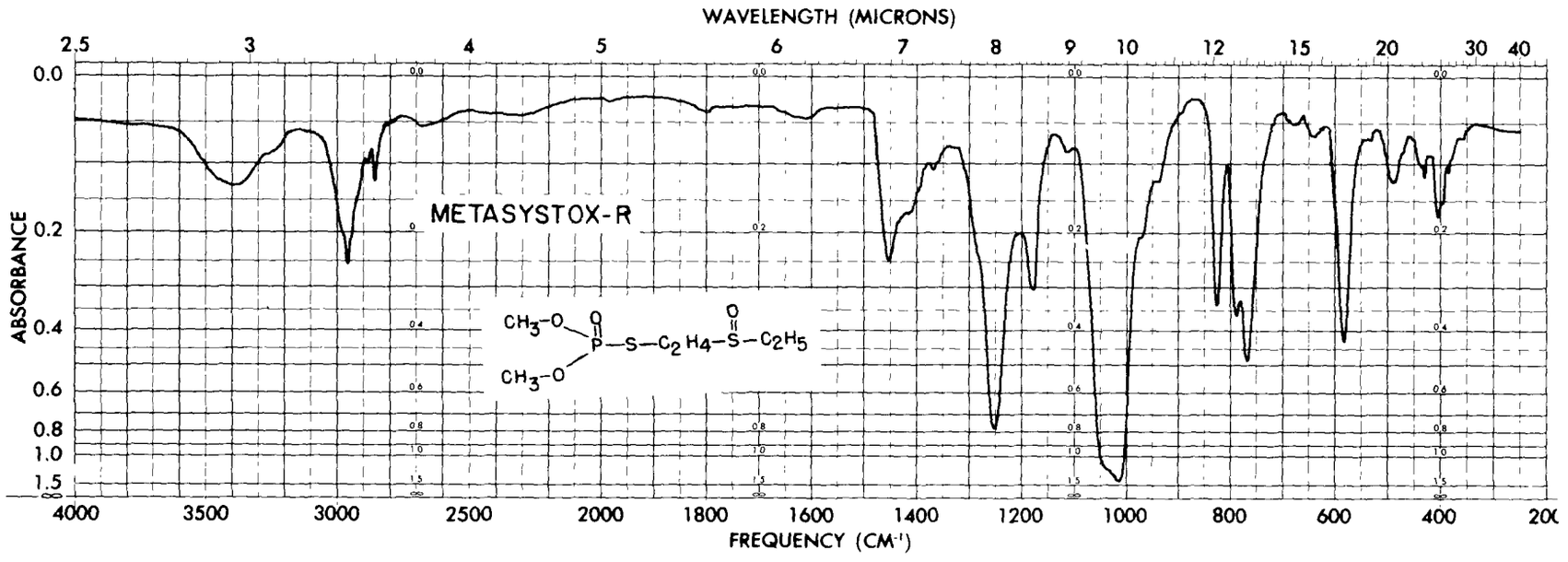

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
MCPP
CH3
O–CH–COOH
CH3
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

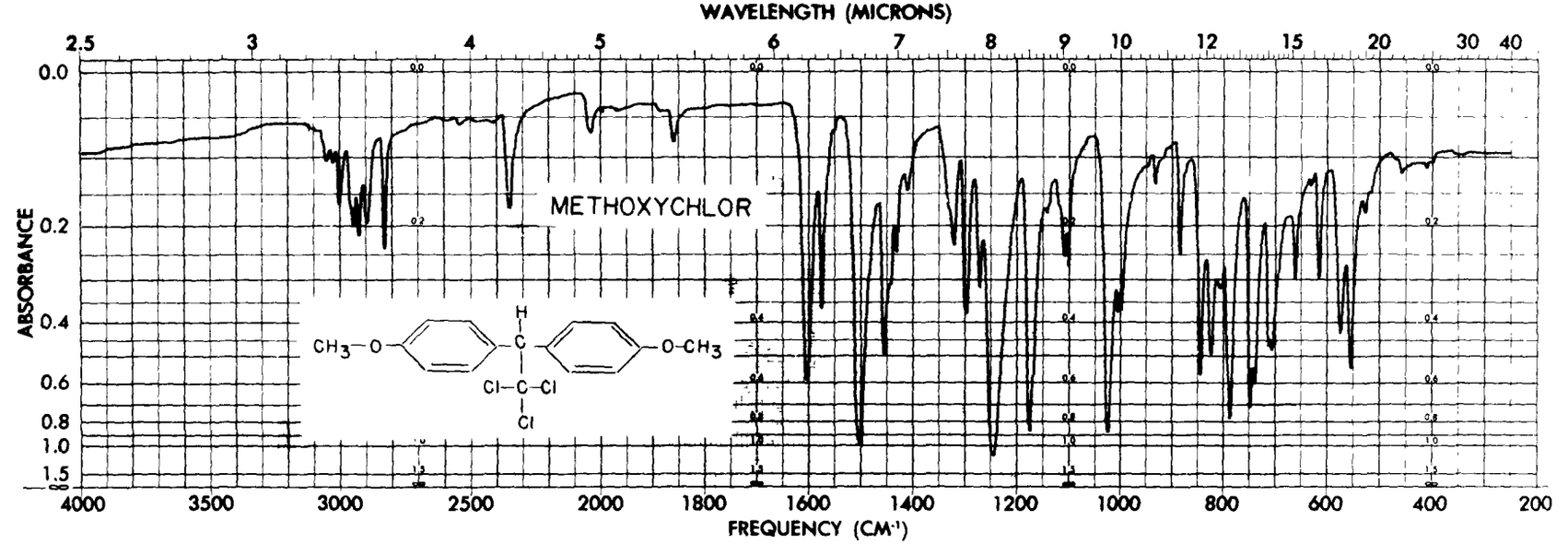

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
MEMMI
Cl
O
Cl
ClCCl
N–Hg–CH3
Cl
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

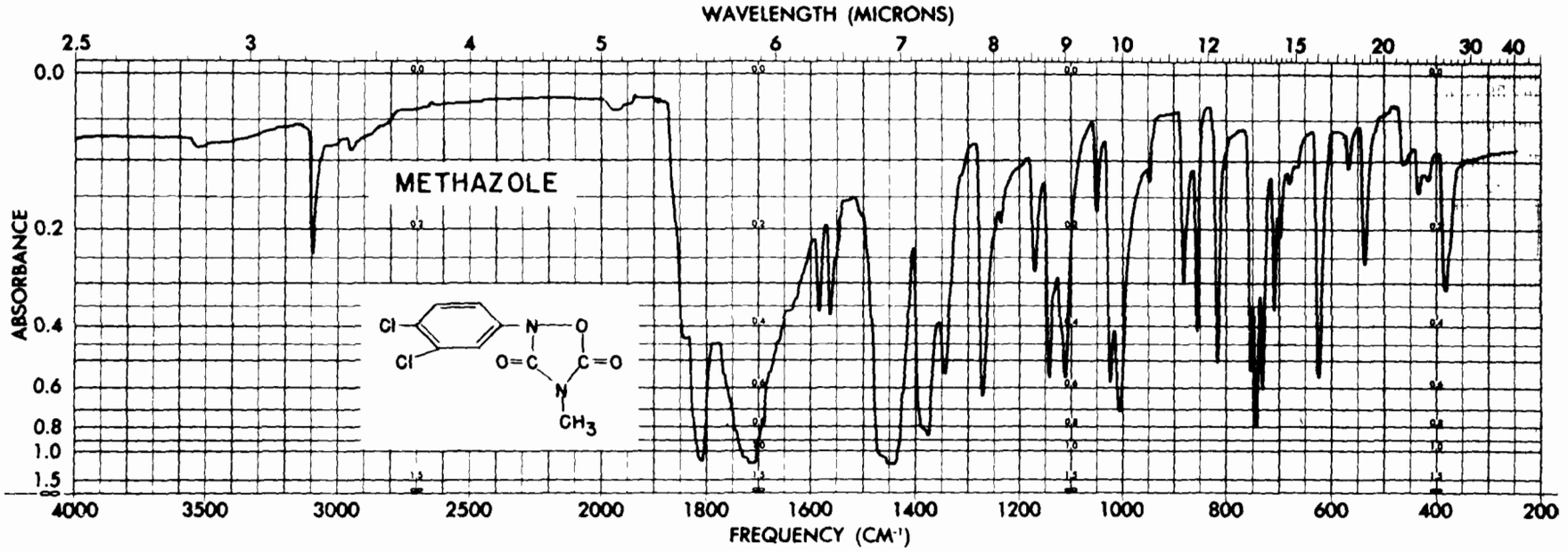

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
MERCURIC CHLORIDE
HgCl2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

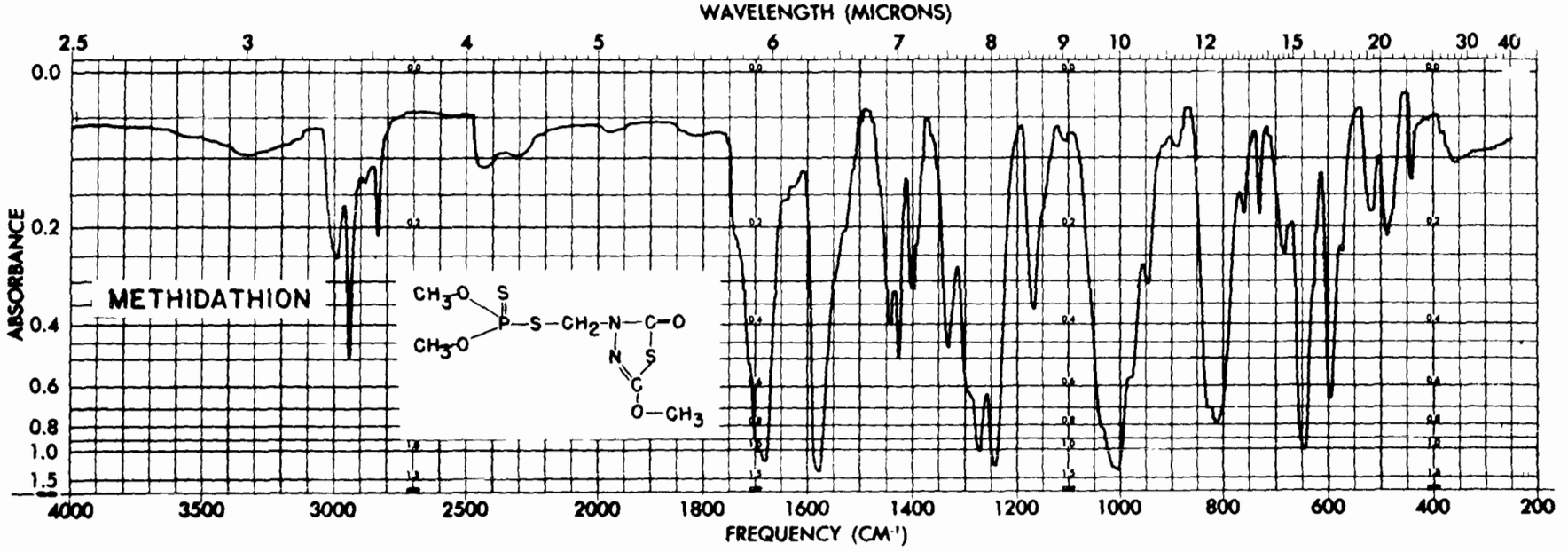

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
MERCURY OXIDE
(YELLOW)
HgO
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

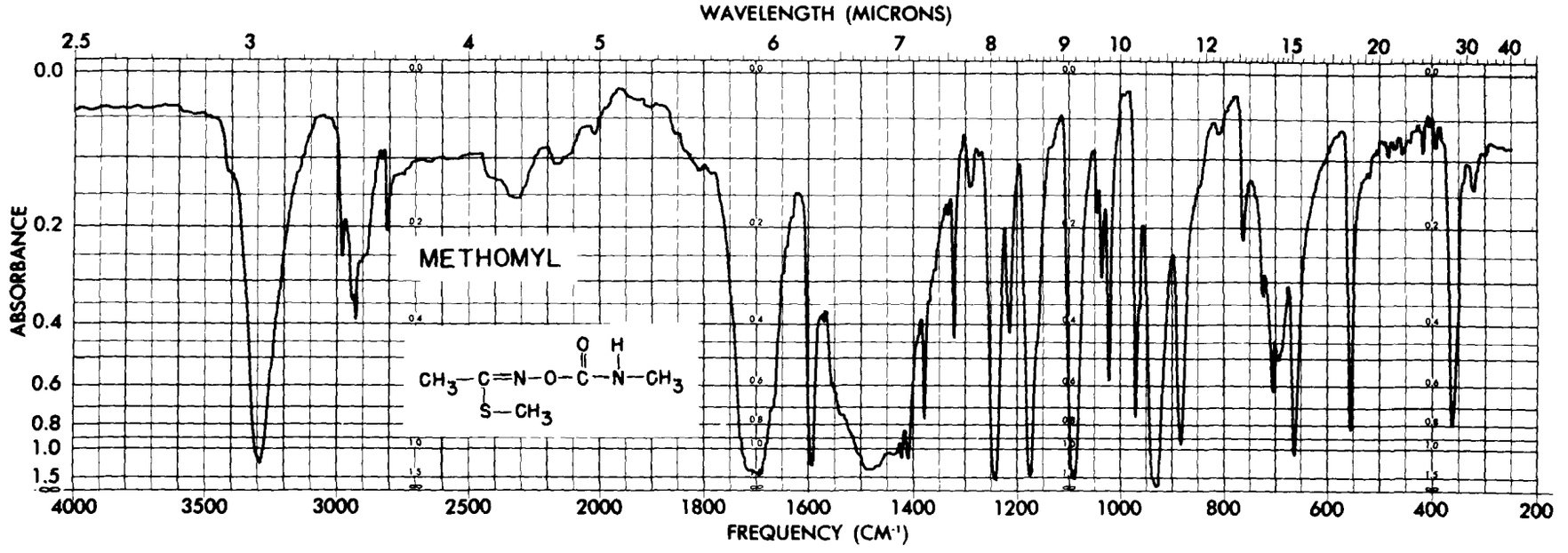

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
MESUROL
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

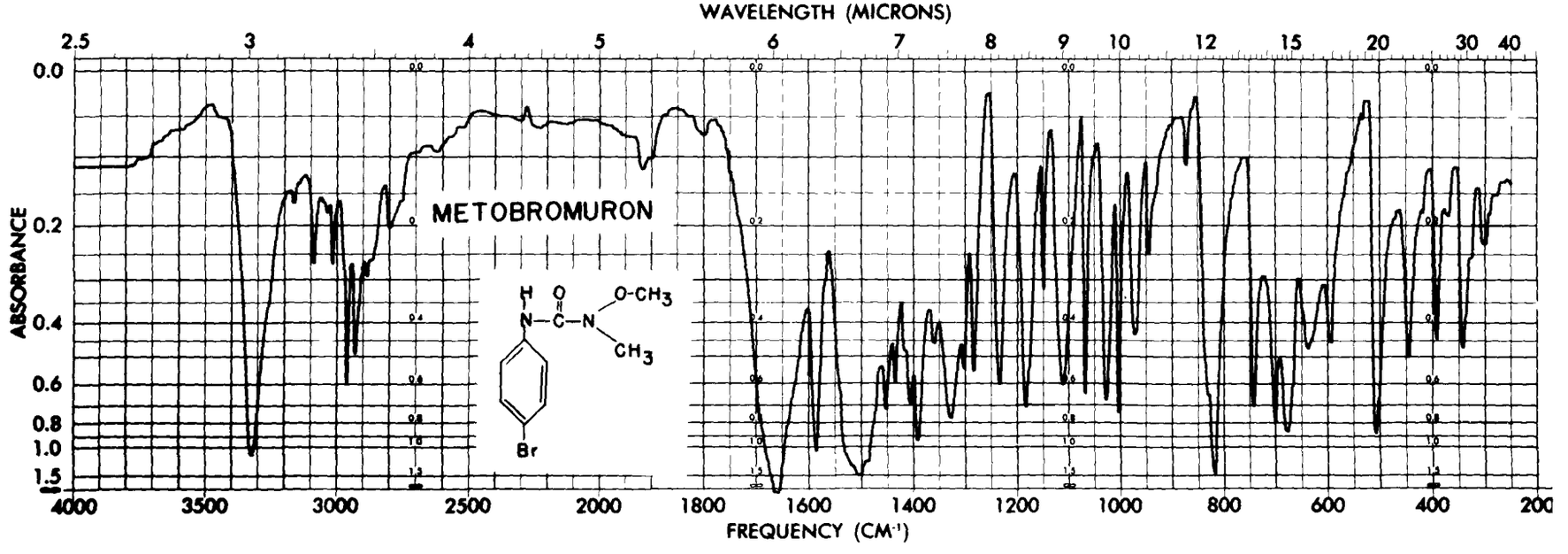

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
METASYSTOX-R
CH3-O
O
P
S-C2H4-S-C2H5
O
CH3-O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

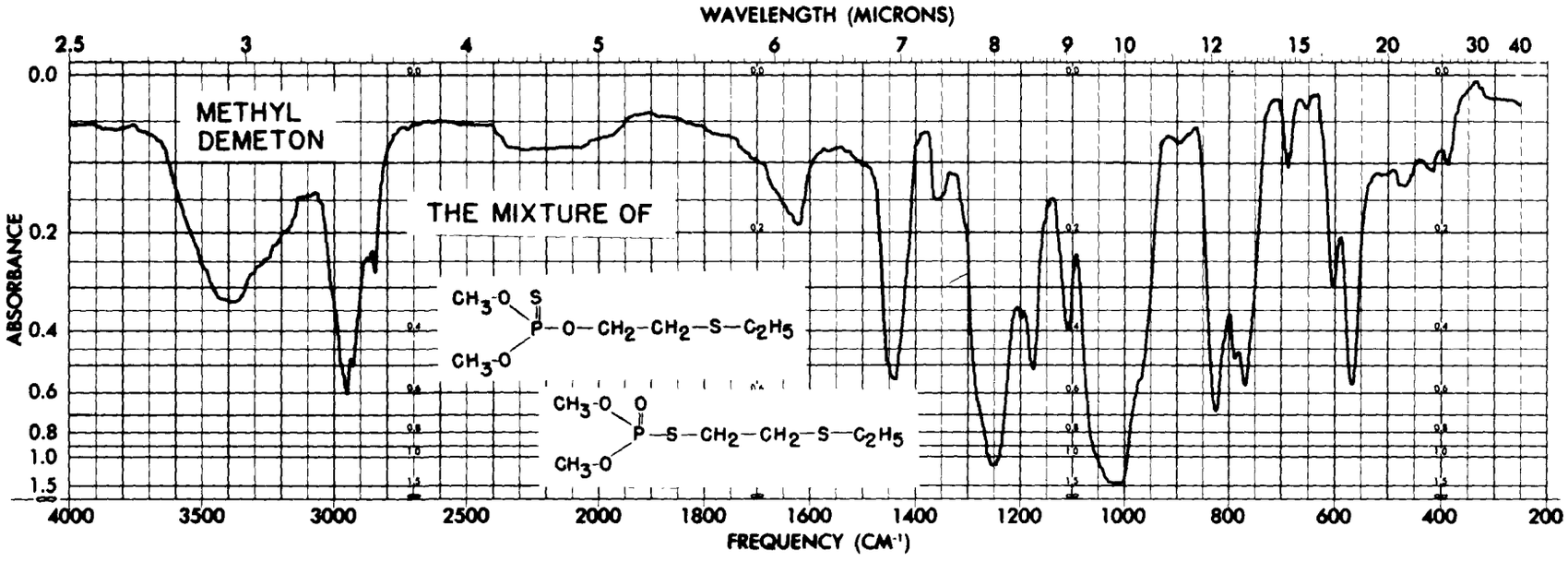

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
METHOXYCHLOR
CH3-O
H
C
O-CH3
Cl-C-Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

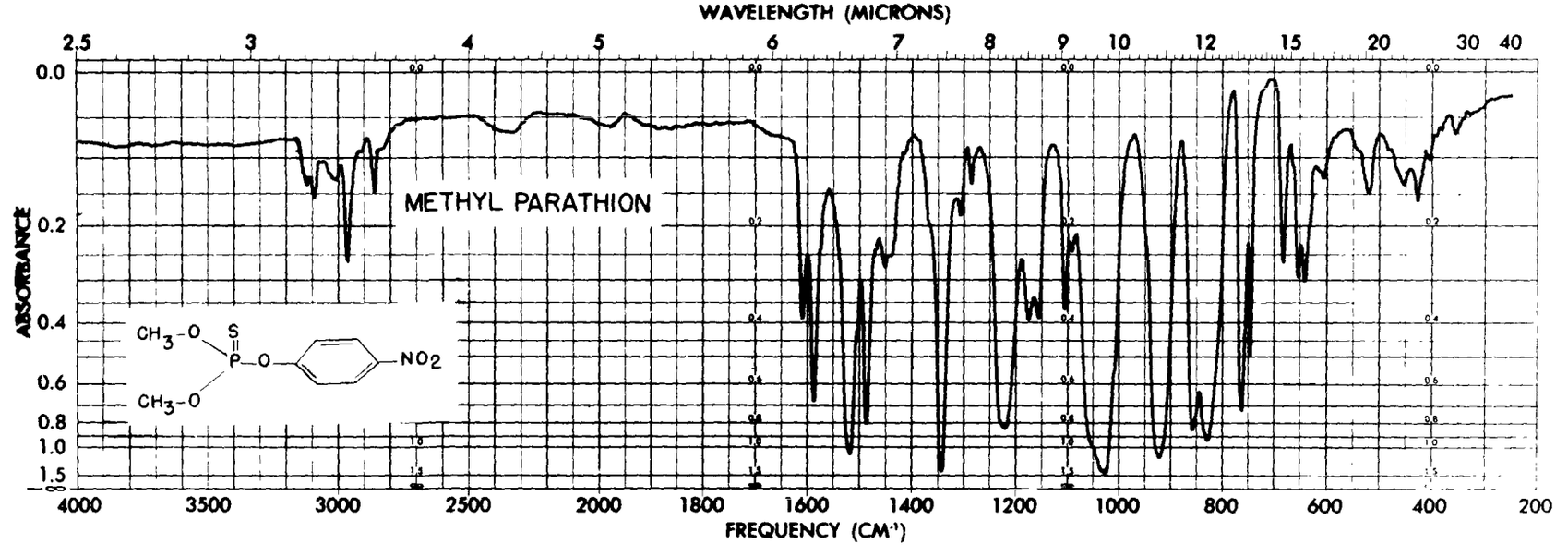

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
METHAZOLE
Cl
Cl
N
O
O=C
C=O
N
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

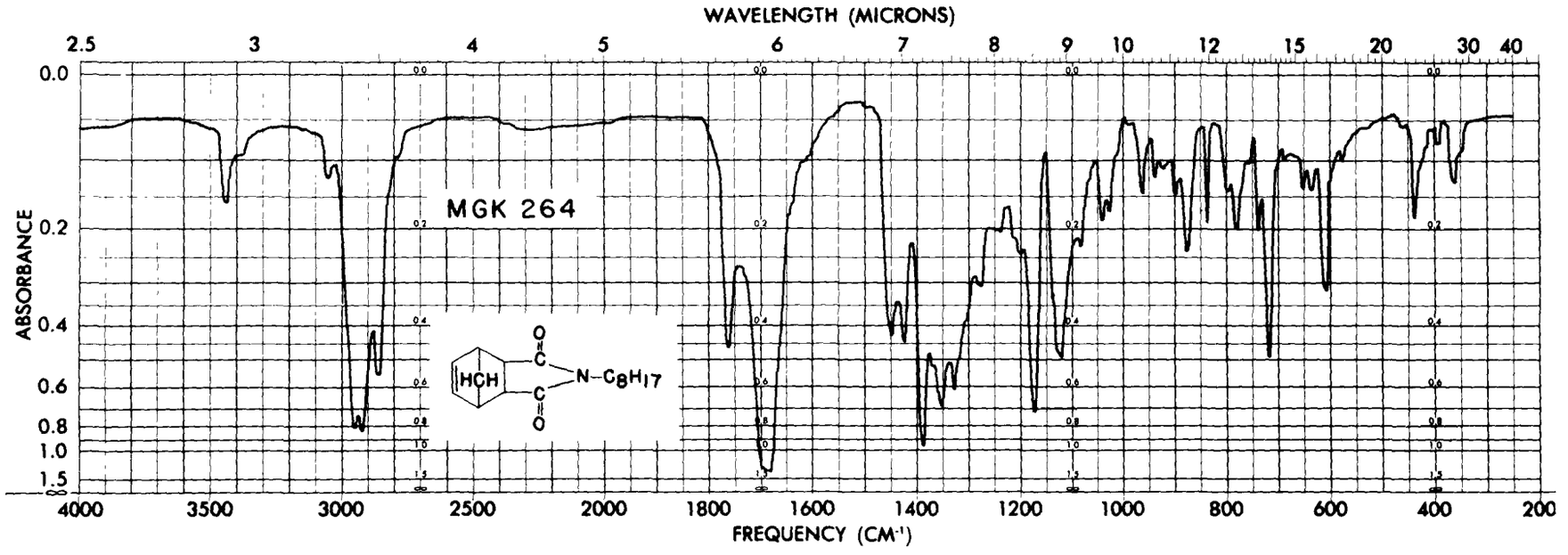

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
METHIDATHION
CH3O
S
P
S
CH2
N
C
O
CH3O
N
S
C
O
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

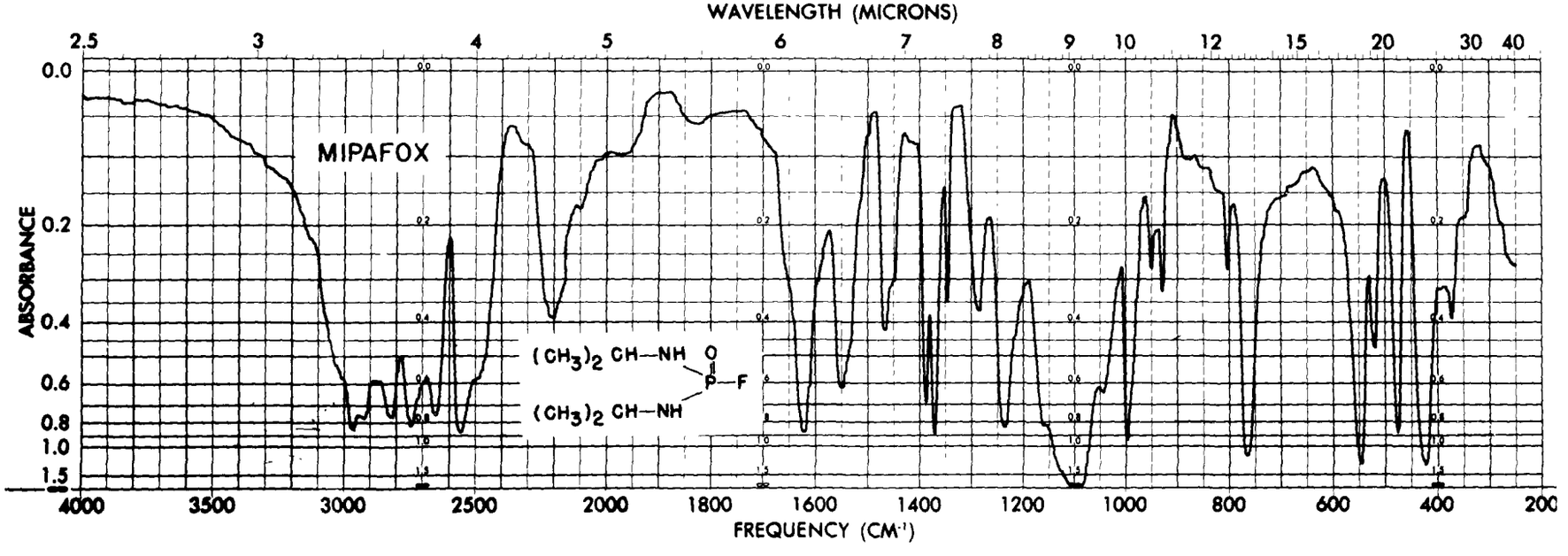

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
METHOMYL
FREQUENCY (CM⁻¹)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200

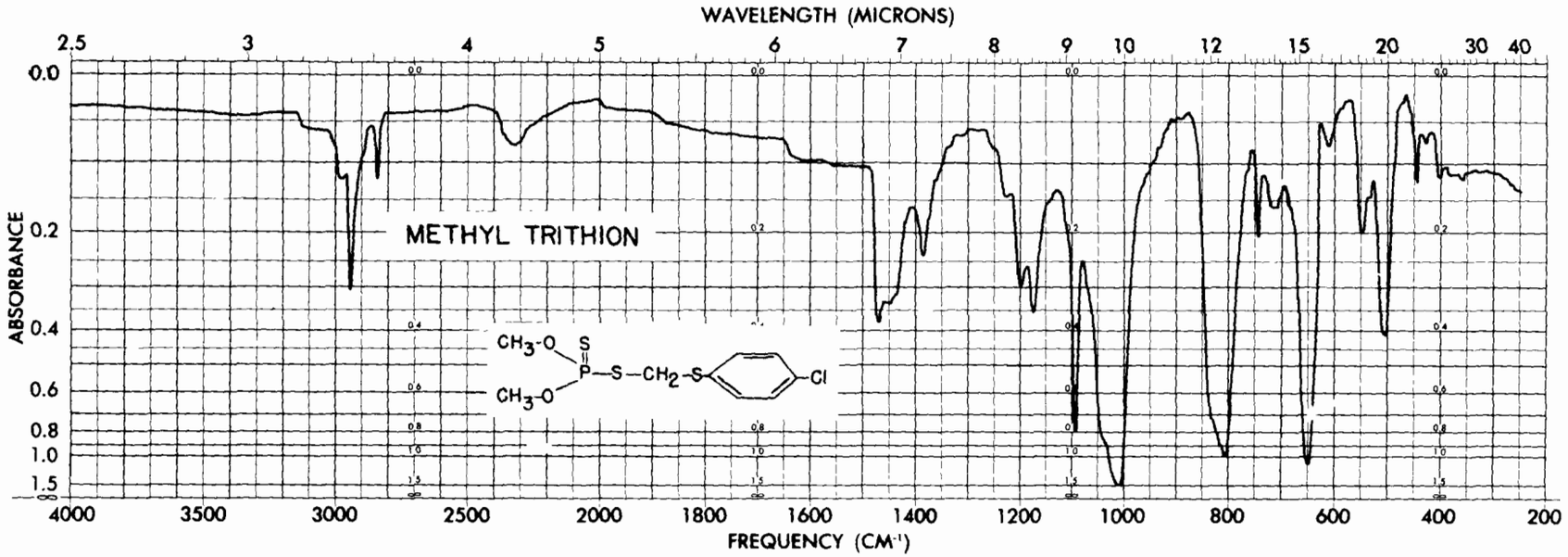

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
METOBROMURON
Br
FREQUENCY (CM⁻¹)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200

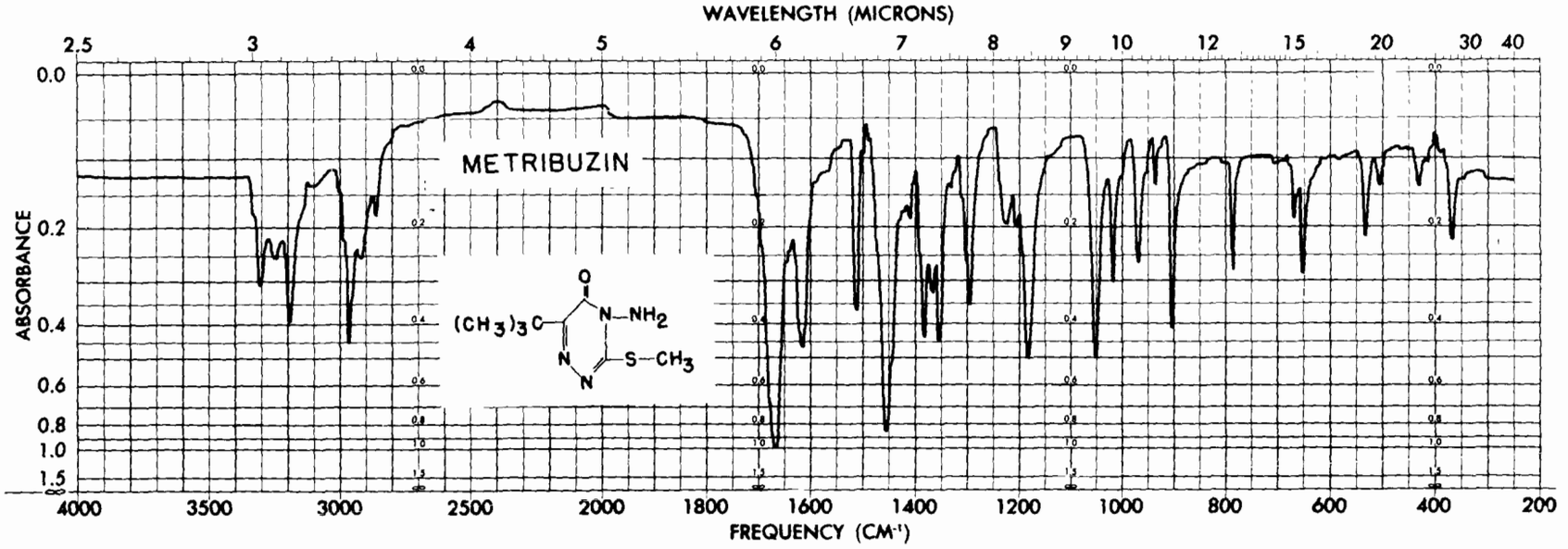

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
METHYL
DEMETON
THE MIXTURE OF
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

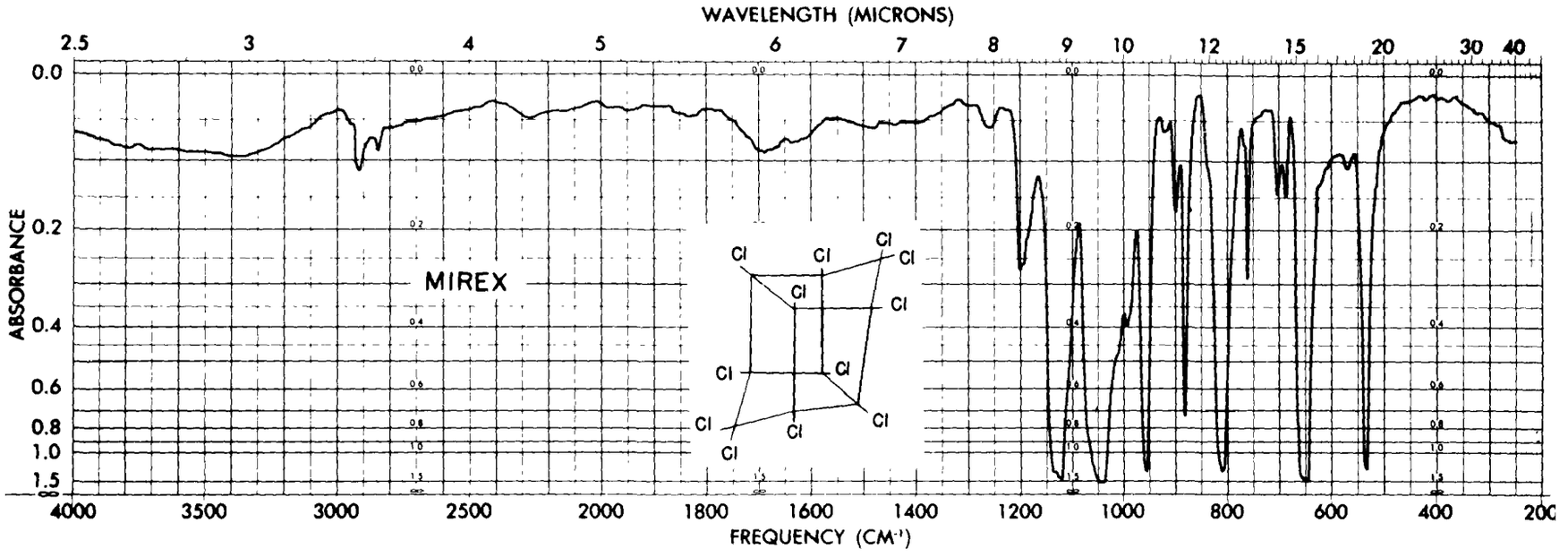

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
METHYL PARATHION
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

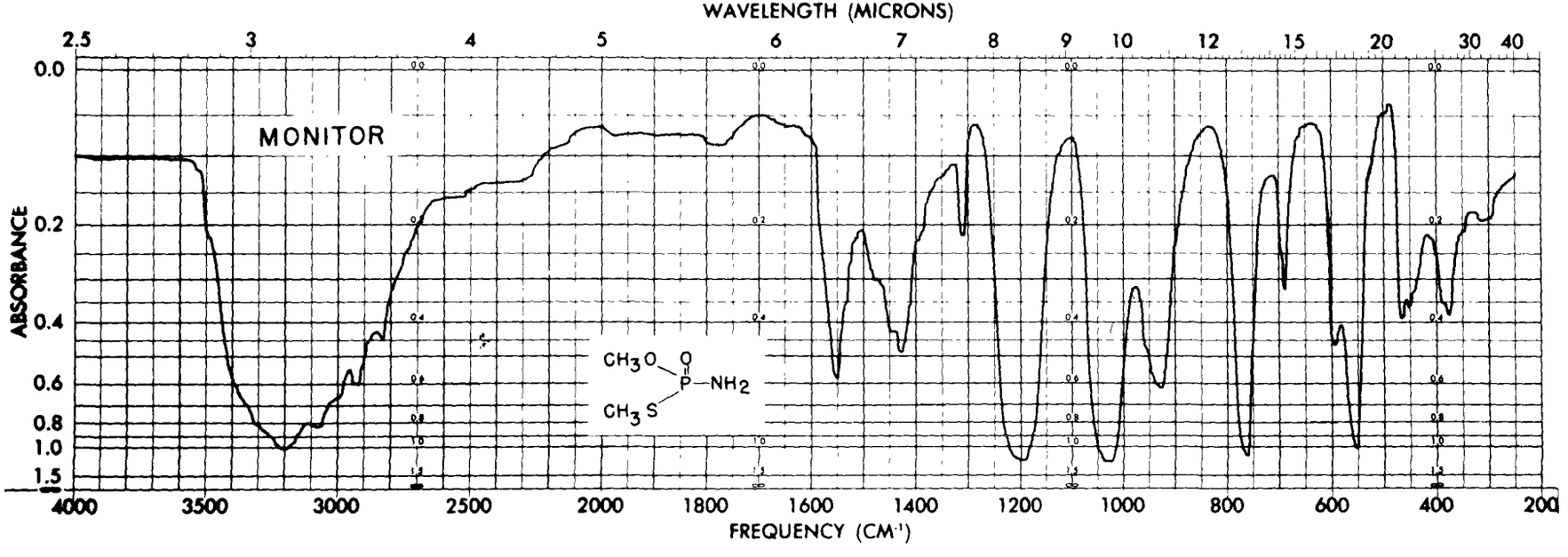

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
MGK 264
HCH
O
C
N–C8H17
C
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

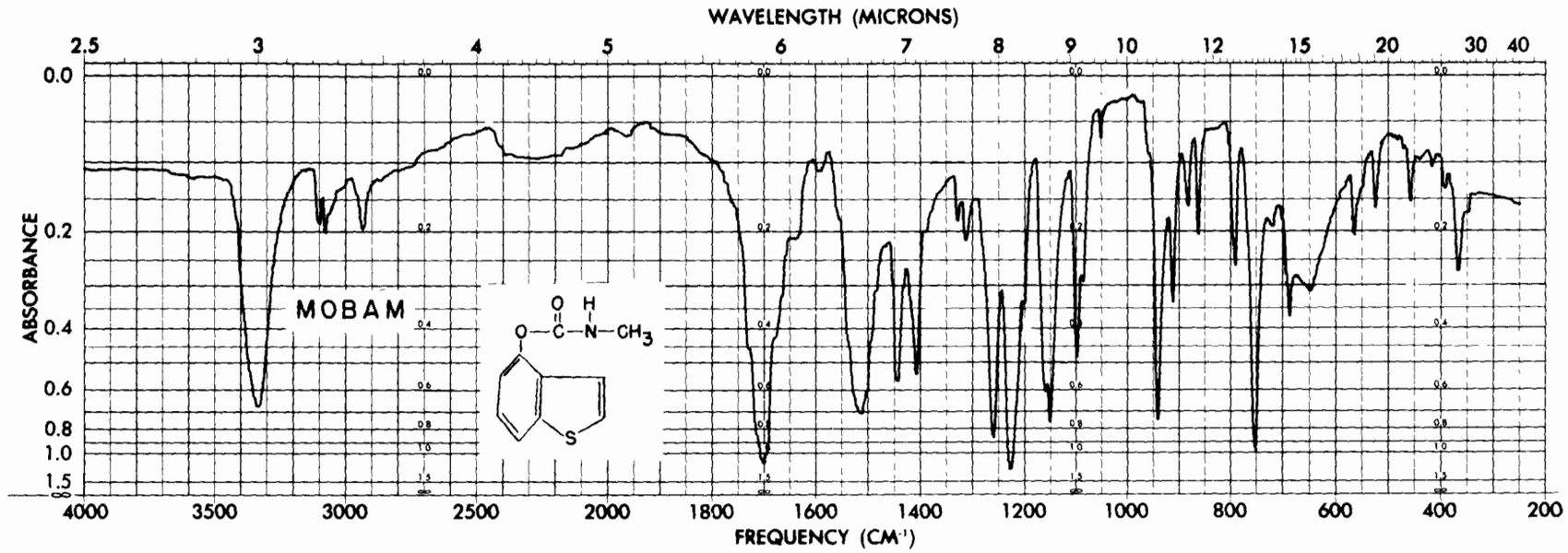

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
MIPAFOX
(CH3)2 CH–NH
O
P–F
(CH3)2 CH–NH
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
METHYL TRITHION
CH3-O
S
P
S
CH2
S
Cl
CH3-O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
METRIBUZIN
O
(CH3)3C
N
NH2
N
S
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
MIREX
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
MONITOR
CH3O
O
P
NH2
CH3 S
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
MOBAM
O H
O—C—N—CH3
S
4000
3500
3000
2500
2000
1800
1600
1400
1200
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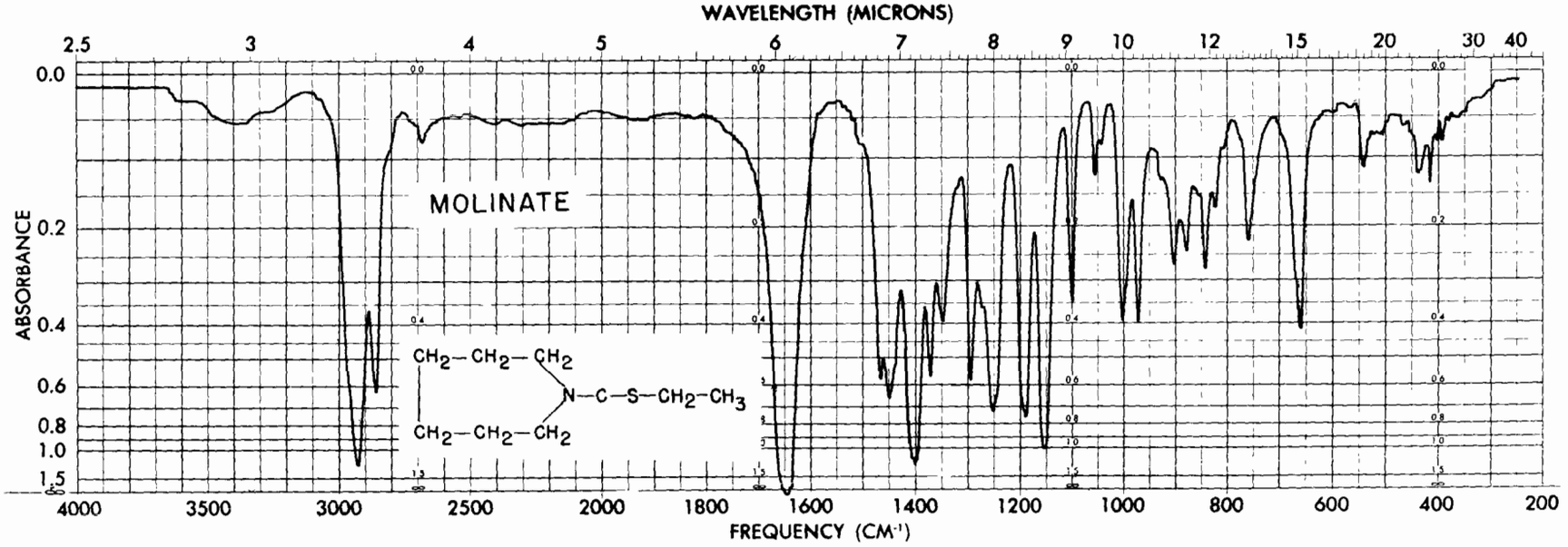
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
MOLINATE
CH2—CH2—CH2
N—C—S—CH2—CH3
CH2—CH2—CH2
4000
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3000
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1800
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800
600
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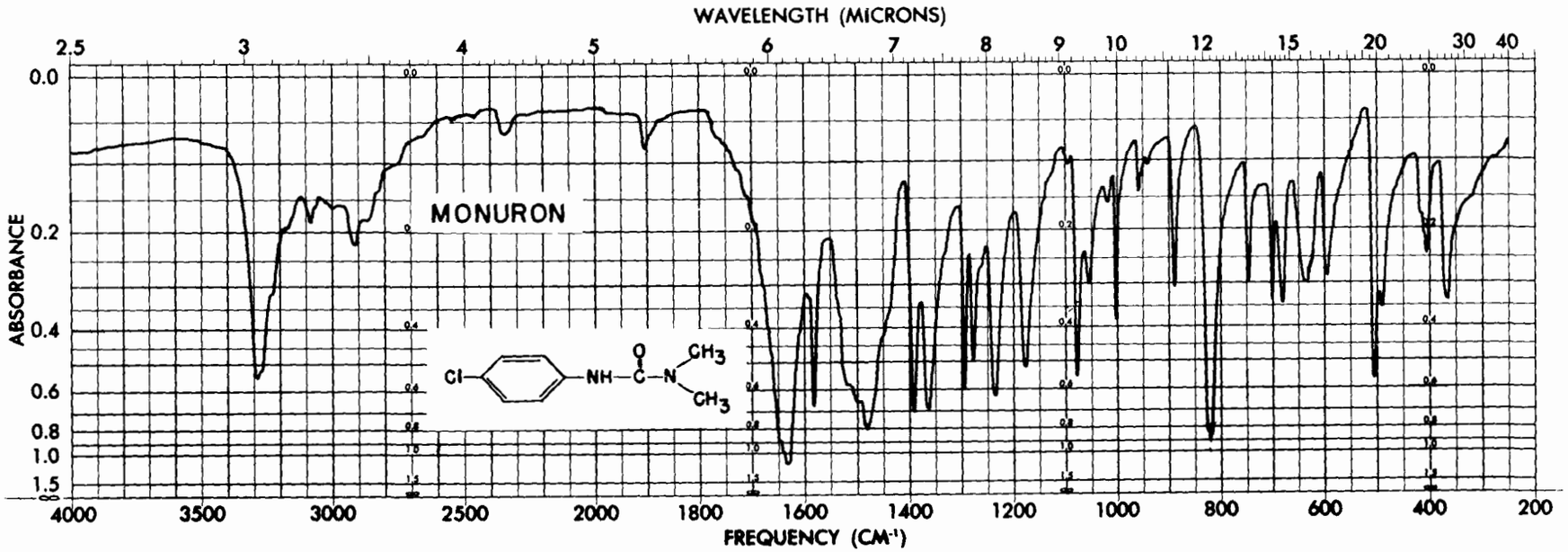
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
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3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
MONURON
Cl
NH
C
O
N
CH3
CH3
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2500
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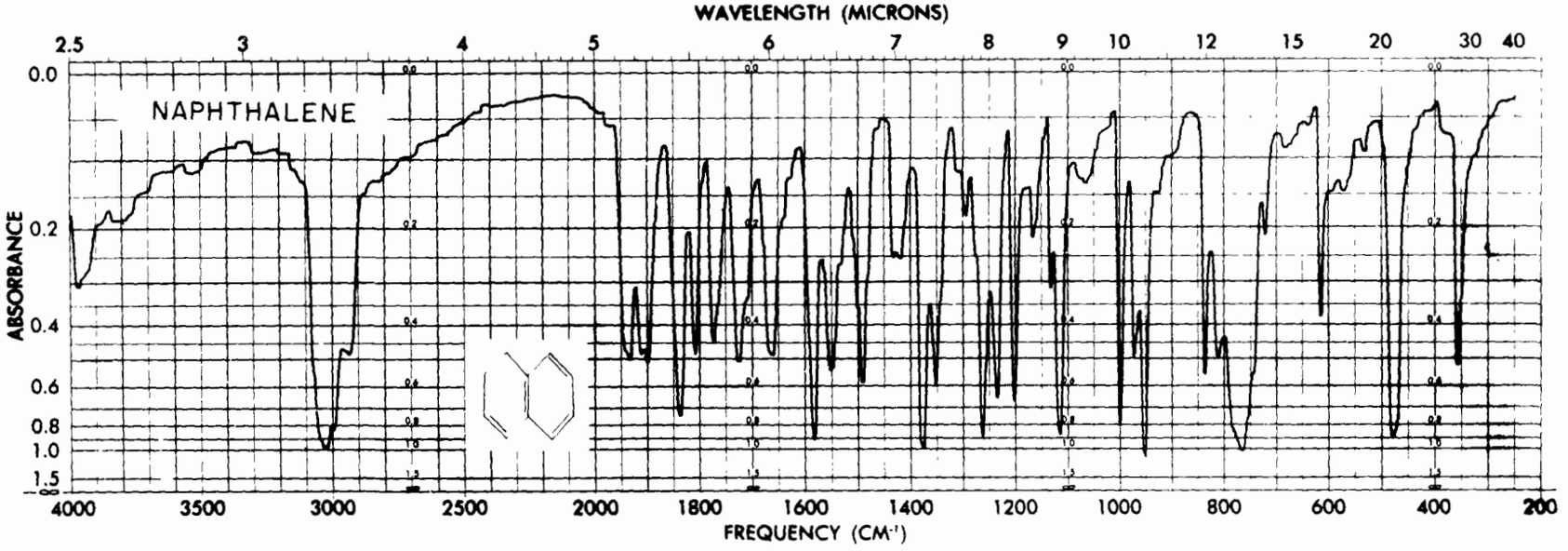
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
4
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7
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9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
NAPHTHALENE
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800
600
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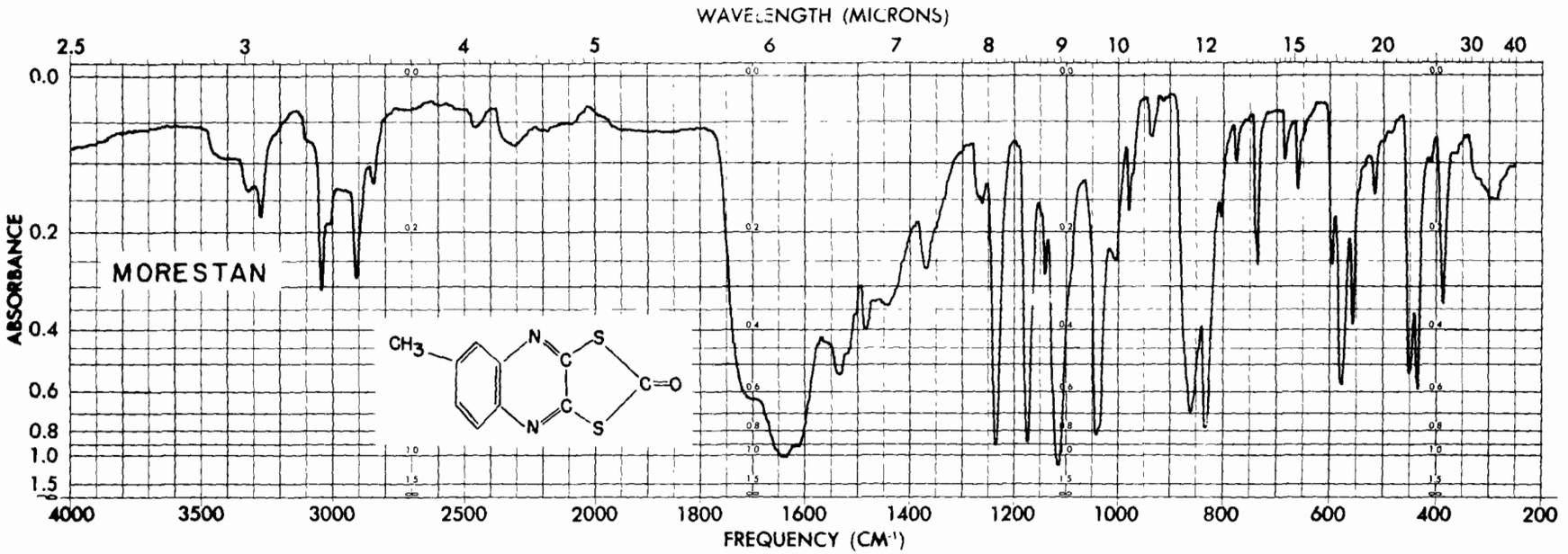
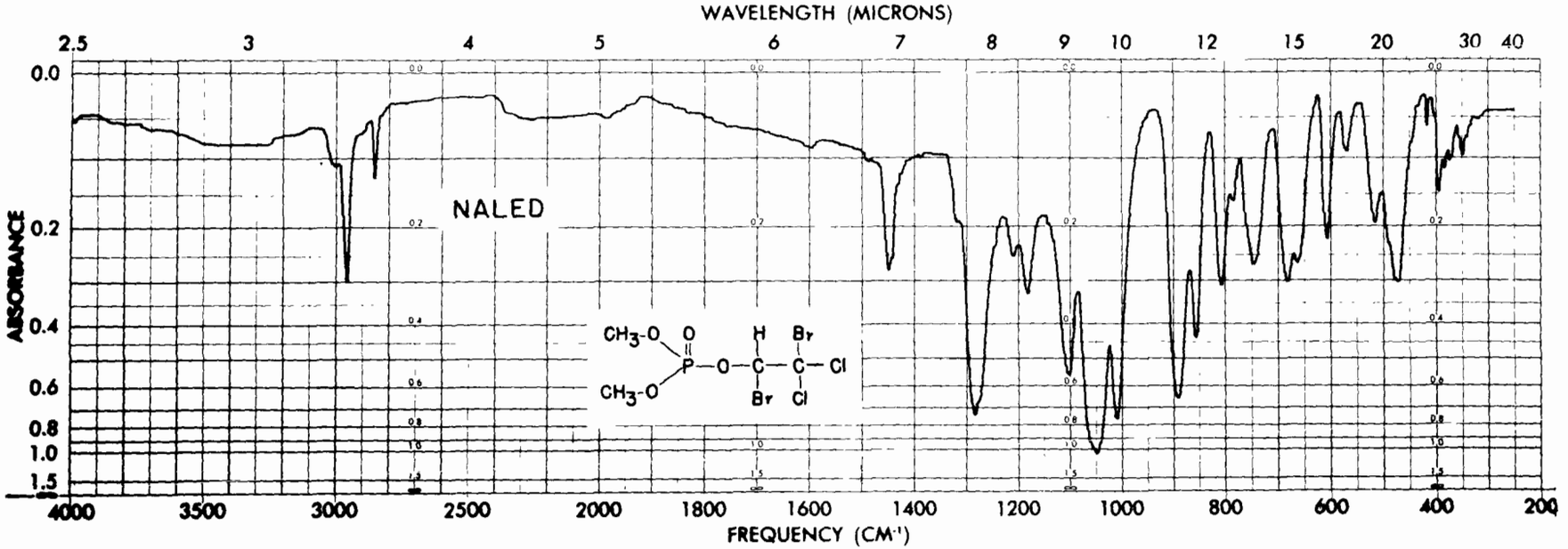
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5 3 4 5 6 7 8 9 10 12 15 20 30 40
ABSORBANCE
0.0 0.2 0.4 0.6 0.8 1.0 1.5
MORESTAN
CH3
N
S
C
C=O
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5 3 4 5 6 7 8 9 10 12 15 20 30 40
ABSORBANCE
0.0 0.2 0.4 0.6 0.8 1.0 1.5
NALED
CH3-O
O
P
O
C
H
Br
Cl
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 200
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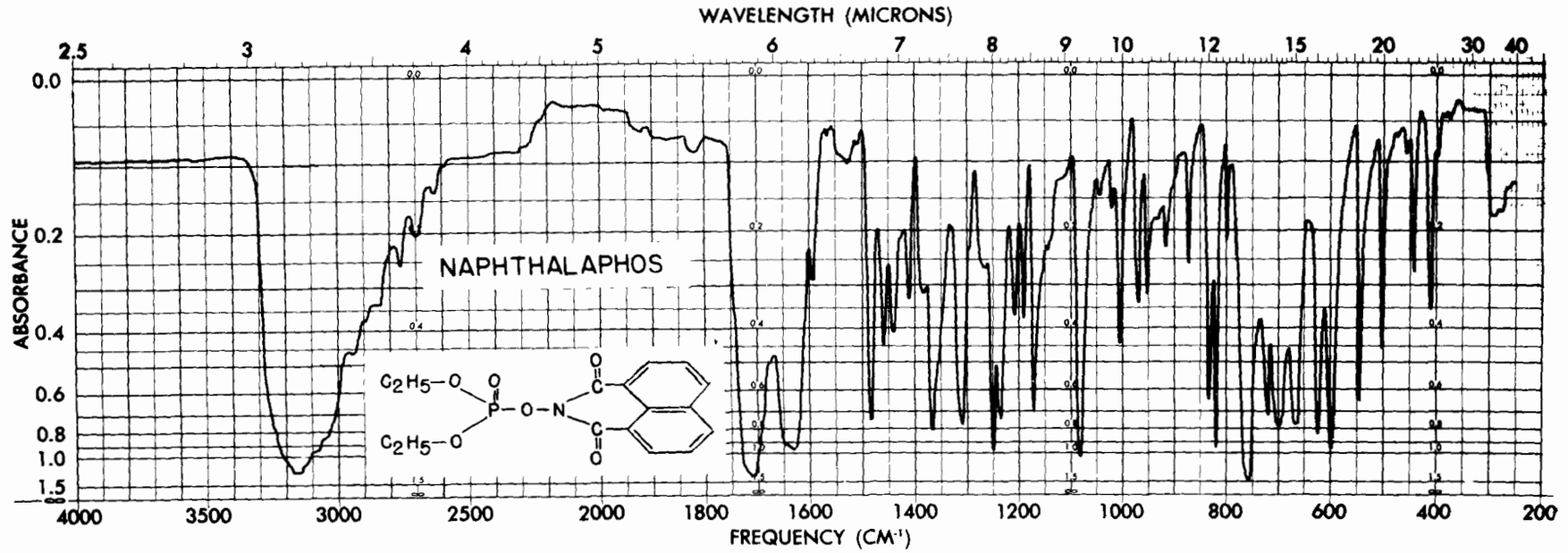
WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
NAPHTHALAPHOS
4000
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3000
2500
2000
1800
1600
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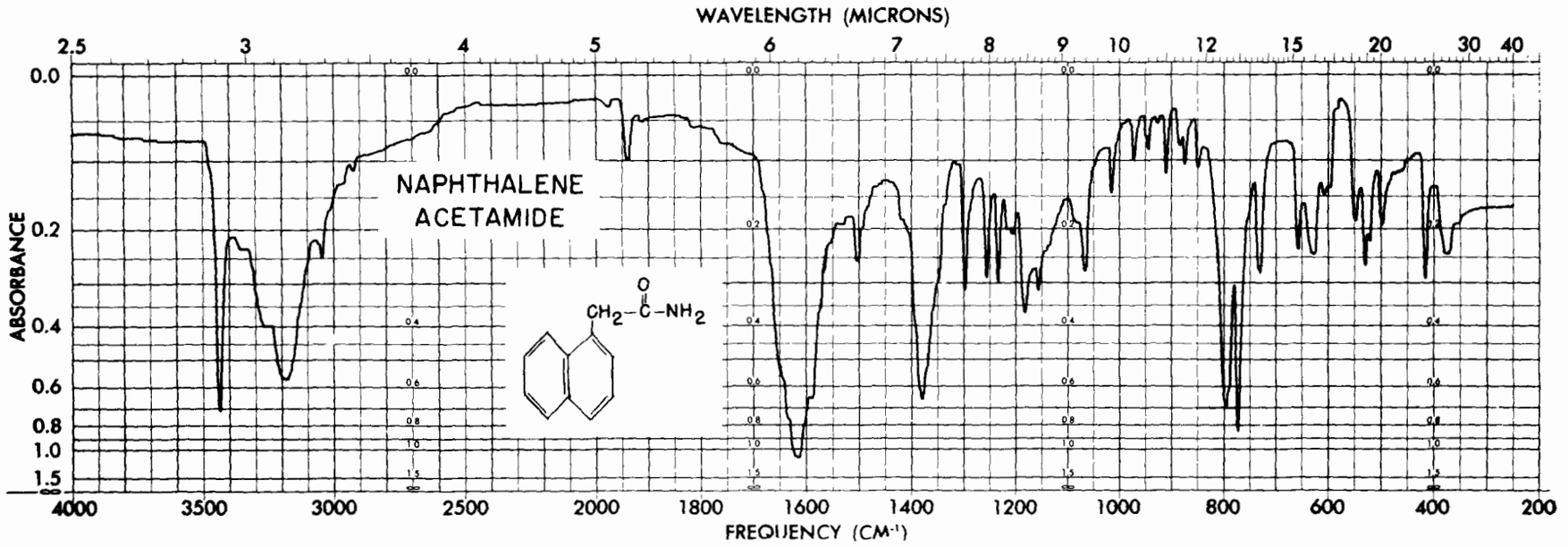
1200
1000
800
600
400
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
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6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
NAPHTHALENE
ACETAMIDE
4000
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3000
2500
2000
1800
1600
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800
600
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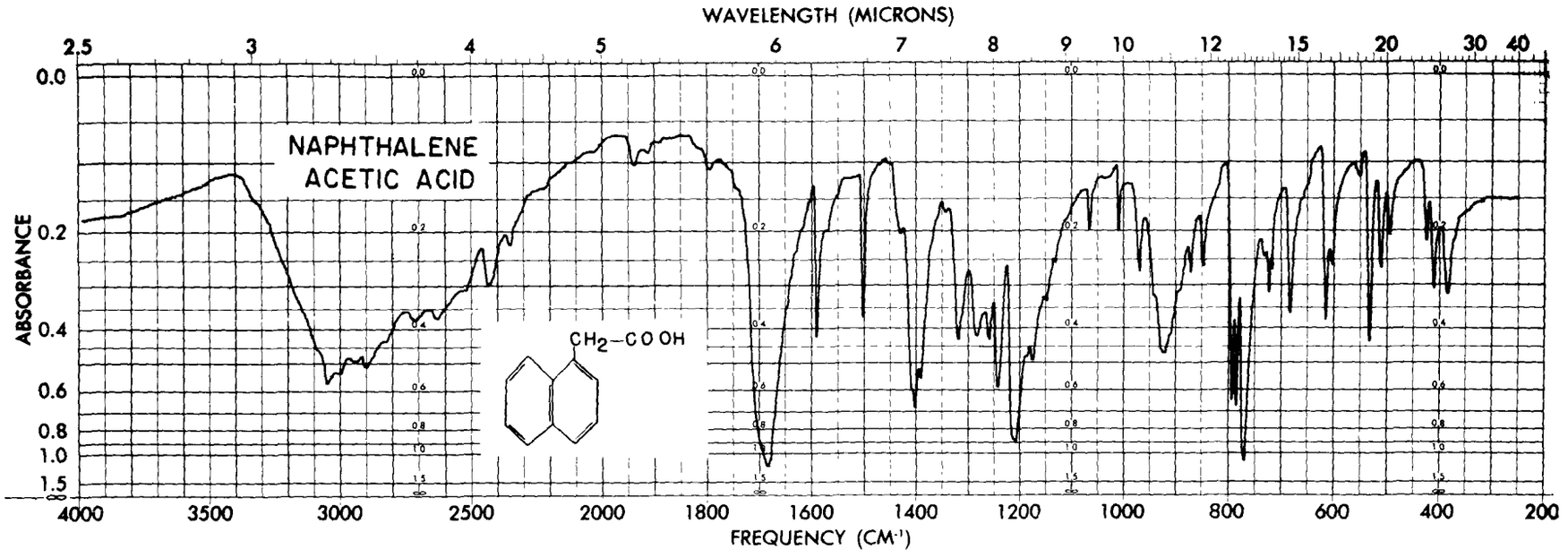
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
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7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
NAPHTHALENE
ACETIC ACID
CH2—COOH
4000
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800
600
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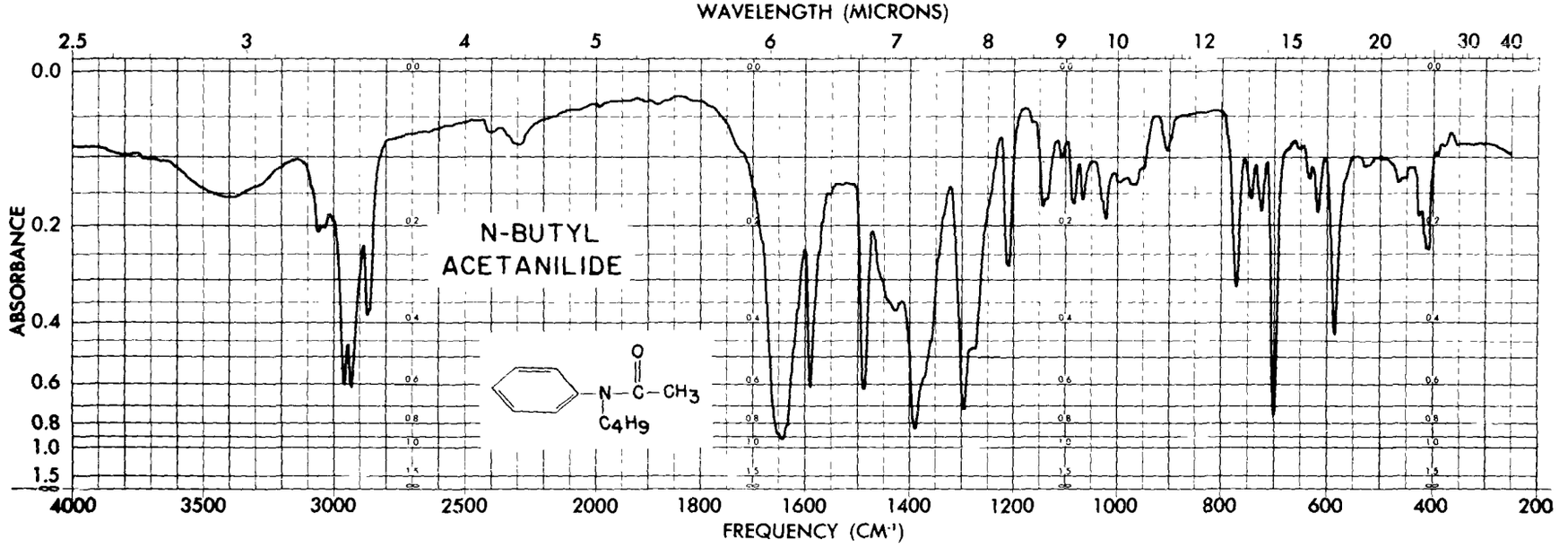
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
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4
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6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
N-BUTYL
ACETANILIDE
O
N—C—CH3
C4H9
4000
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3000
2500
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1200
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800
600
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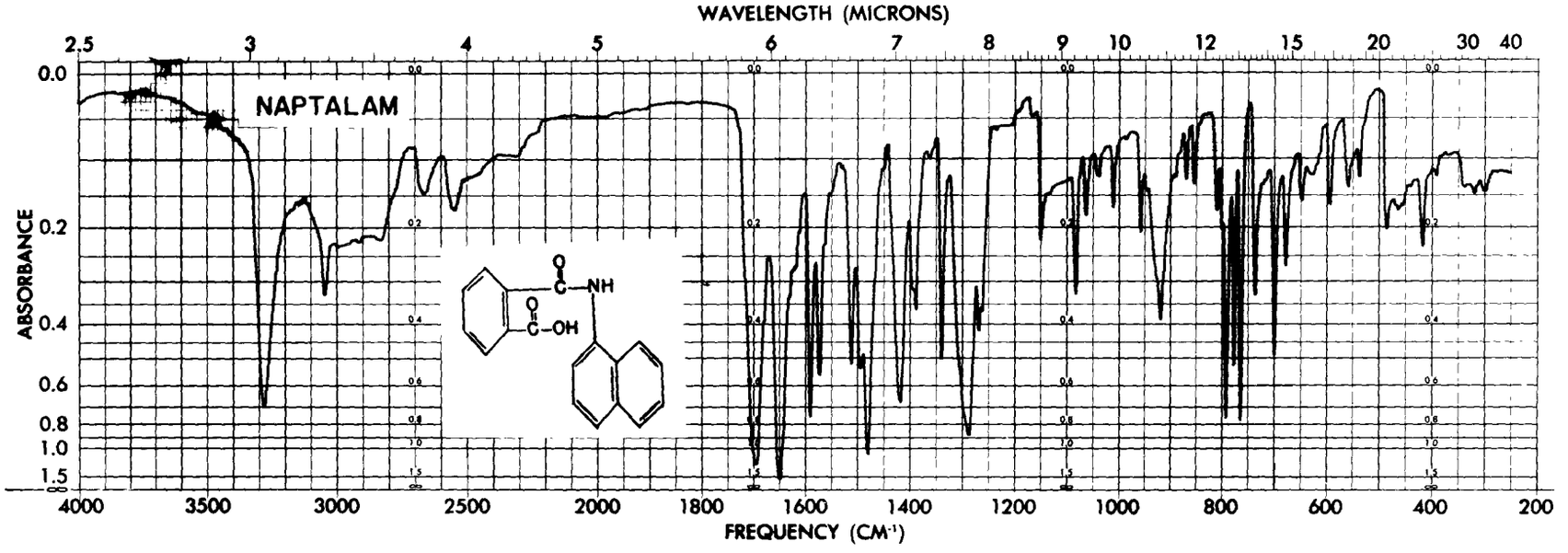
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
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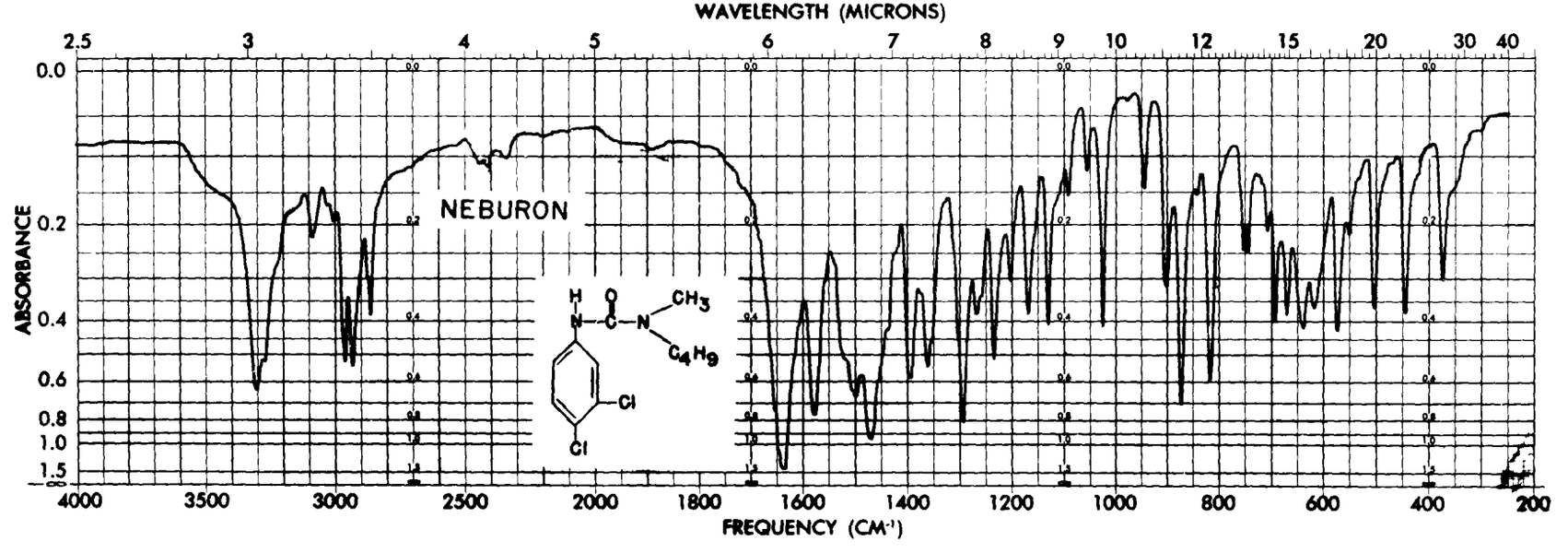
9
10
12
15
20
30
40
NAPTALAM
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)


WAVELENGTH (MICRONS)
2.5
3
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9
10
12
15
20
30
40
NEBURON
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
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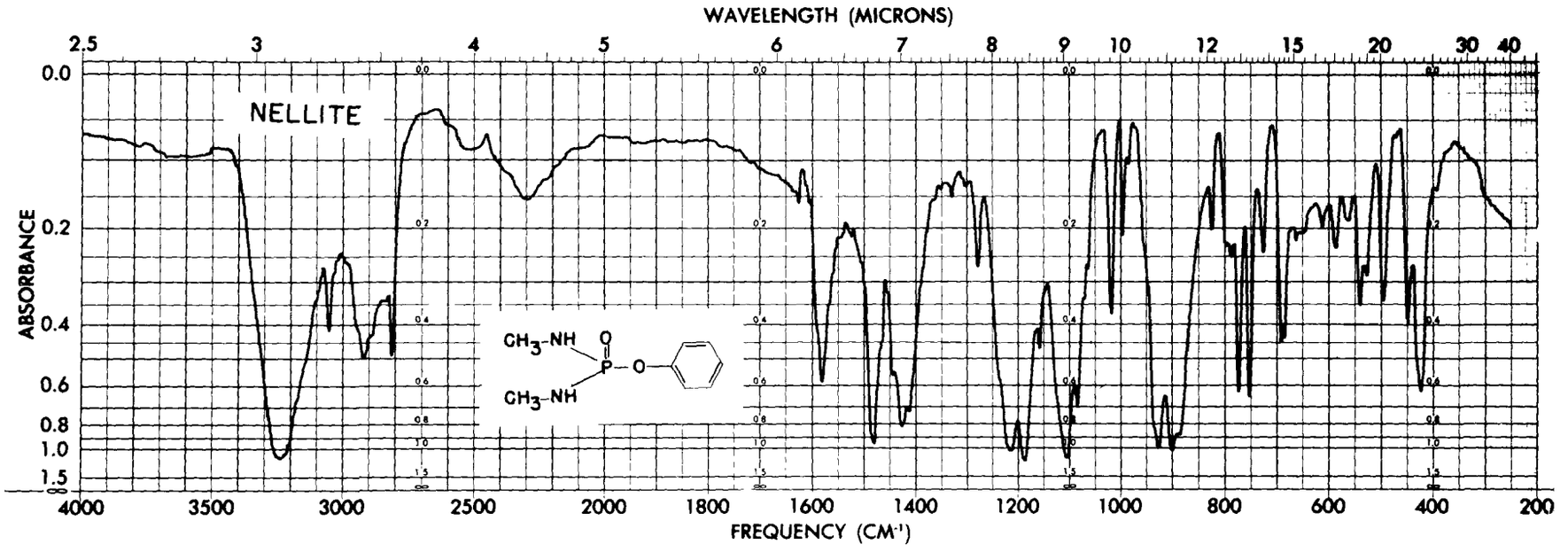
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)


WAVELENGTH (MICRONS)
2.5
3
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7
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9
10
12
15
20
30
40
NELLITE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CH3-NH
O
P
O
CH3-NH
4000
3500
3000
2500
2000
1800
1600
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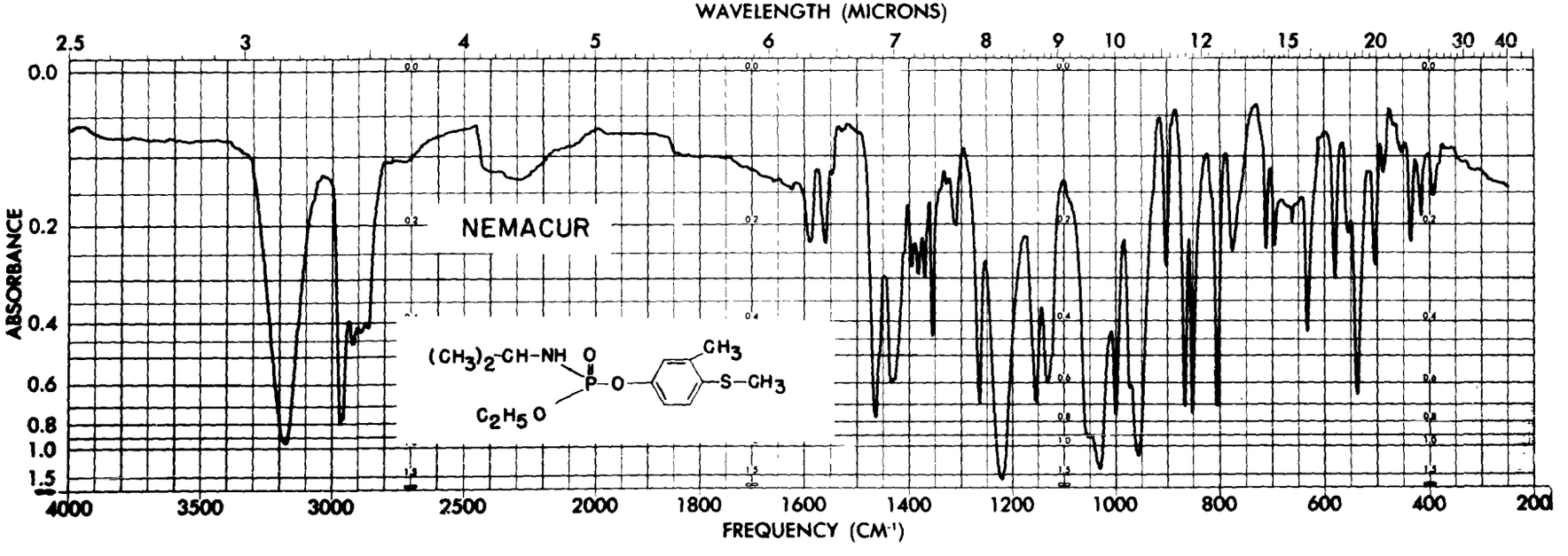
800
600
400
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
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8
9
10
12
15
20
30
40
NEMACUR
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
(CH3)2-CH-NH
O
P
O
CH3
S-CH3
C2H5O
4000
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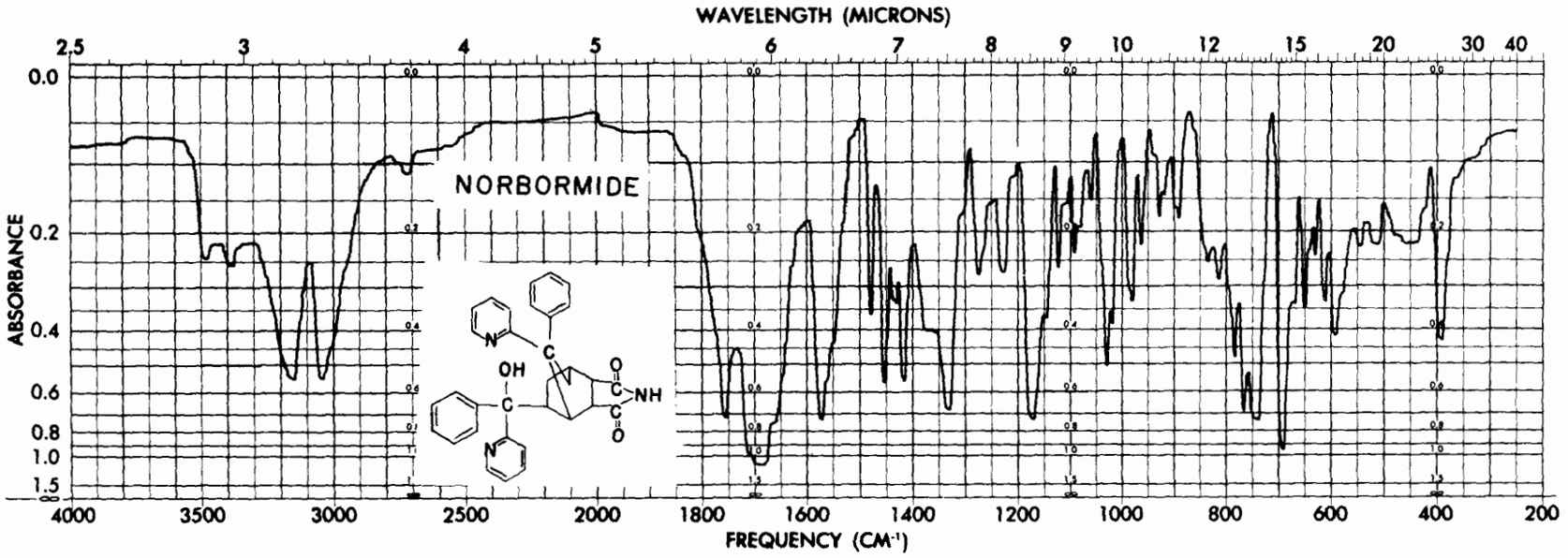
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
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3
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7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
NORBORMIDE
OH
NH
4000
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800
600
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200
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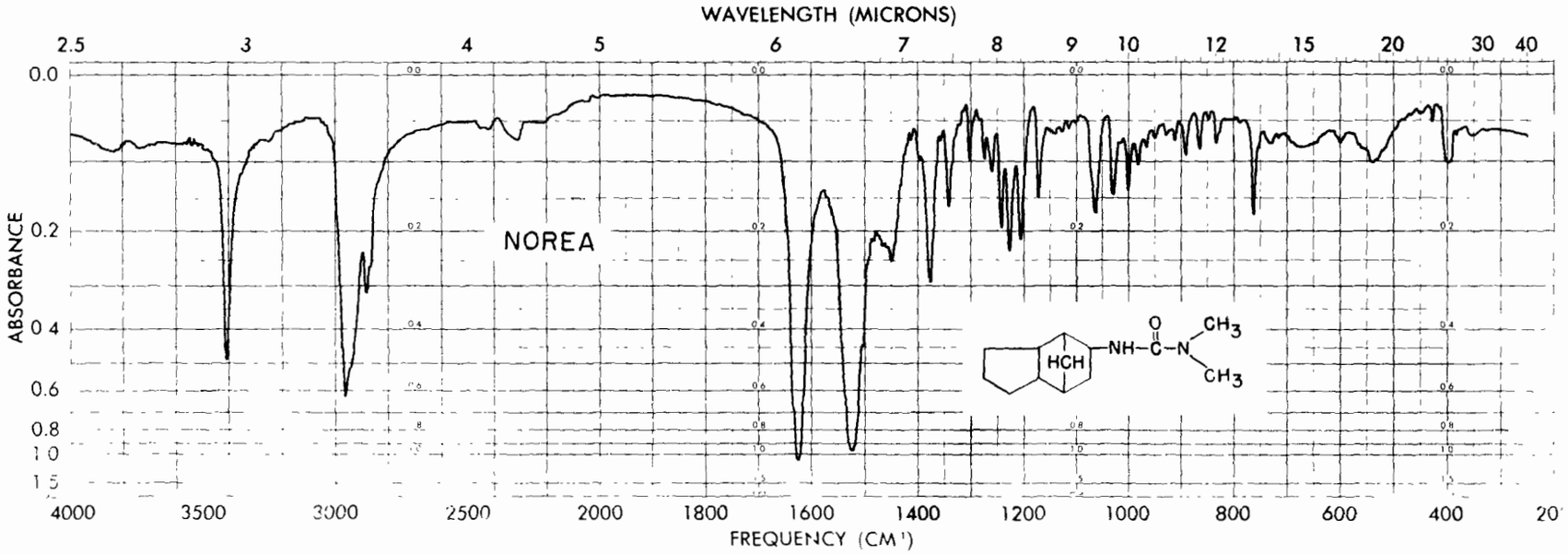
WAVELENGTH (MICRONS)
2.5
3
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6
7
8
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10
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15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
NOREA
HCH
NH
CH3
CH3
4000
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2500
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1800
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1400
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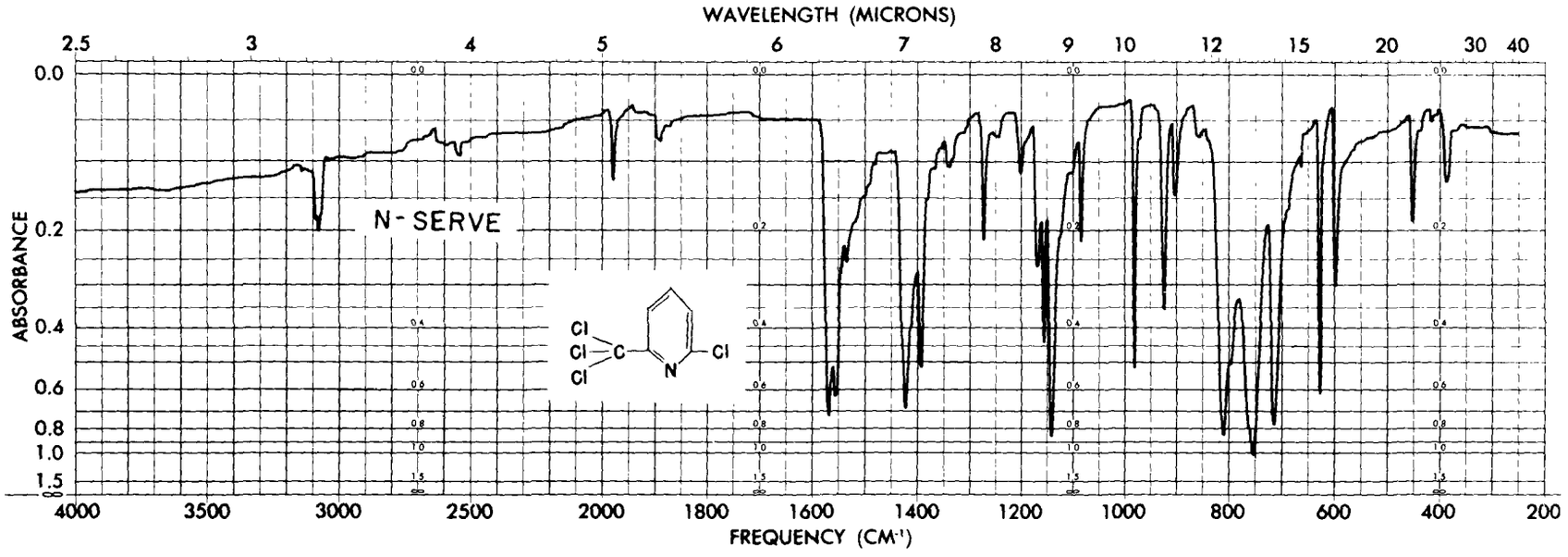
800
600
400
FREQUENCY (CM⁻¹)


WAVELENGTH (MICRONS)
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3
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8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
N-SERVE
Cl
Cl
Cl
C
N
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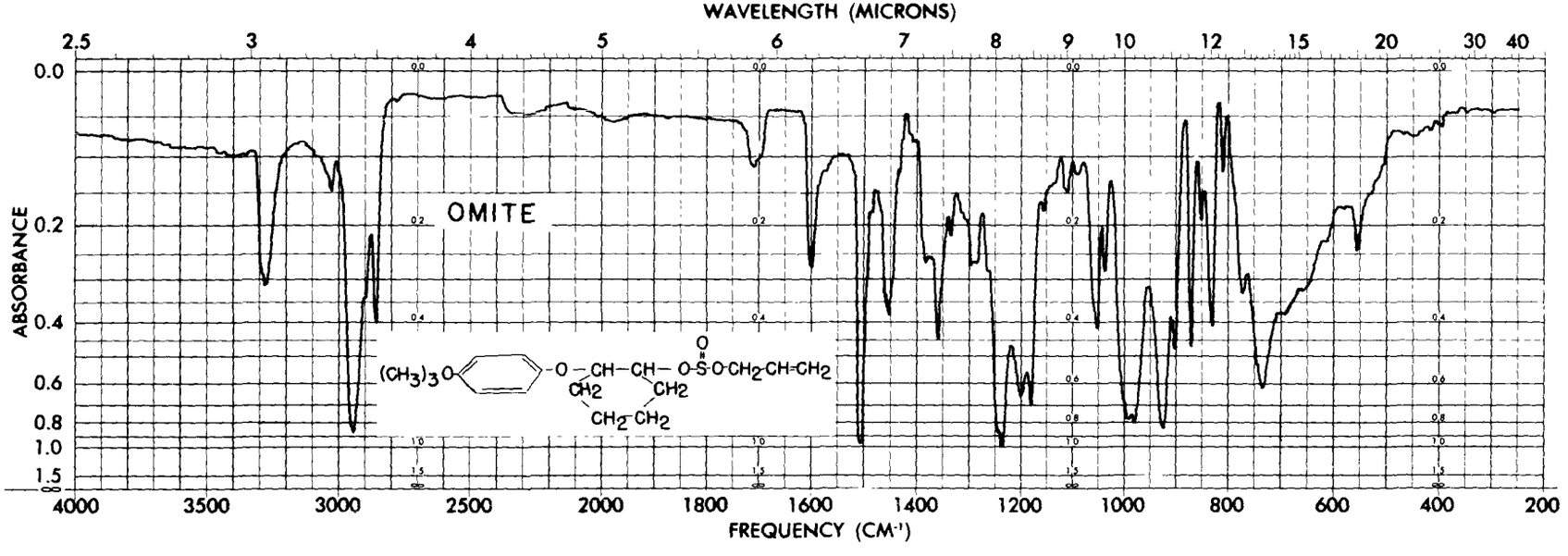
WAVELENGTH (MICRONS)
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8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
OMITE
(CH3)3O
O
CH
CH
O
S
O
CH2
CH=CH2
CH2
CH2
CH2
CH2
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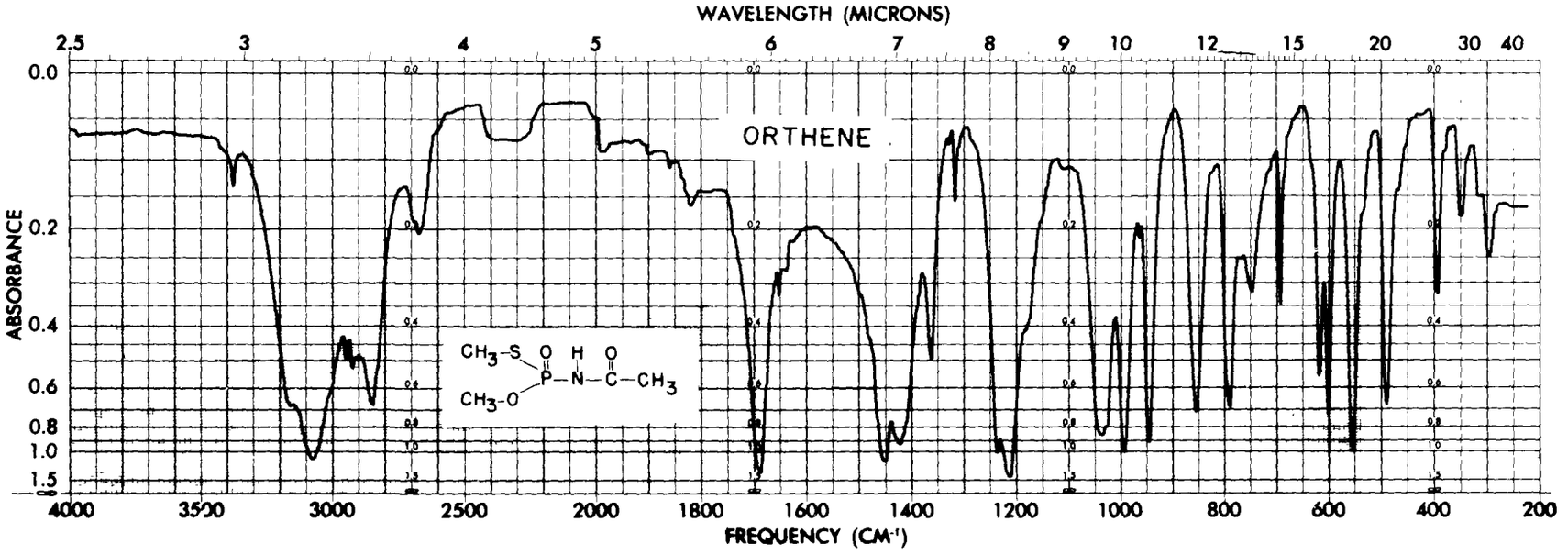
WAVELENGTH (MICRONS)
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15
20
30
40
ORTHENE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
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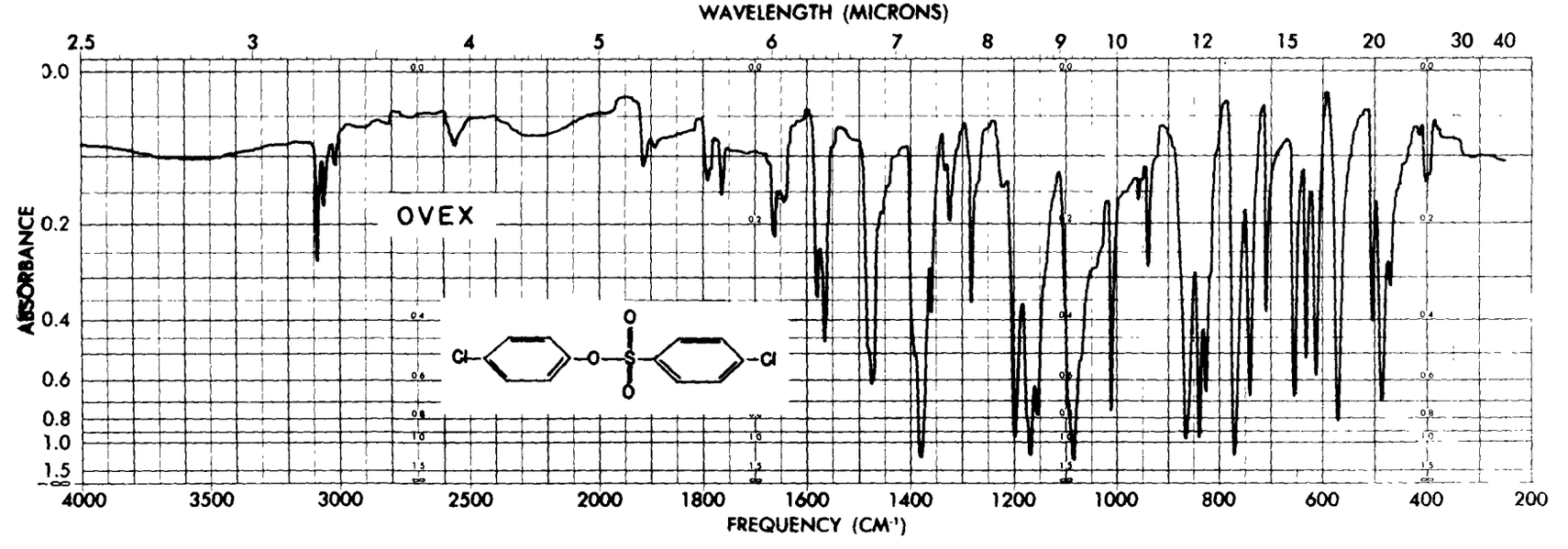
WAVELENGTH (MICRONS)
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6
7
8
9
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15
20
30
40
OVEX
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
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800
600
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200
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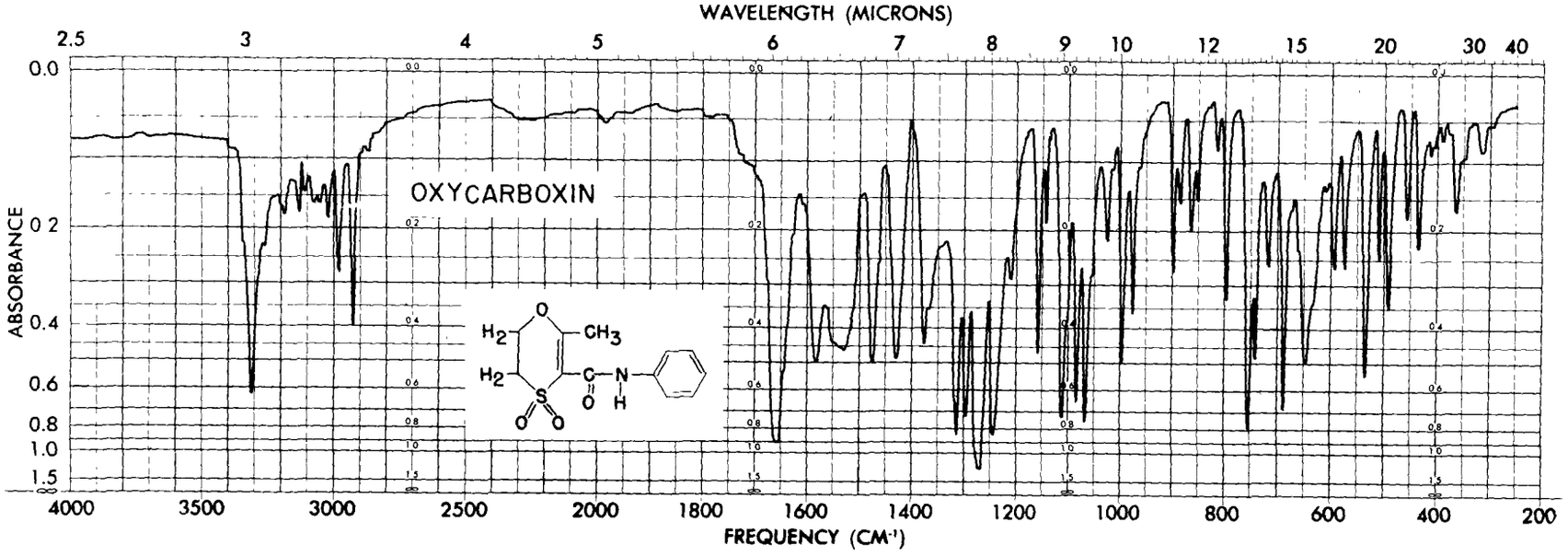
WAVELENGTH (MICRONS)
2.5
3
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6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
OXYCARBOXIN
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800
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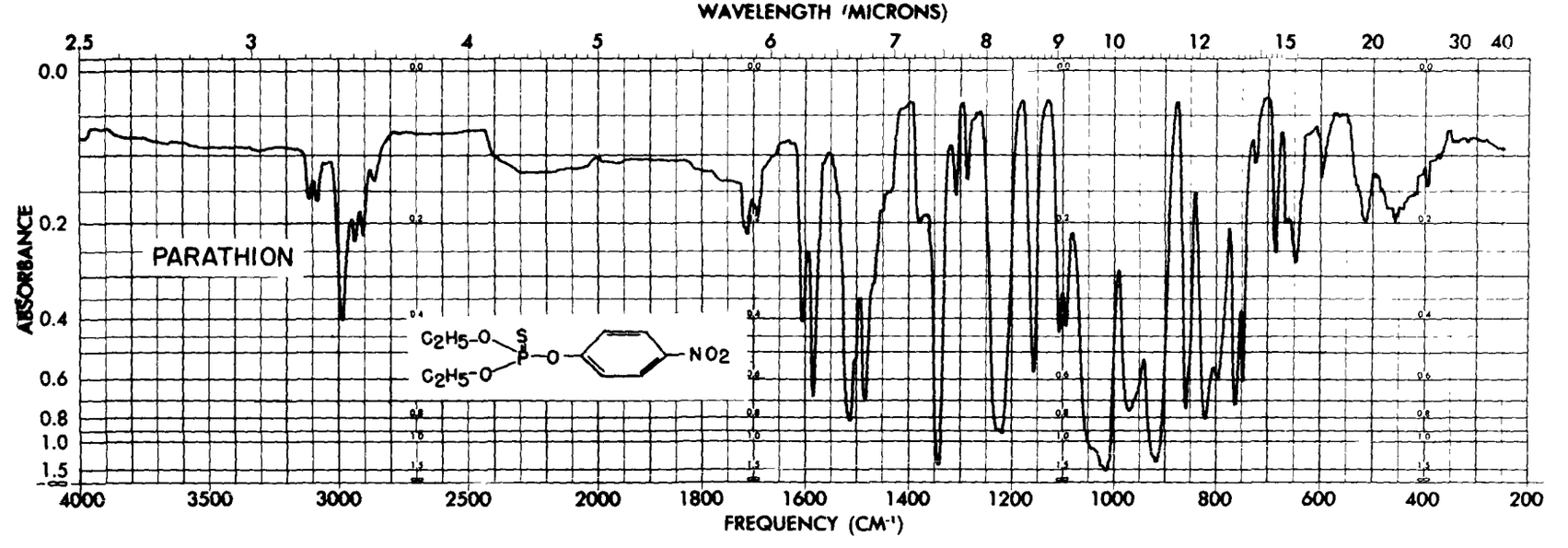
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
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10
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15
20
30
40
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0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
PARATHION
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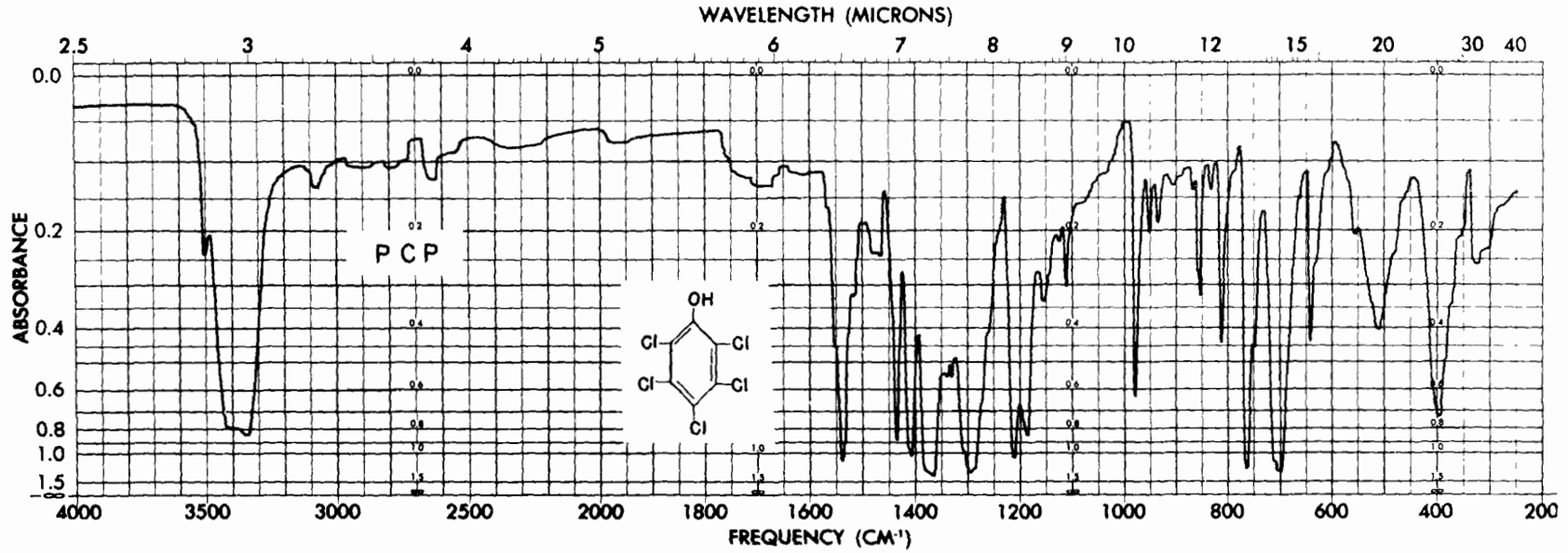
WAVELENGTH (MICRONS)
2.5
3
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6
7
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15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
PCP
OH
Cl
Cl
Cl
Cl
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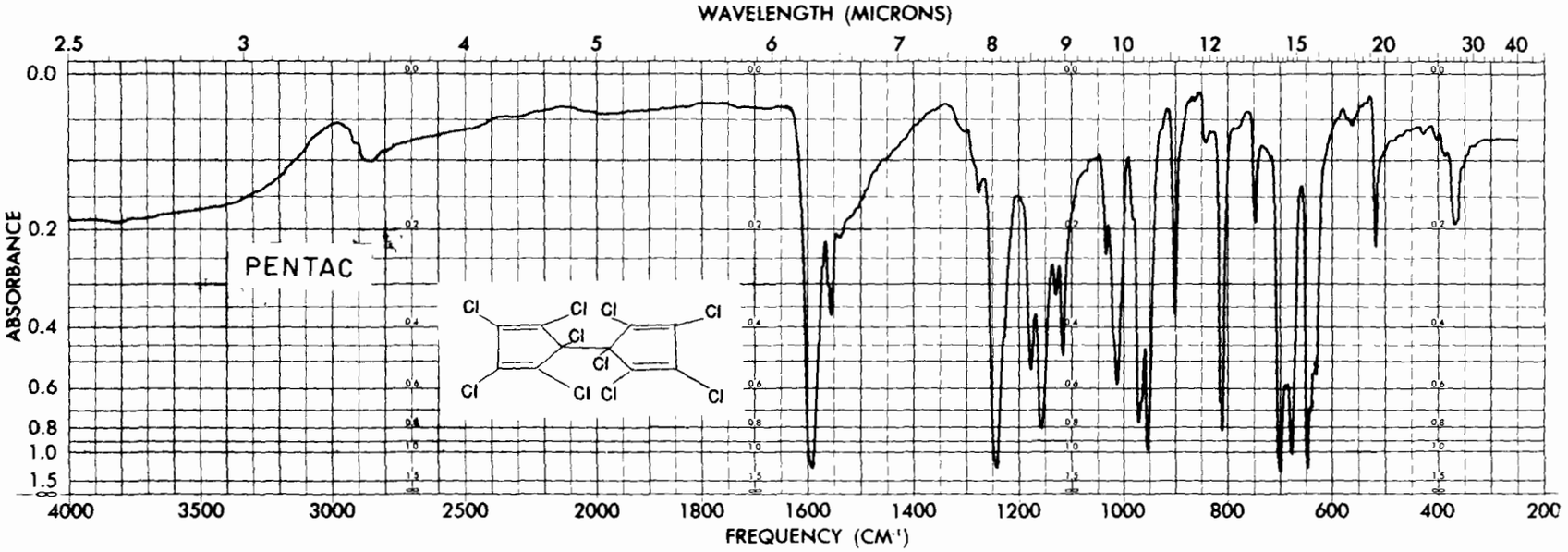
WAVELENGTH (MICRONS)
2.5
3
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30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
PENTAC
Cl
Cl
Cl
Cl
Cl
Cl
Cl
Cl
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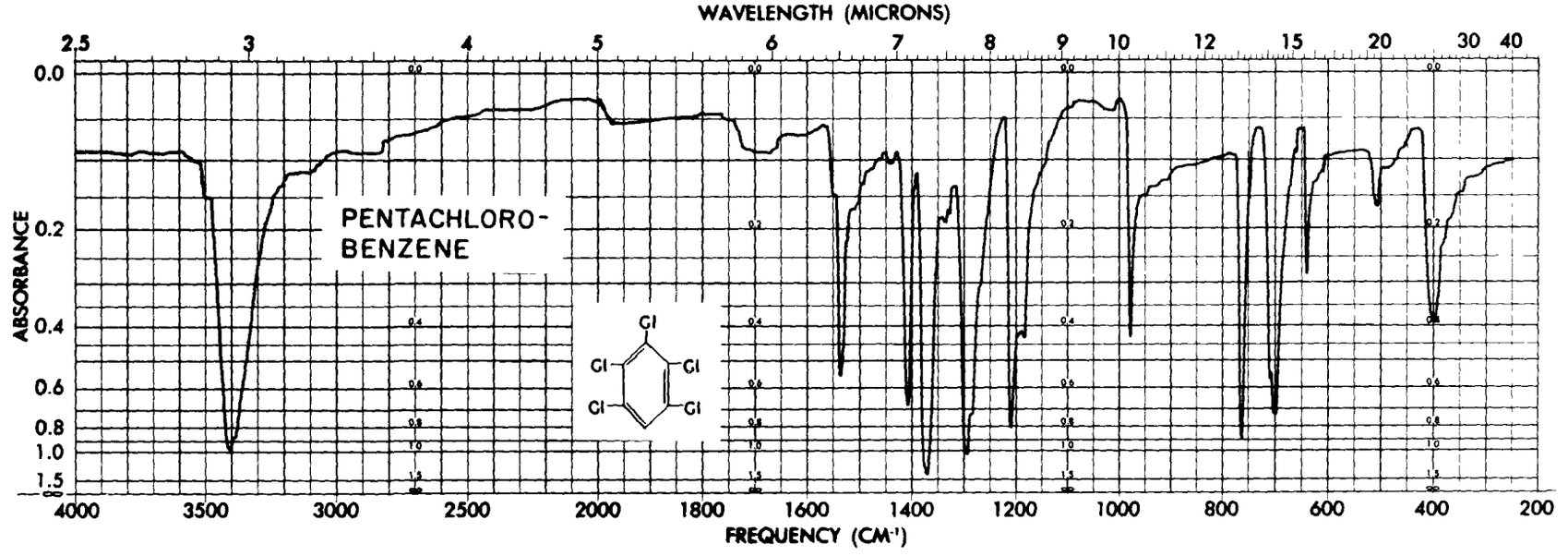
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
4
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6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
PENTACHLORO-
BENZENE
Cl
Cl
Cl
Cl
Cl
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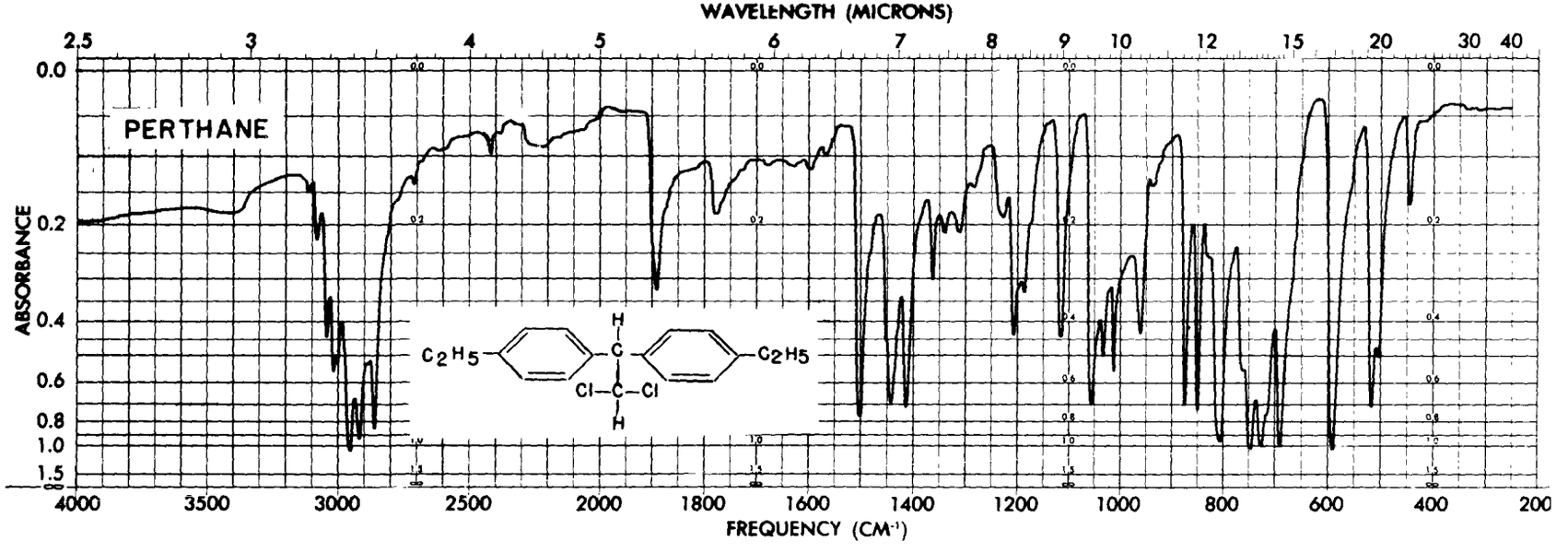
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
4
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6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
PERTHANE
C2H5
C2H5
H
C
Cl
C
Cl
H
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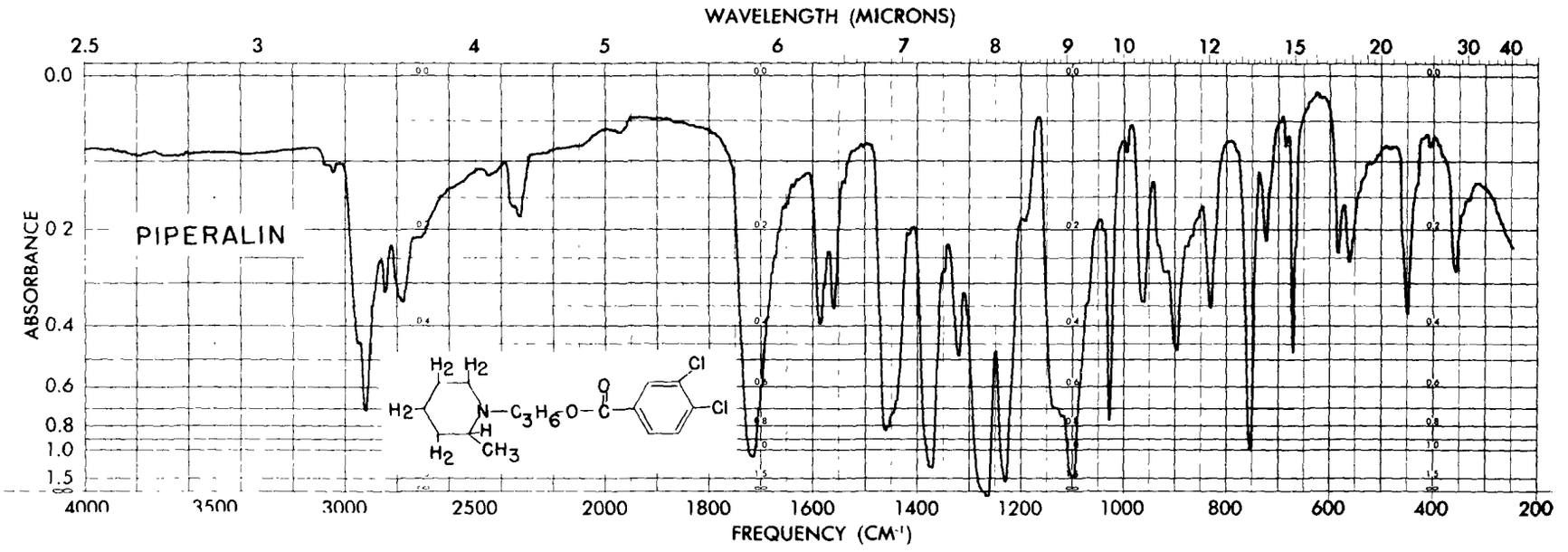
WAVELENGTH (MICRONS)
2.5
3
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8
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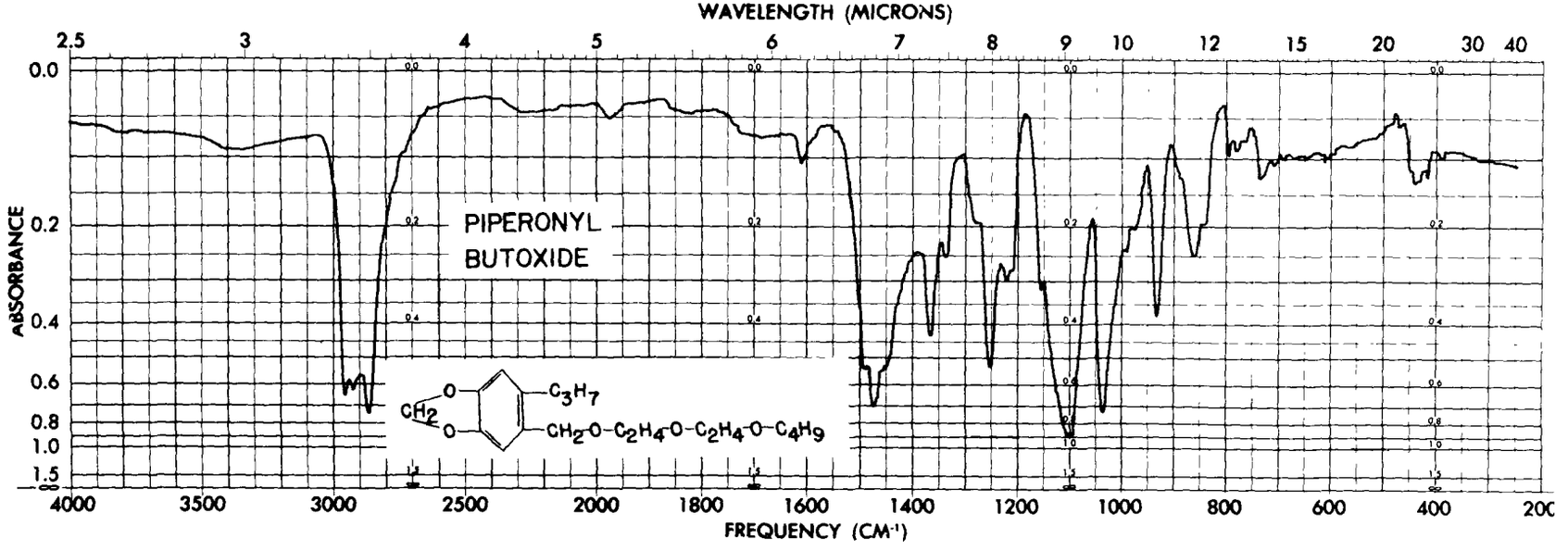
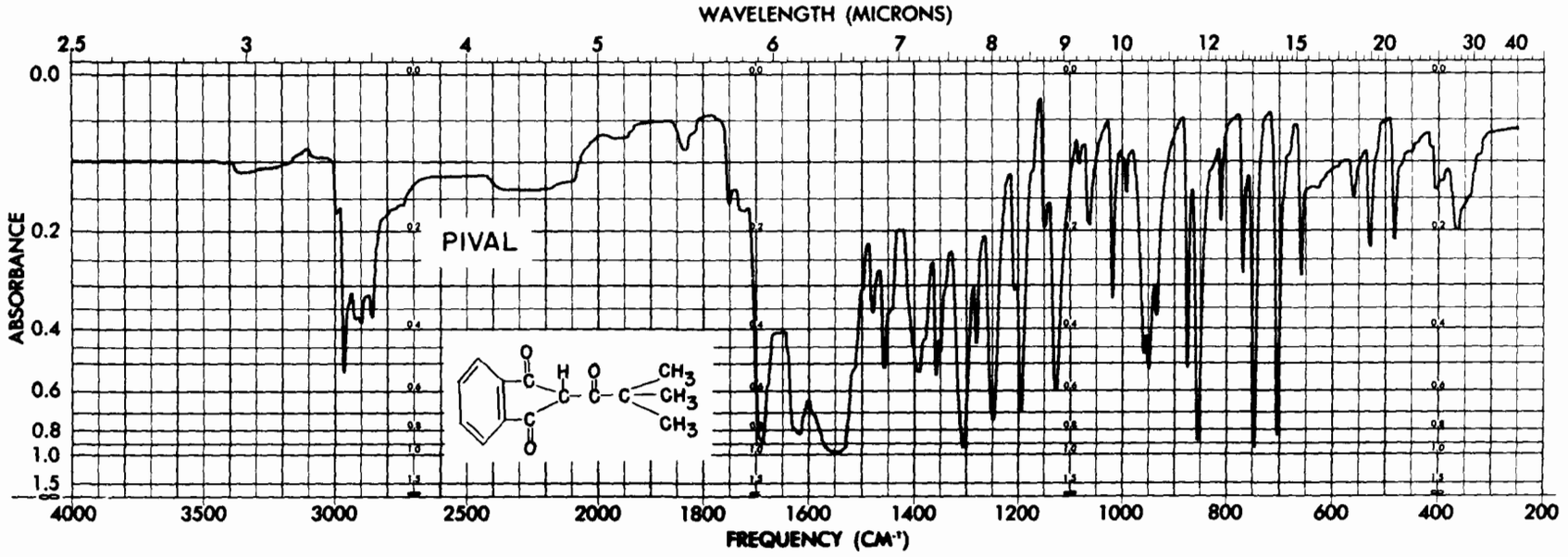
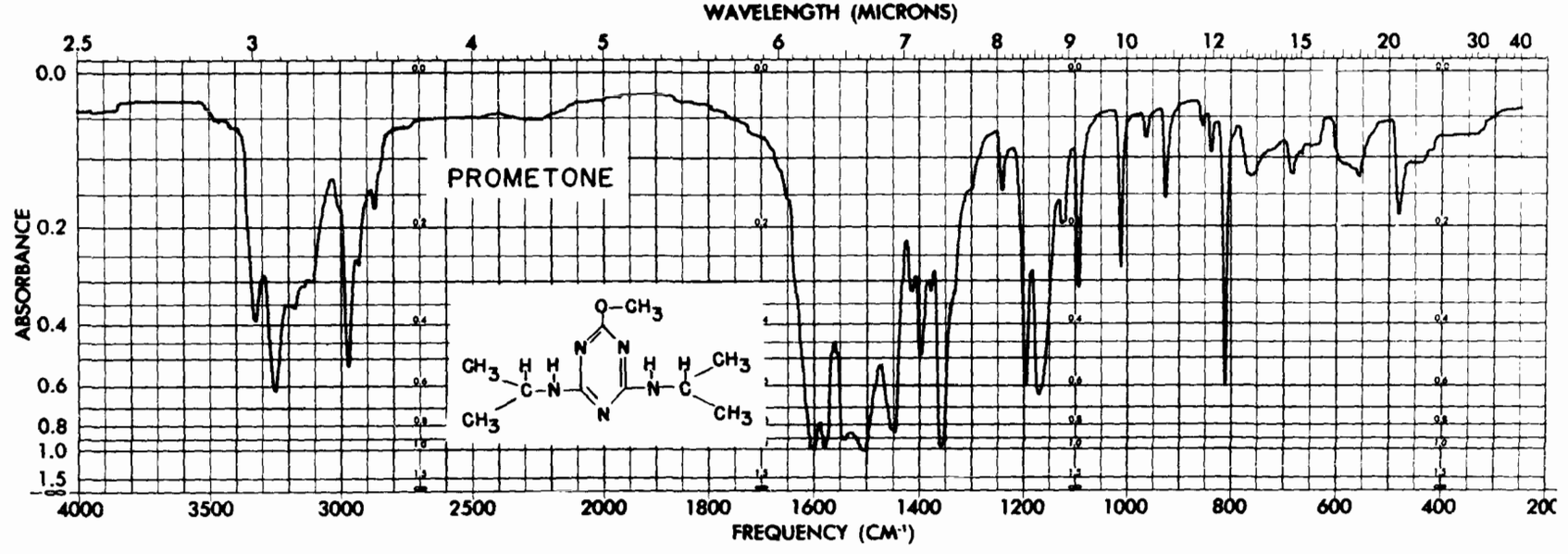
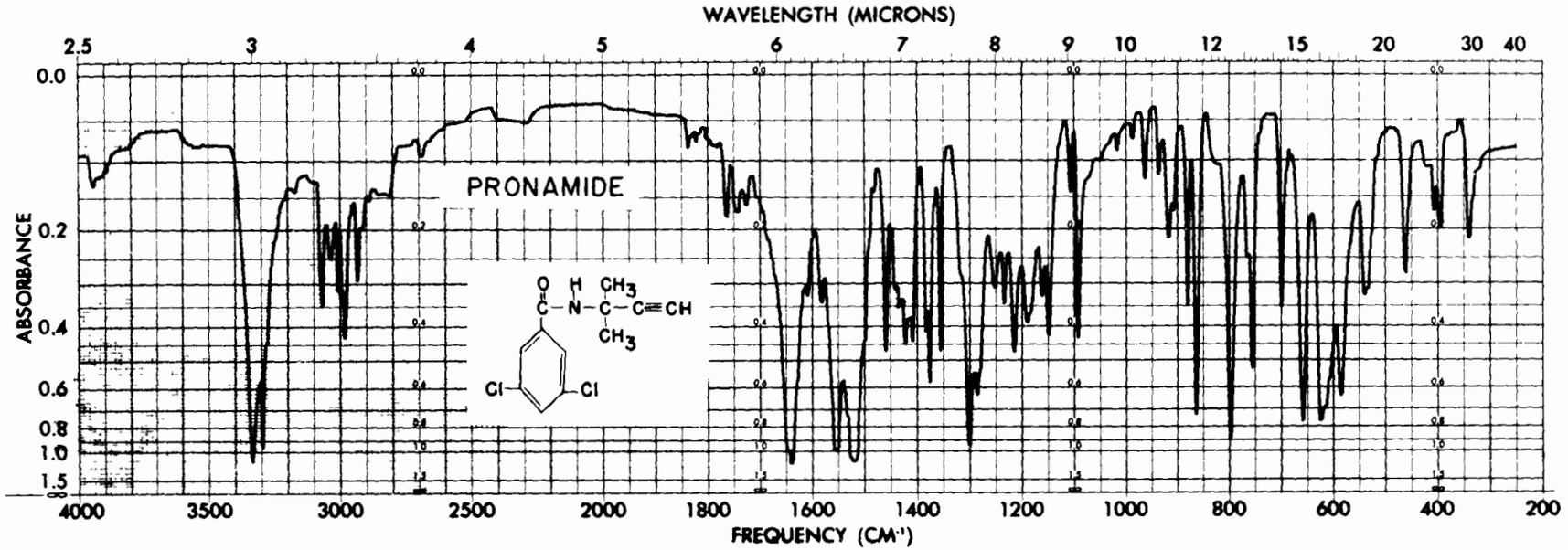
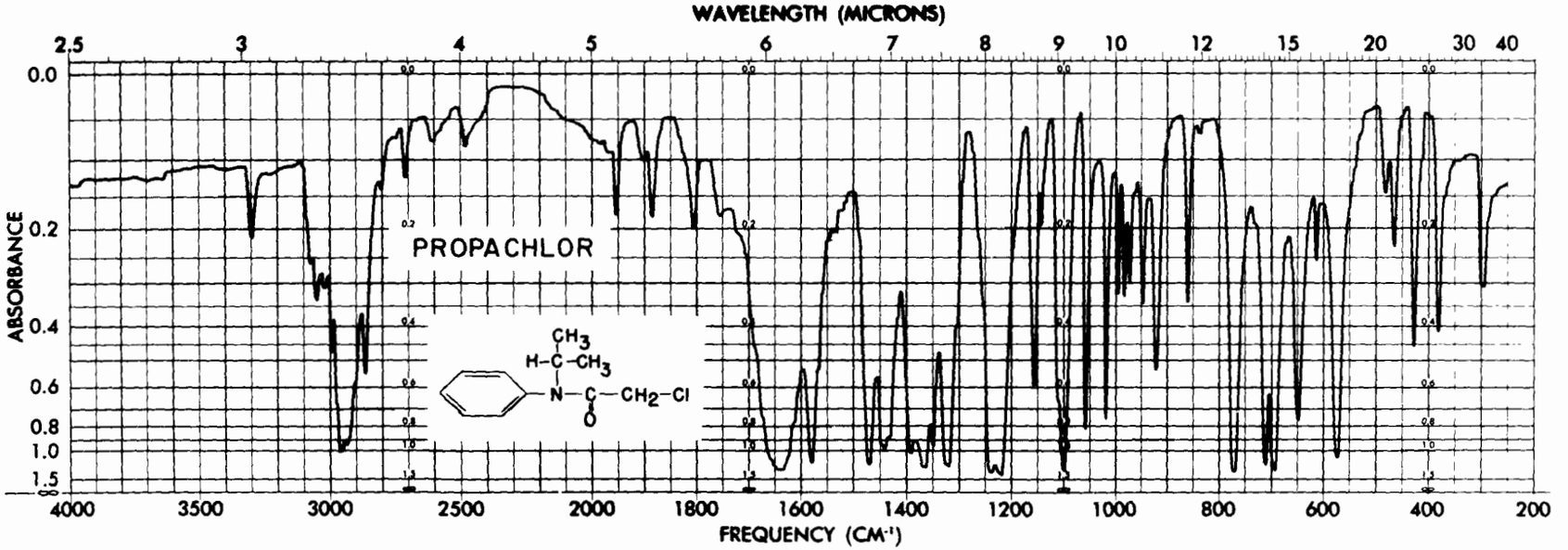
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
PIPERALIN
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

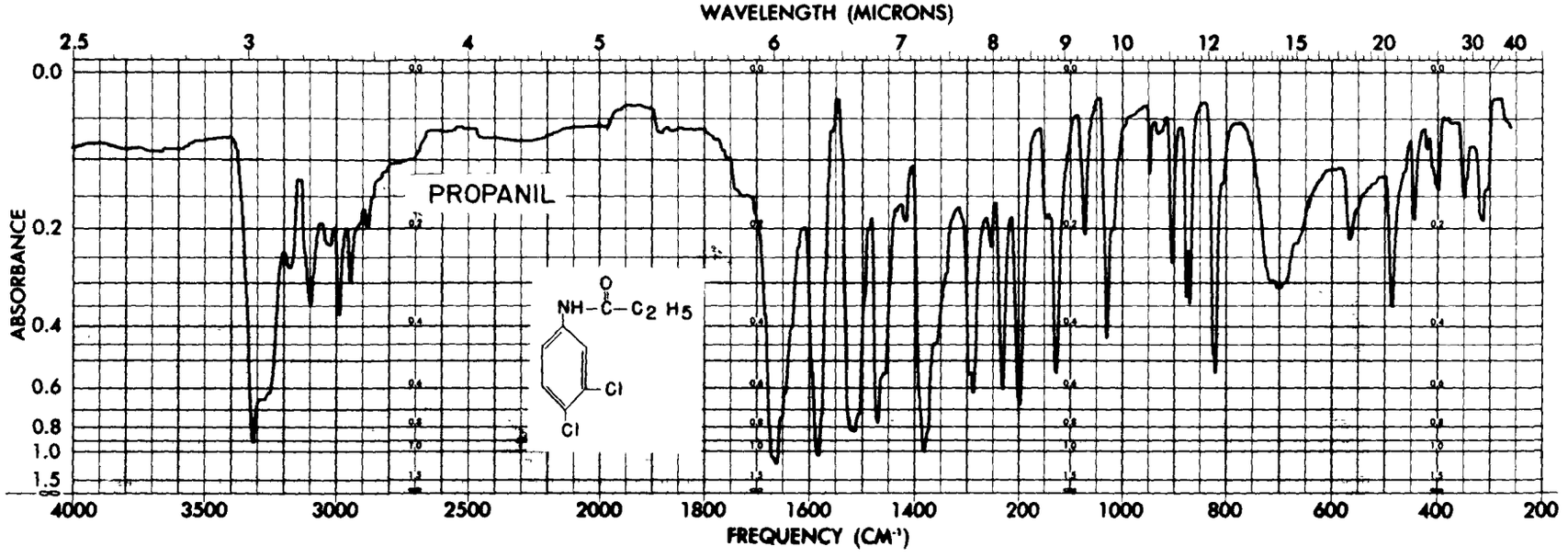

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
PIPERONYL
BUTOXIDE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
FREQUENCY (CM-1)

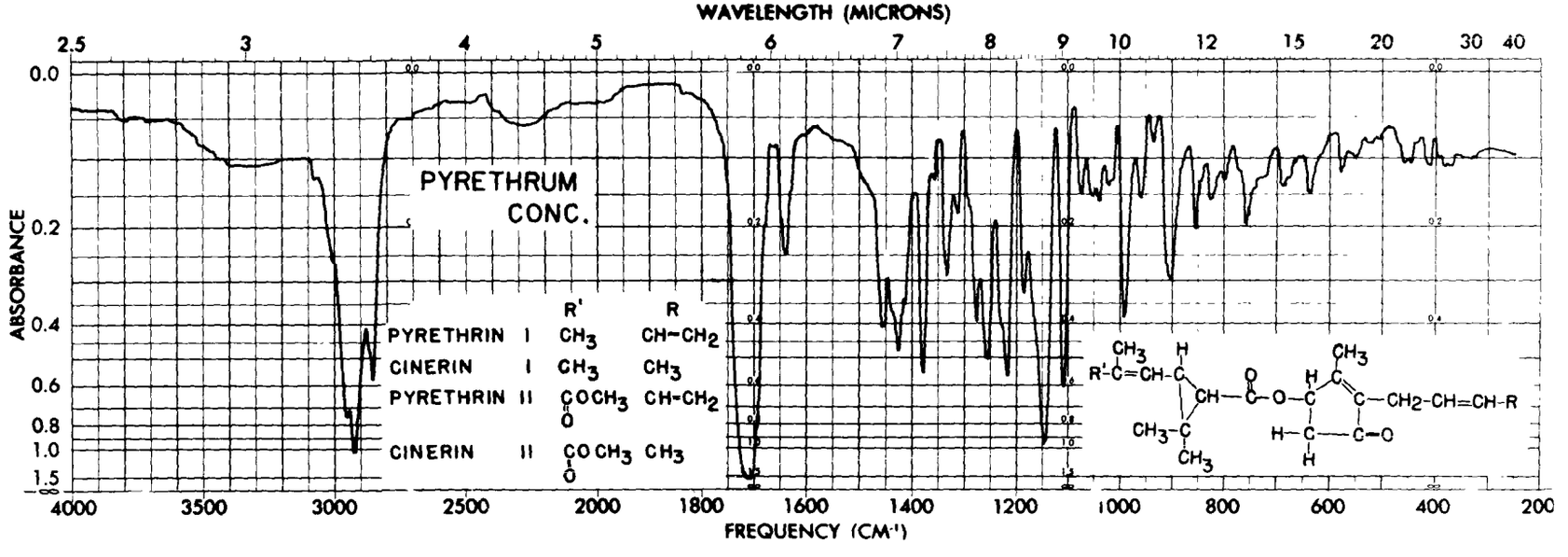

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
PIVAL
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

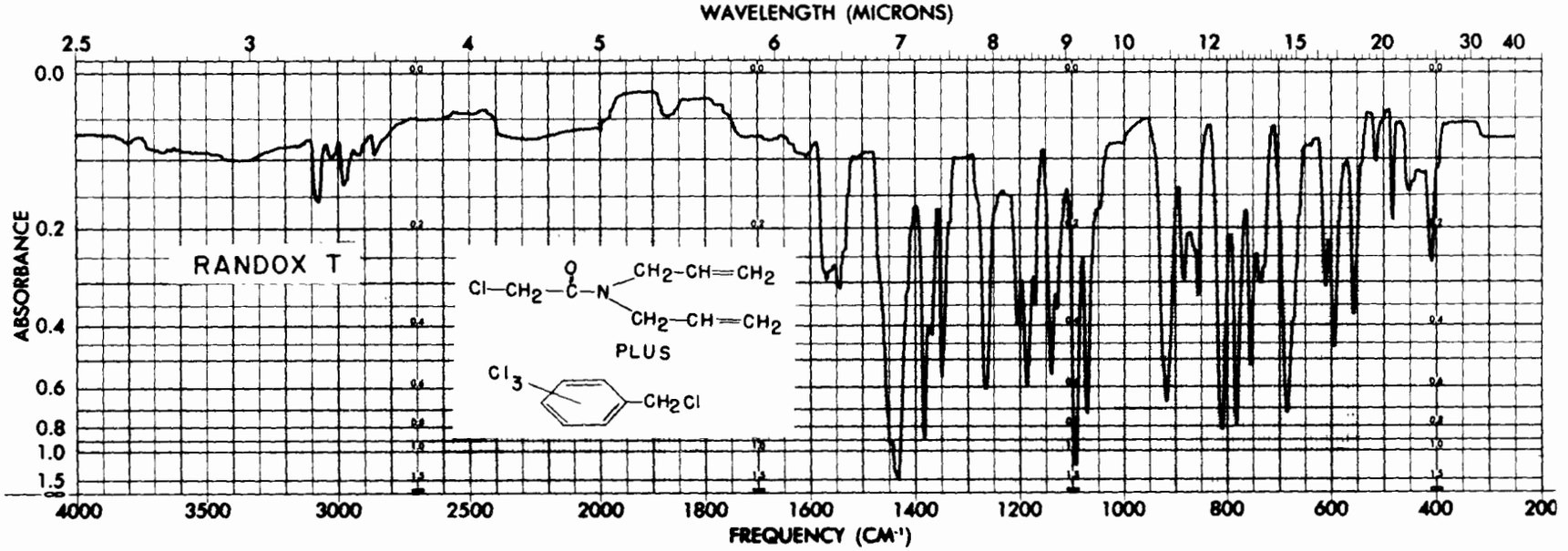

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
PROMETONE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
FREQUENCY (CM⁻¹)

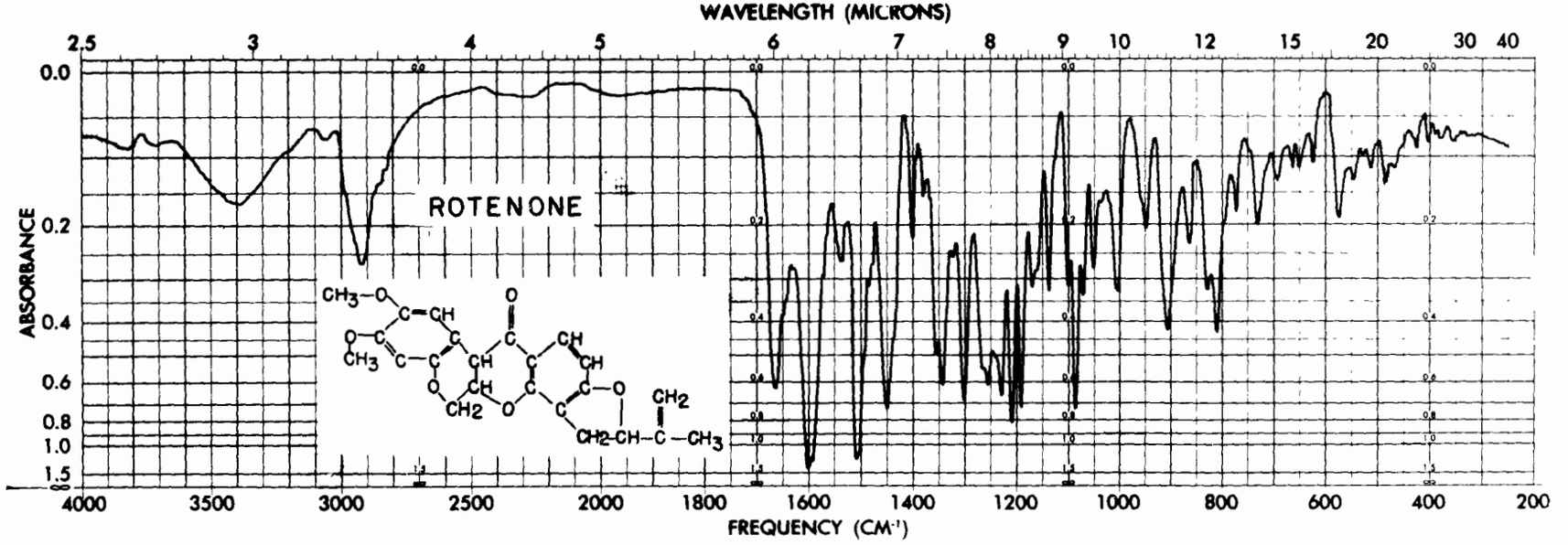

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
PRONAMIDE
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

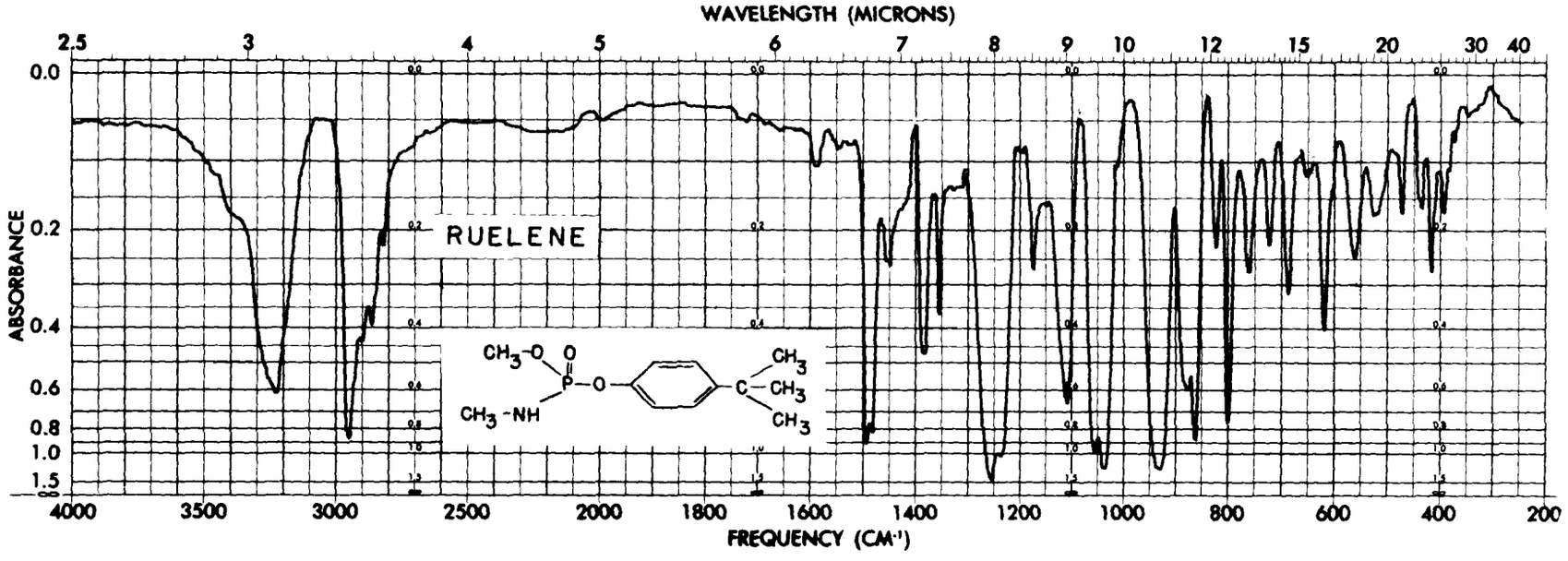

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
PROPACHLOR
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

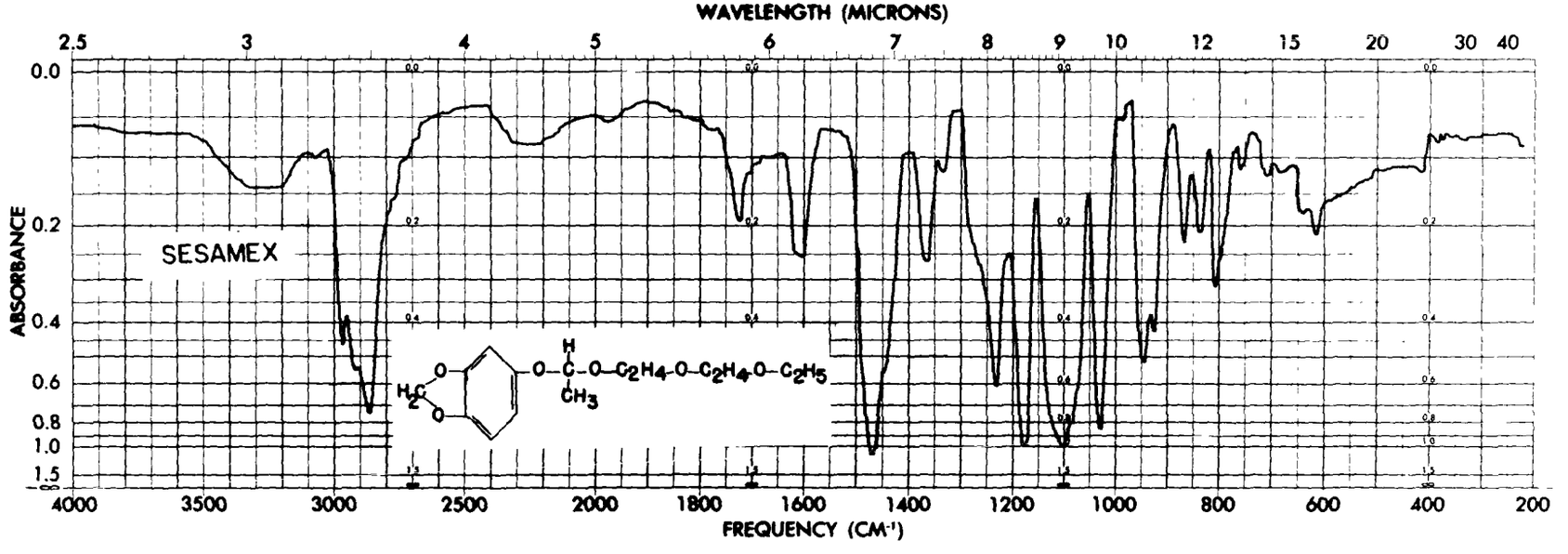

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
PROPANIL
NH–C–C2 H5
O
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
200
1000
800
600
400
200
FREQUENCY (CM-1)

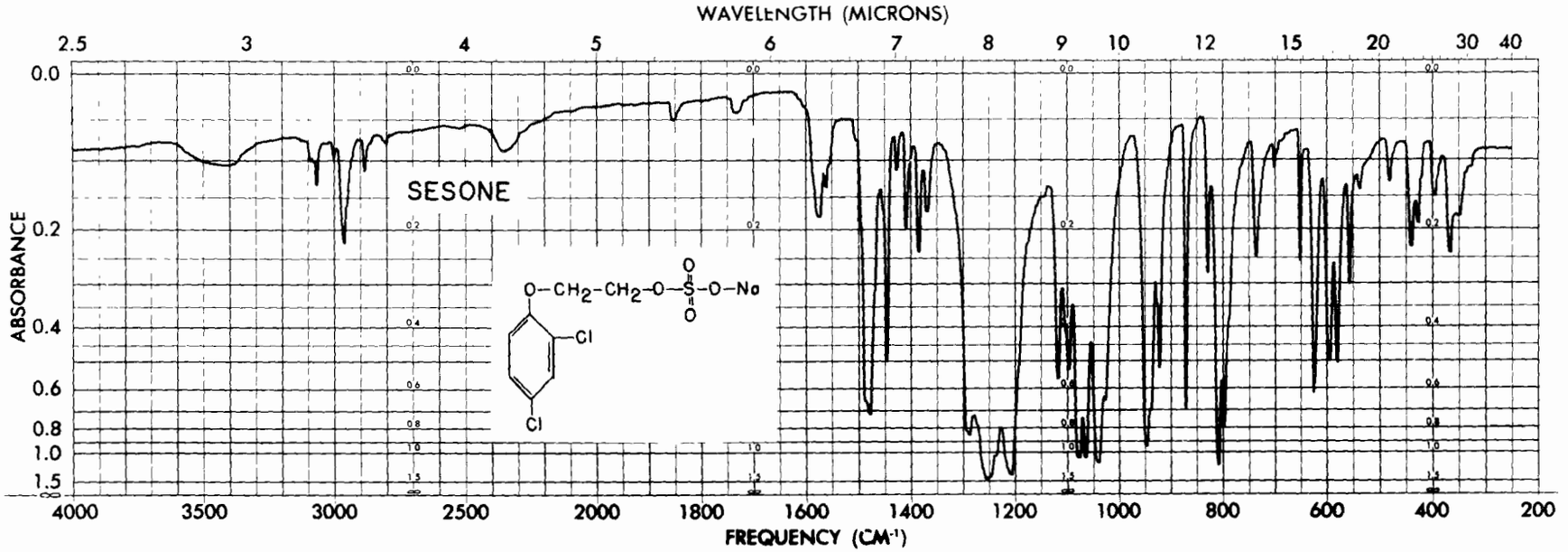

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
PYRETHRUM
CONC.
R'
R
PYRETHRIN I
CH3
CH–CH2
CINERIN I
CH3
CH3
PYRETHRIN II
COCH3
CH–CH2
O
CINERIN II
CO CH3
CH3
O
CH3
R'–C=CH–C
H
CH–C–O–O–C
H
CH3
C–CH2–CH=CH–R
CH3–C
CH3
H–C–C=O
H
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

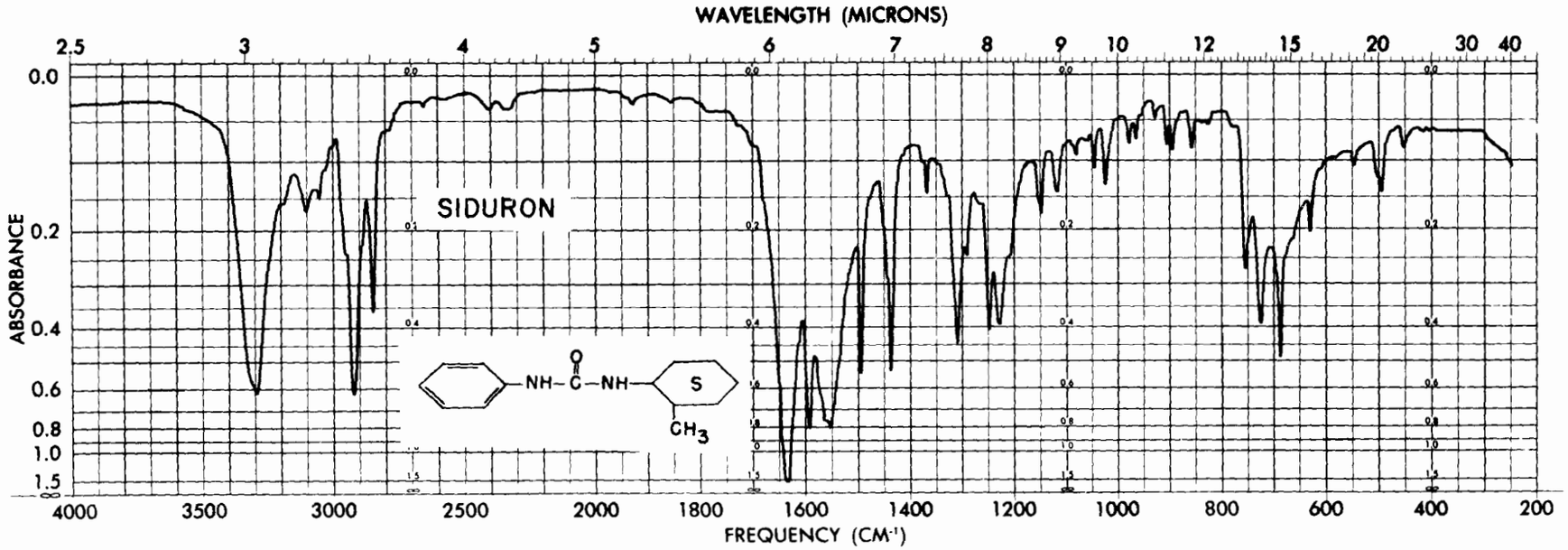

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
RANDOX T
PLUS
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

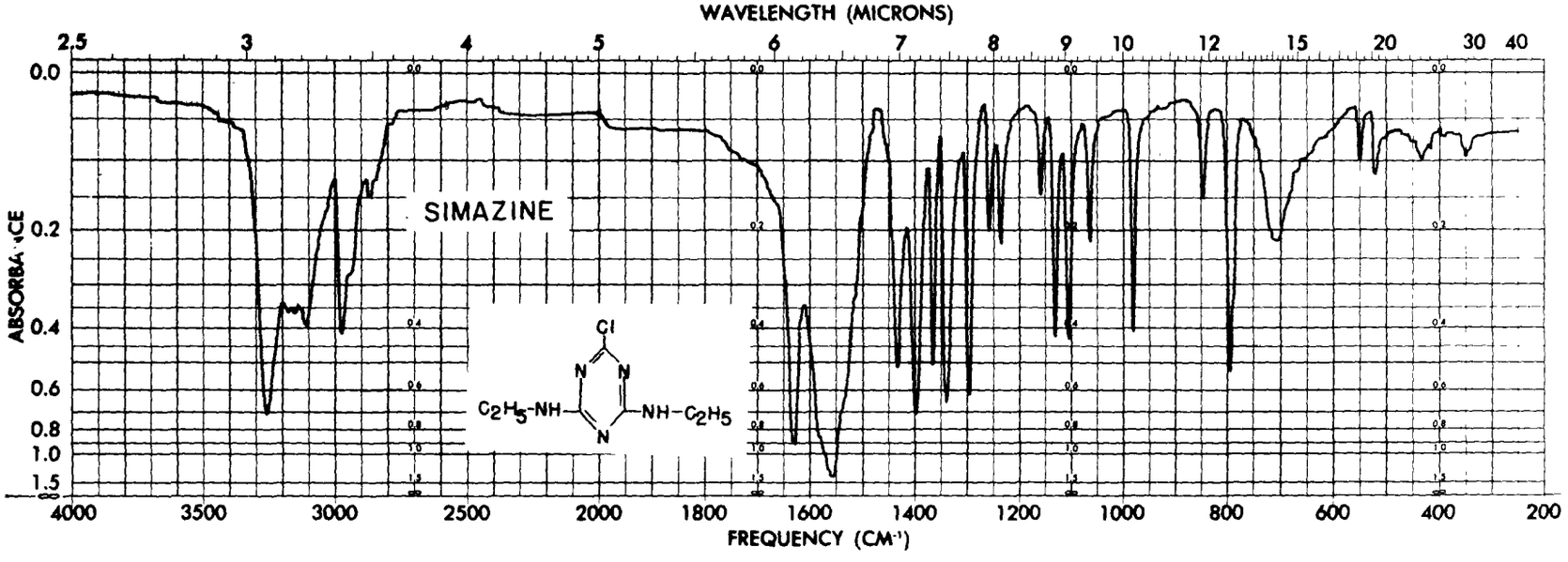

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
ROTENONE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

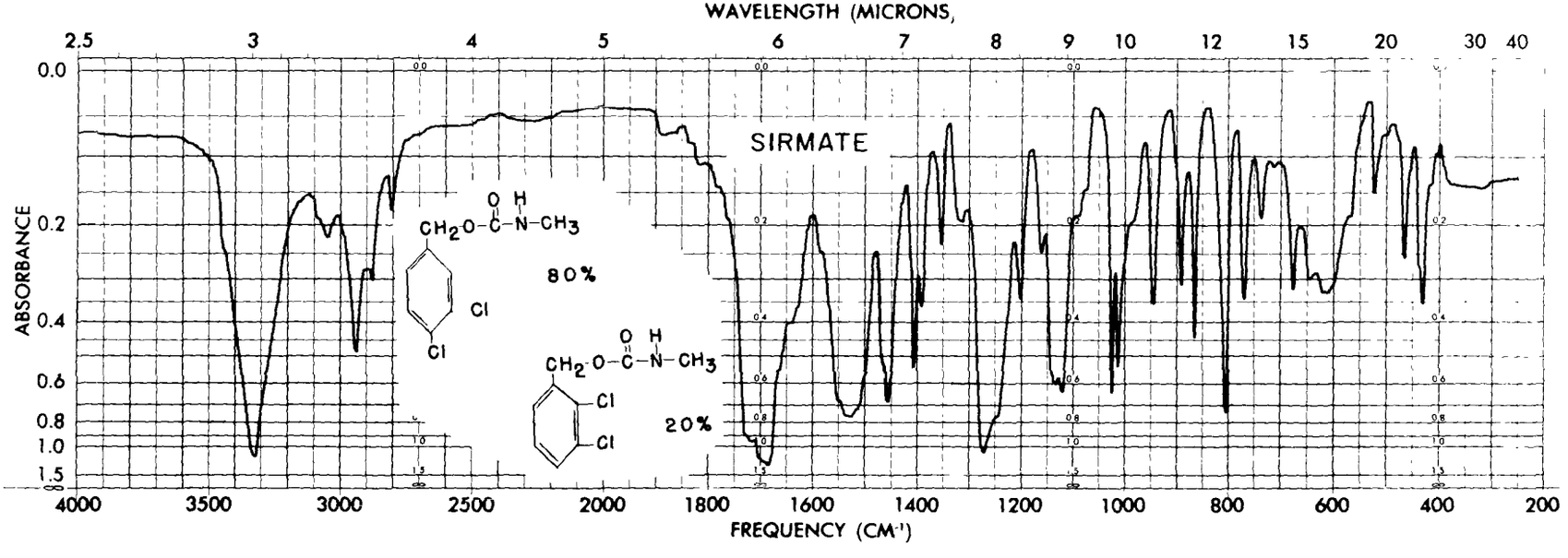

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
RUELENE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

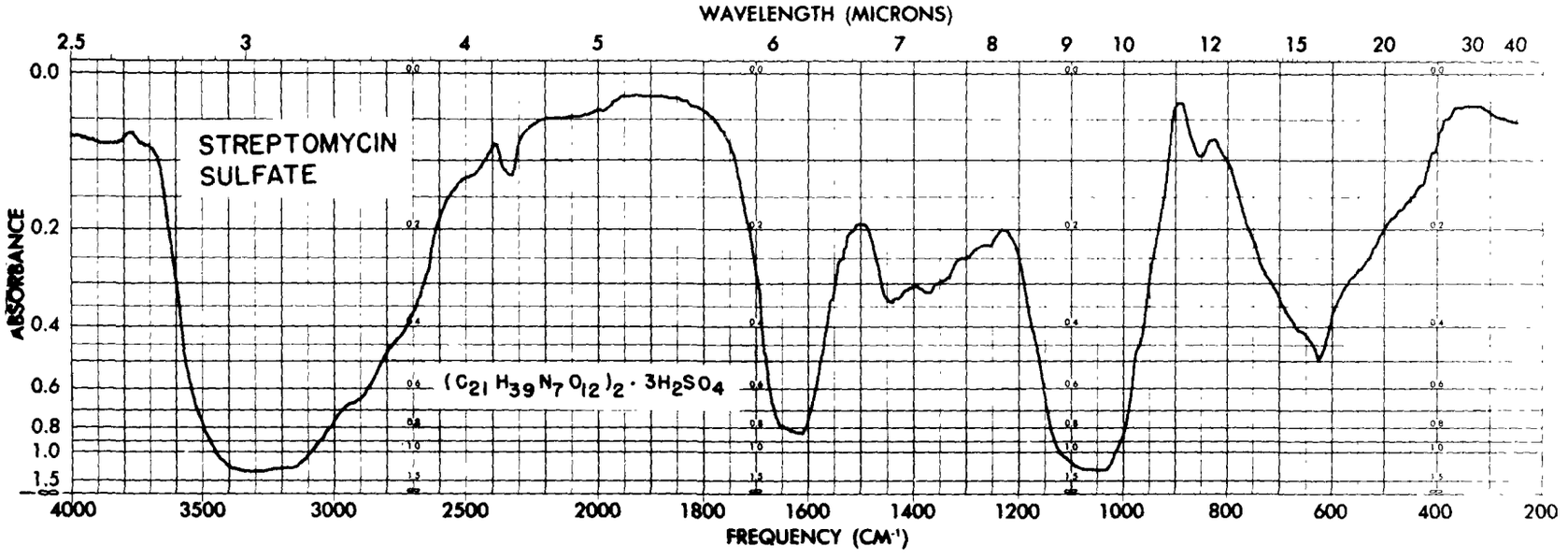

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
SESAMEX
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

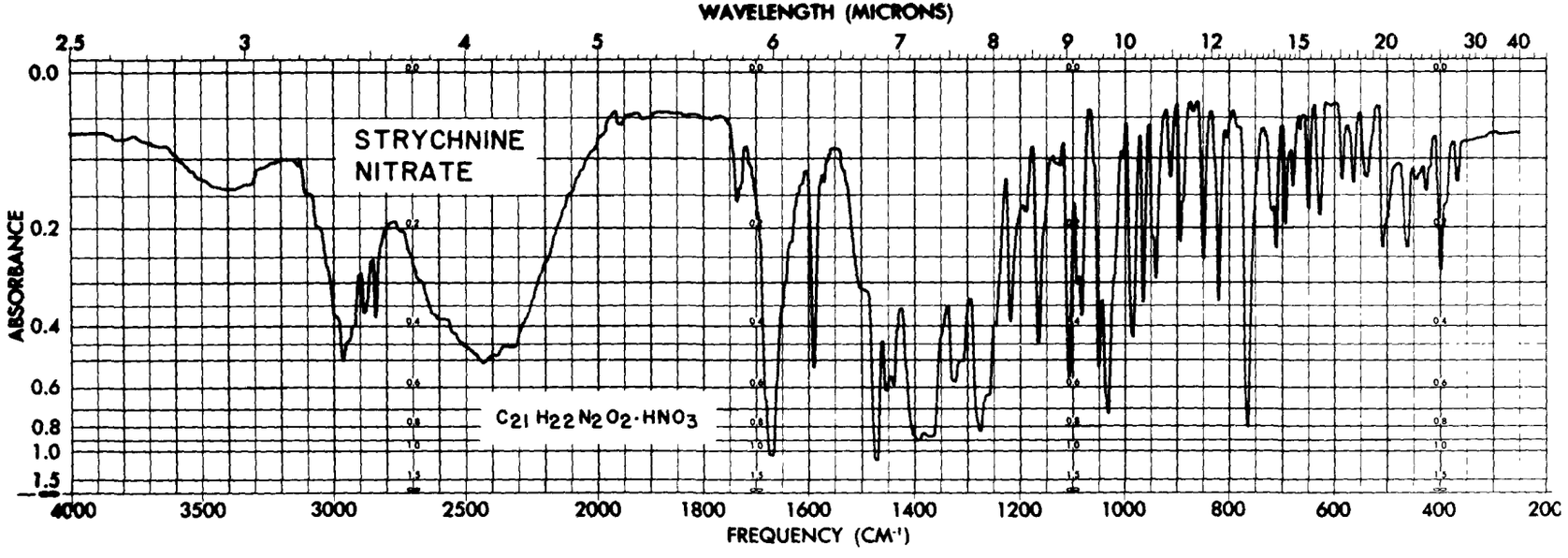

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
SESONE
O–CH2–CH2–O–S–O–Na
O
O
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

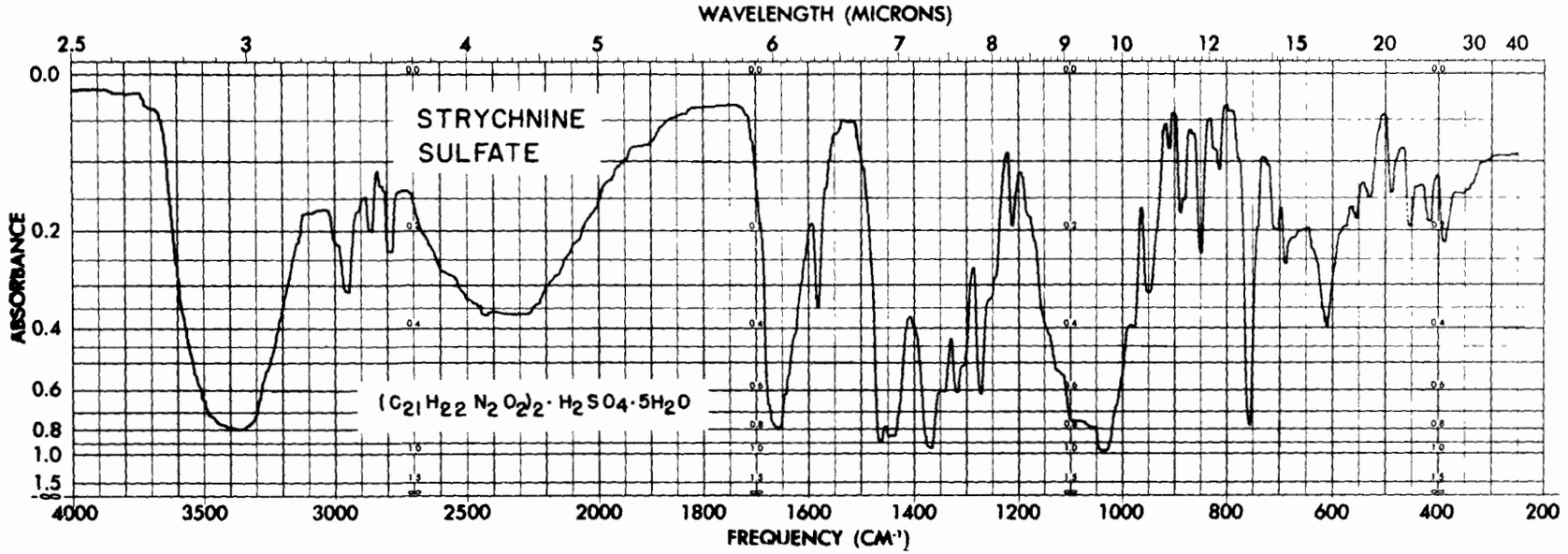

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
SIDURON
O
NH–C–NH
S
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

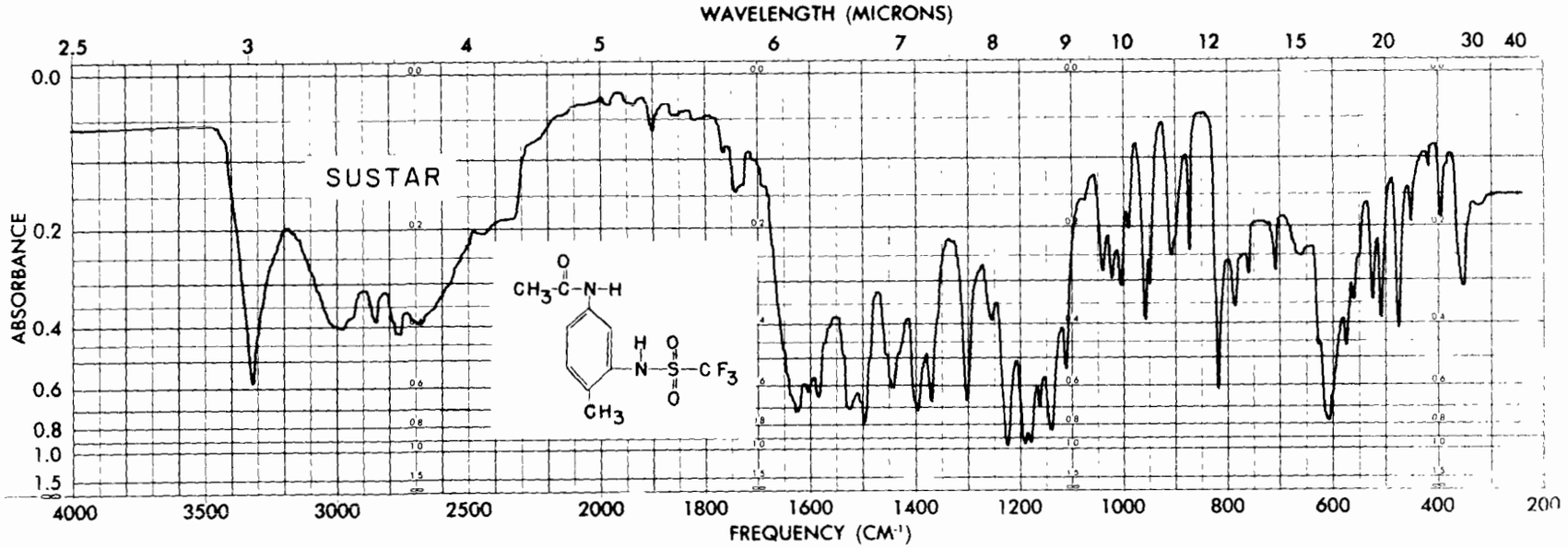

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
SIMAZINE
Cl
N
N
C2H5-NH
NH-C2H5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

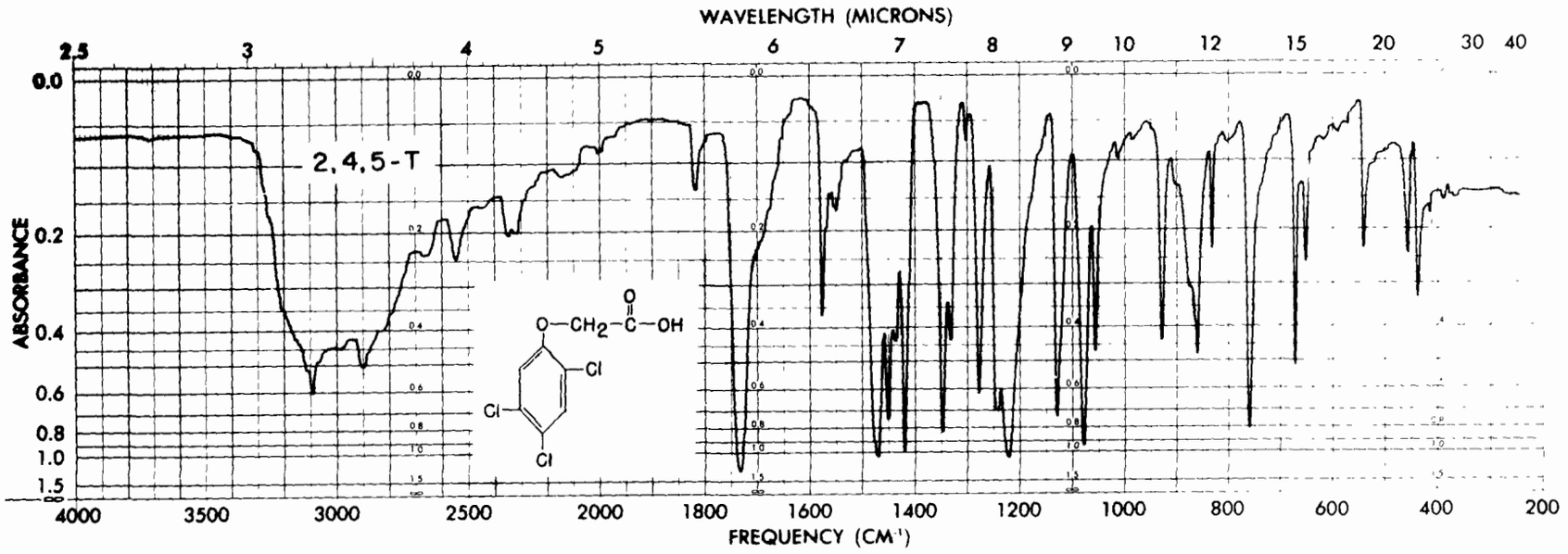

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
SIRMATE
O H
CH2-O-C-N-CH3
80%
Cl
Cl
O H
CH2-O-C-N-CH3
Cl
Cl
20%
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

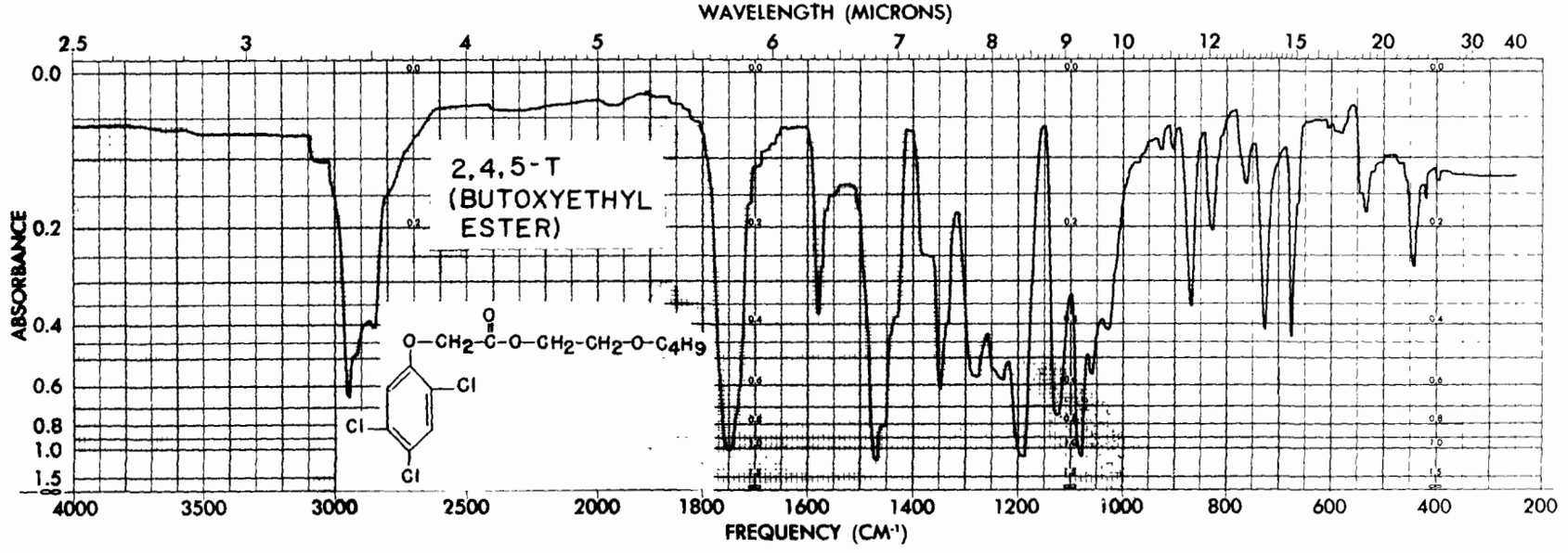

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
STREPTOMYCIN
SULFATE
$(C_{21}H_{39}N_7O_{12})_2 \cdot 3H_2SO_4$
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

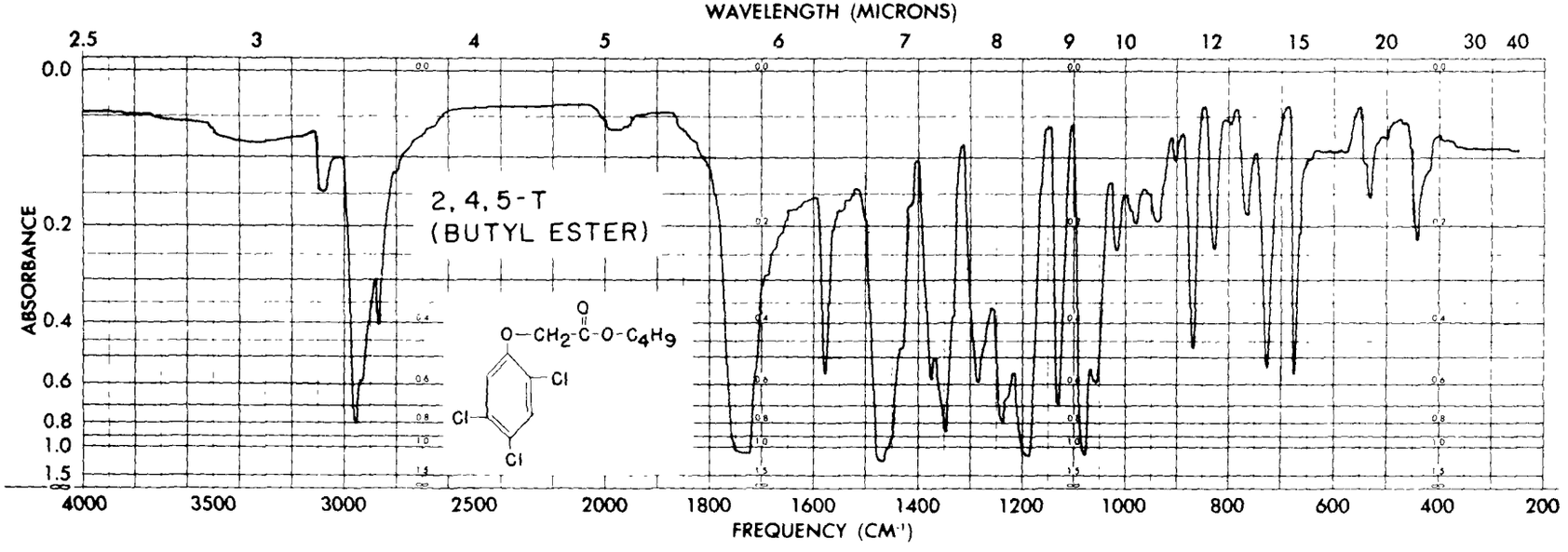

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
STRYCHNINE
NITRATE
$C_{21}H_{22}N_2O_2 \cdot HNO_3$
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

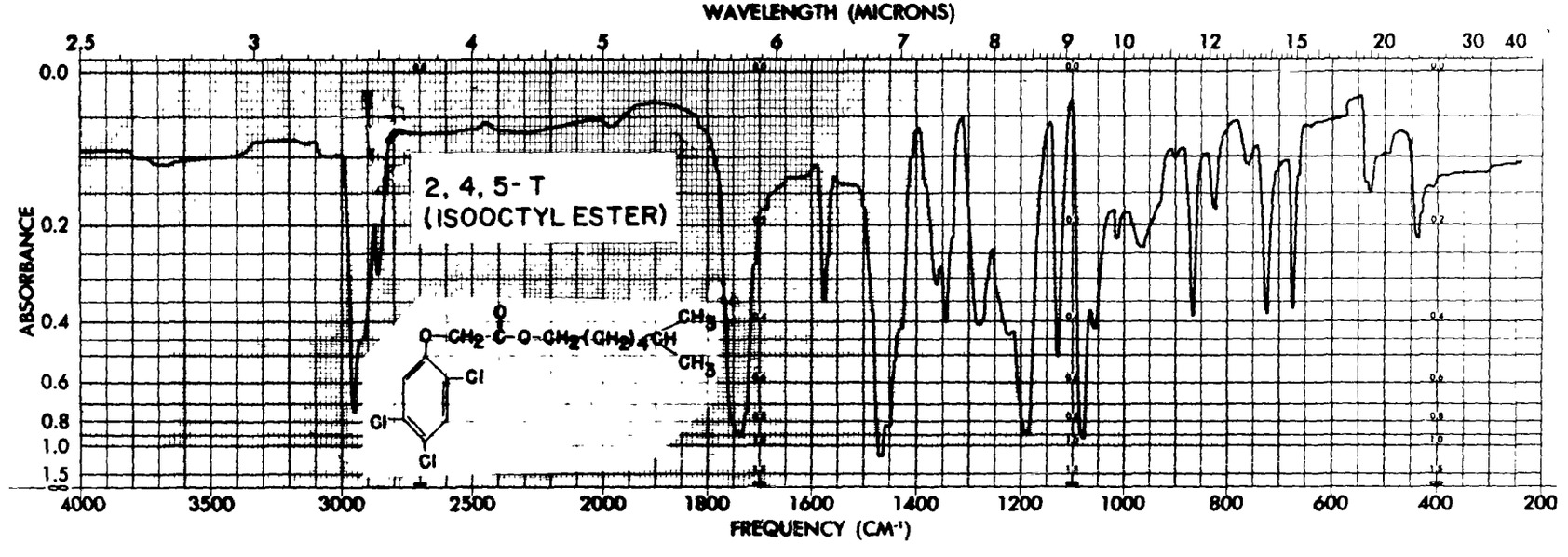

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
STRYCHNINE
SULFATE
$(C_{21}H_{22}N_2O_2)_2 \cdot H_2SO_4 \cdot 5H_2O$
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

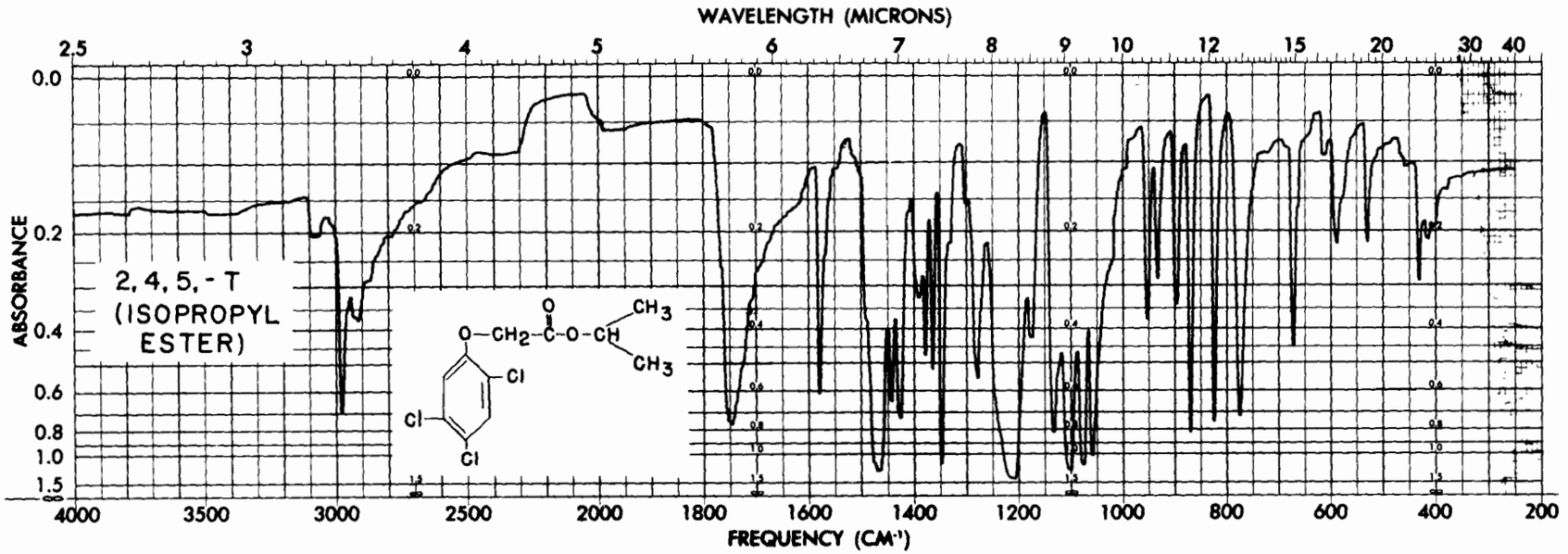

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
SUSTAR
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM^{-1})

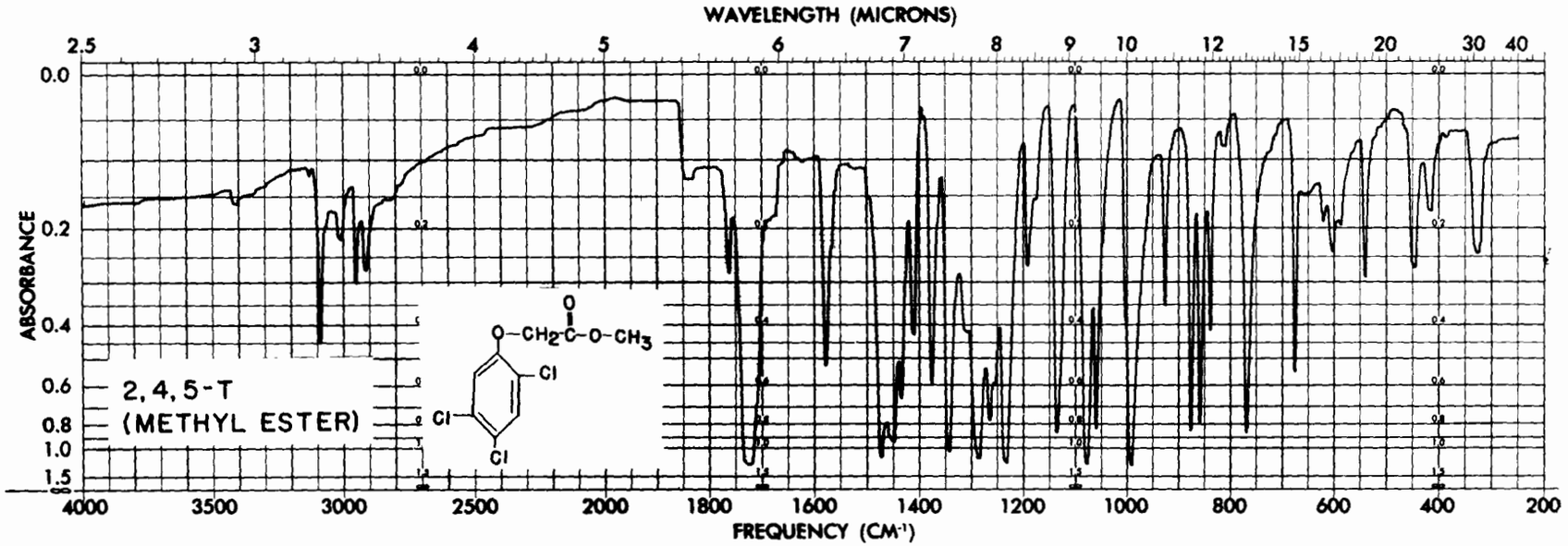

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
2,4,5-T
O—CH2—C—OH
O
Cl
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

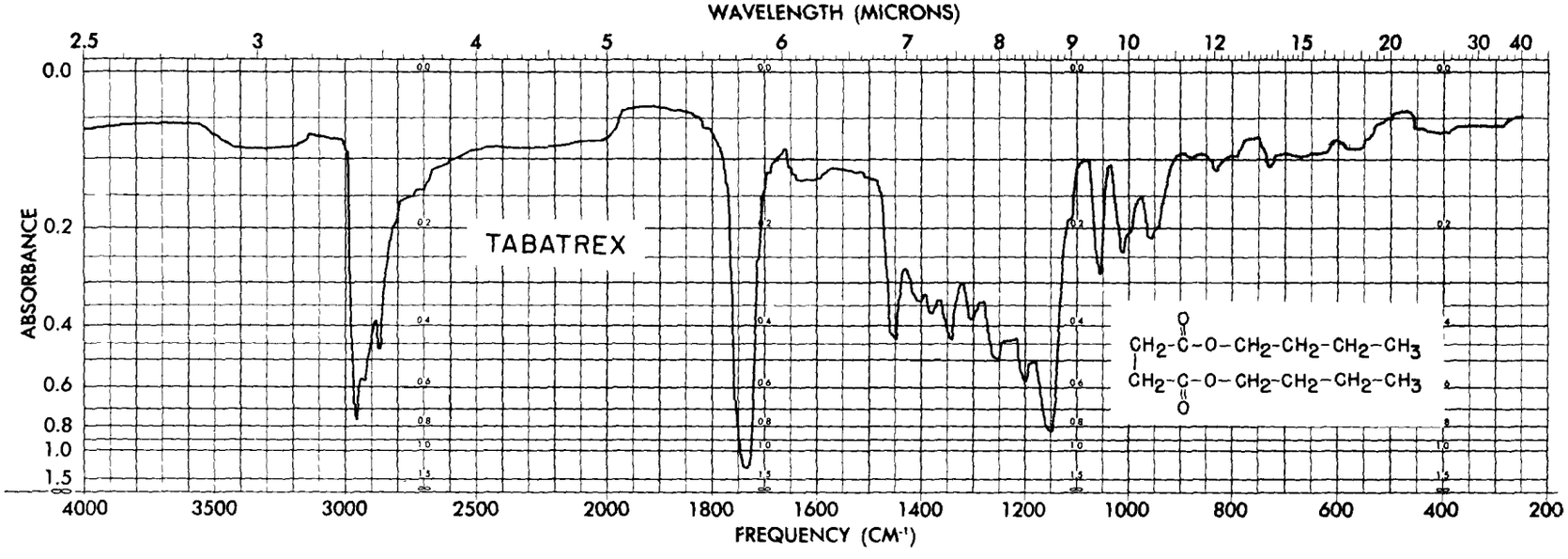

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
2,4,5-T
(BUTOXYETHYL
ESTER)
O
O—CH2—C—O—CH2—CH2—O—C4H9
Cl
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

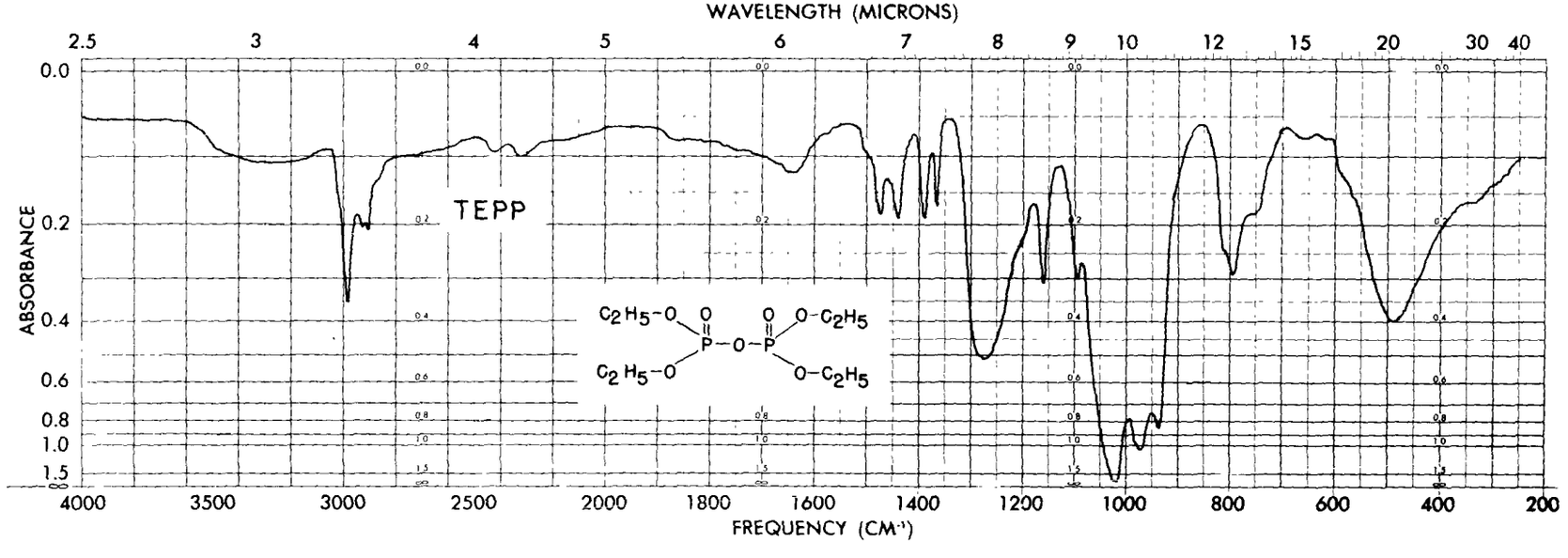

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
2, 4, 5-T
(BUTYL ESTER)
O—CH2-C-O-C4H9
Cl
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

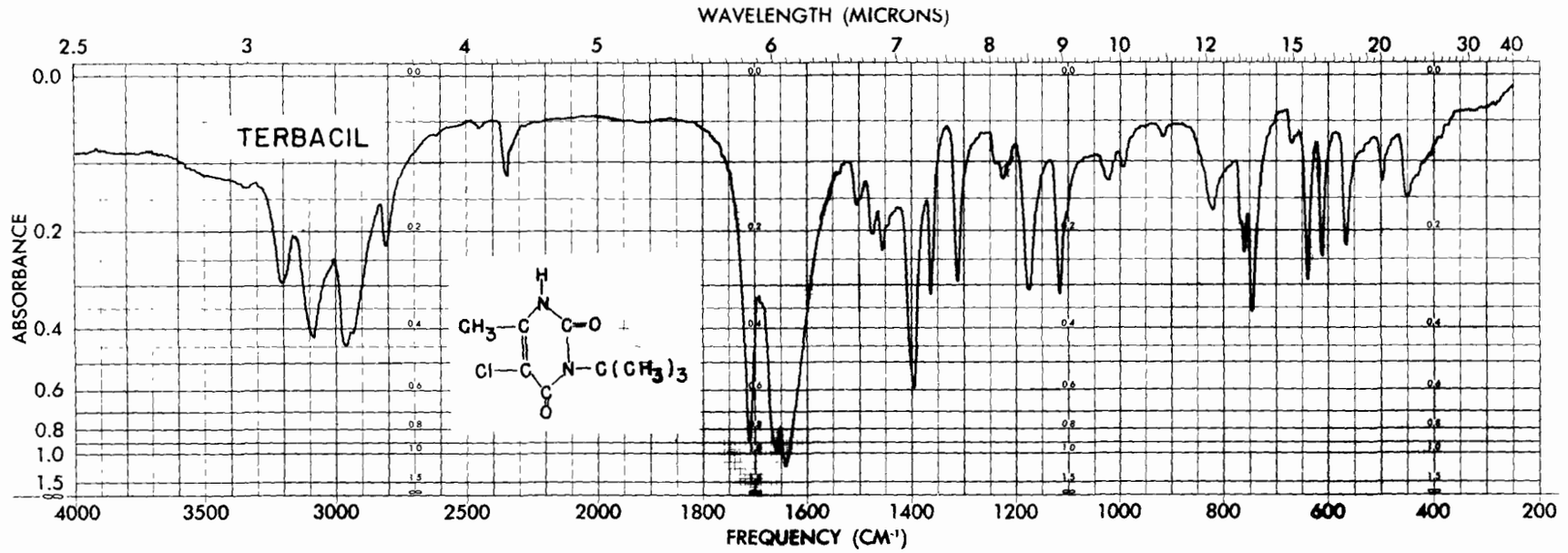

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
2, 4, 5-T
(ISOOCTYL ESTER)
O—CH2-C-O-CH2(CH2)4CH
CH3
CH3
Cl
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

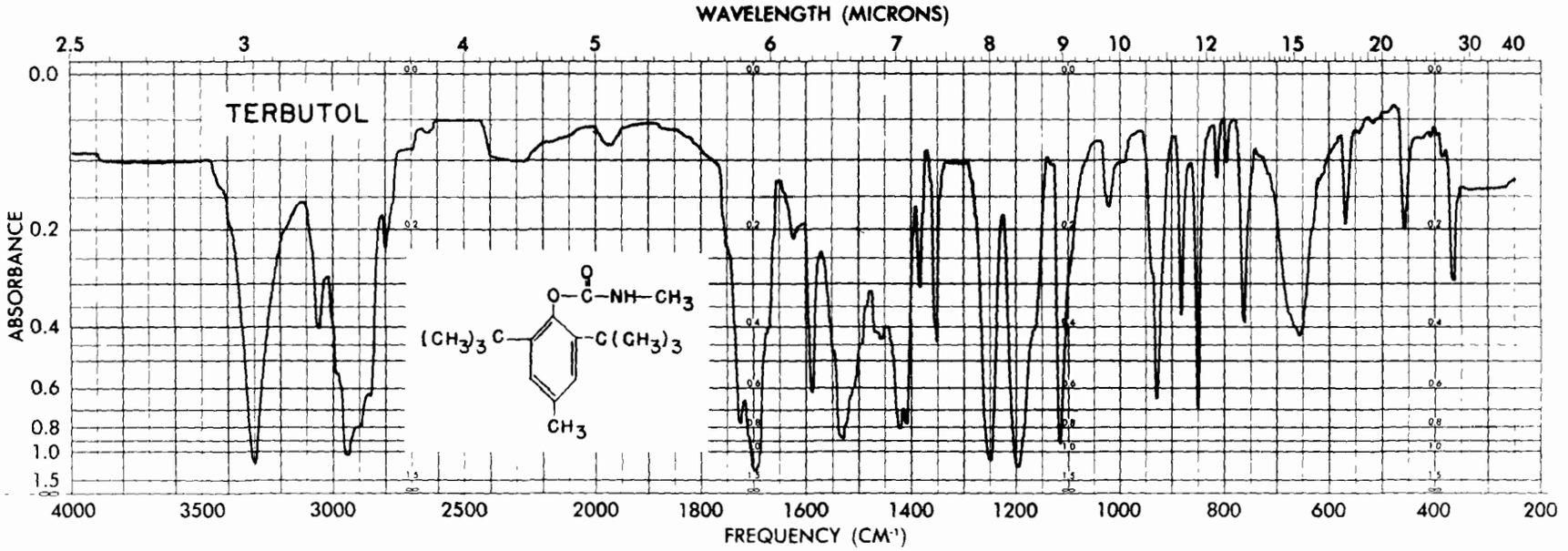

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
2, 4, 5, - T
(ISOPROPYL
ESTER)
O
O-CH2-C-O-CH
CH3
CH3
Cl
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

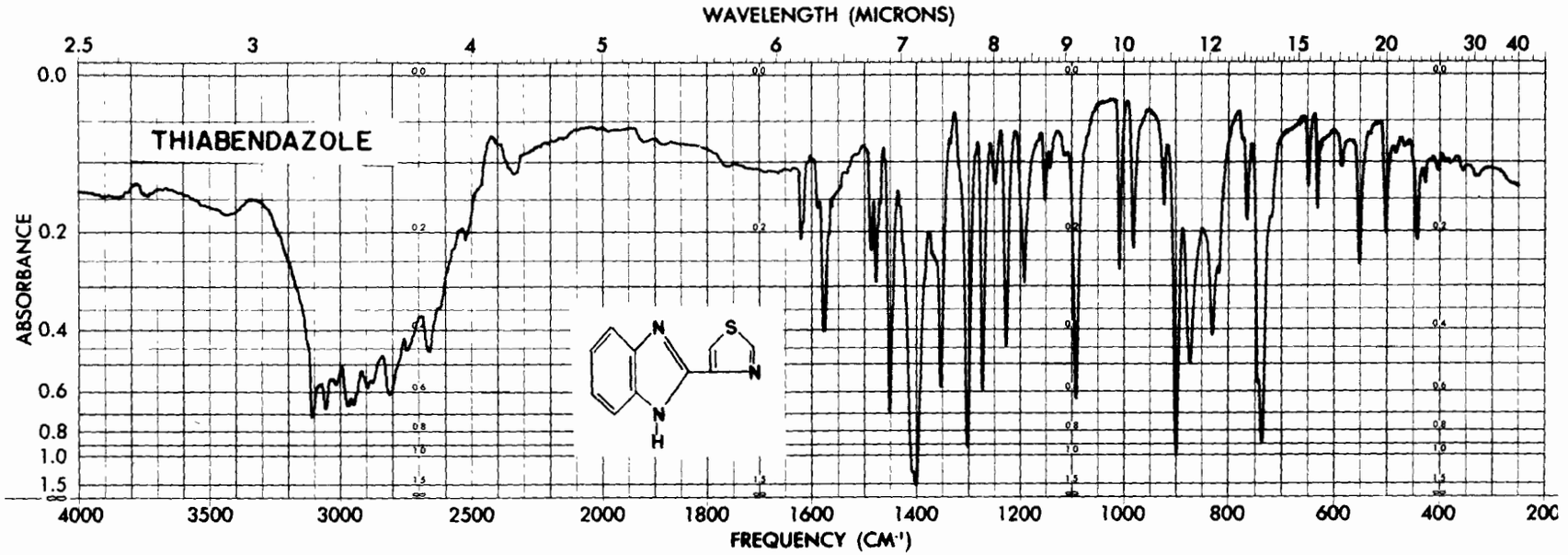

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ABSORBANCE
2, 4, 5-T
(METHYL ESTER)
O
O-CH2-C-O-CH3
Cl
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)

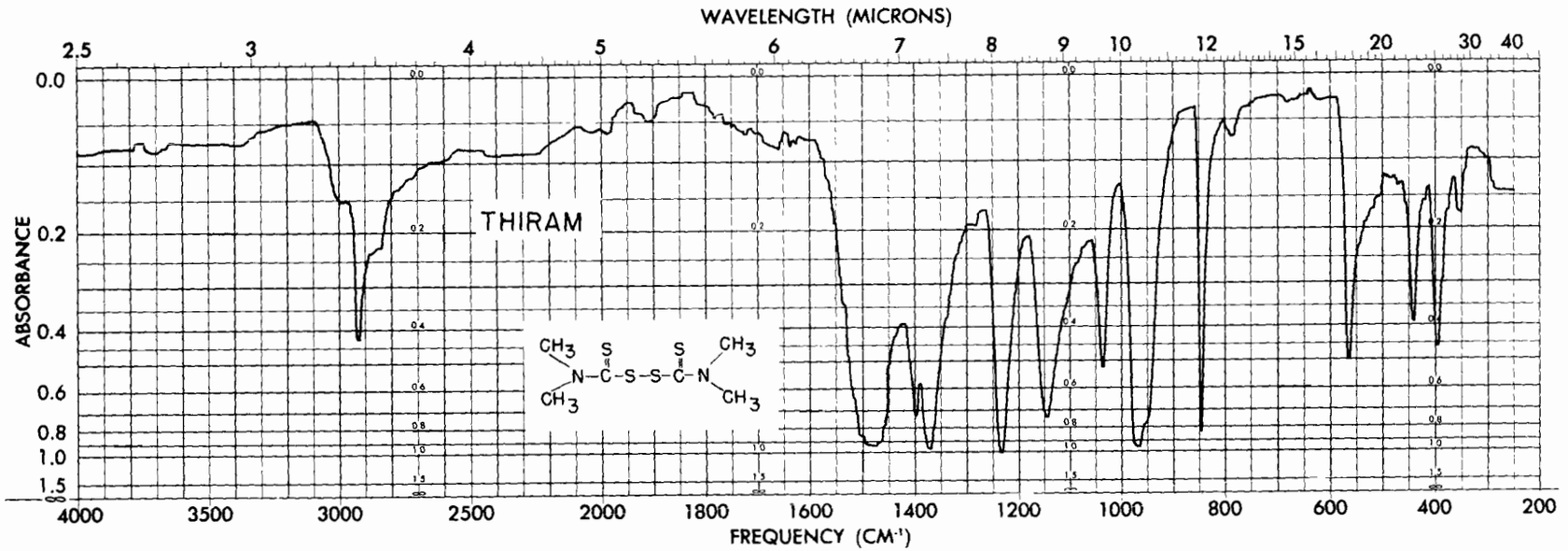

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
TABATREX
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

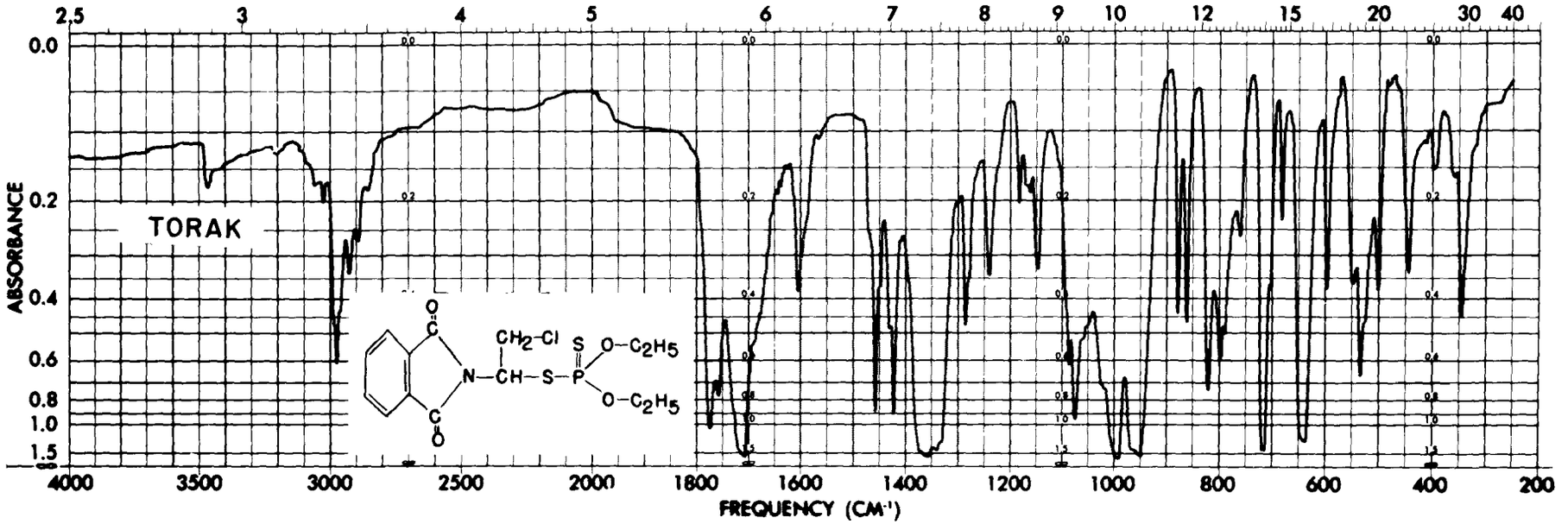

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
TEPP
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

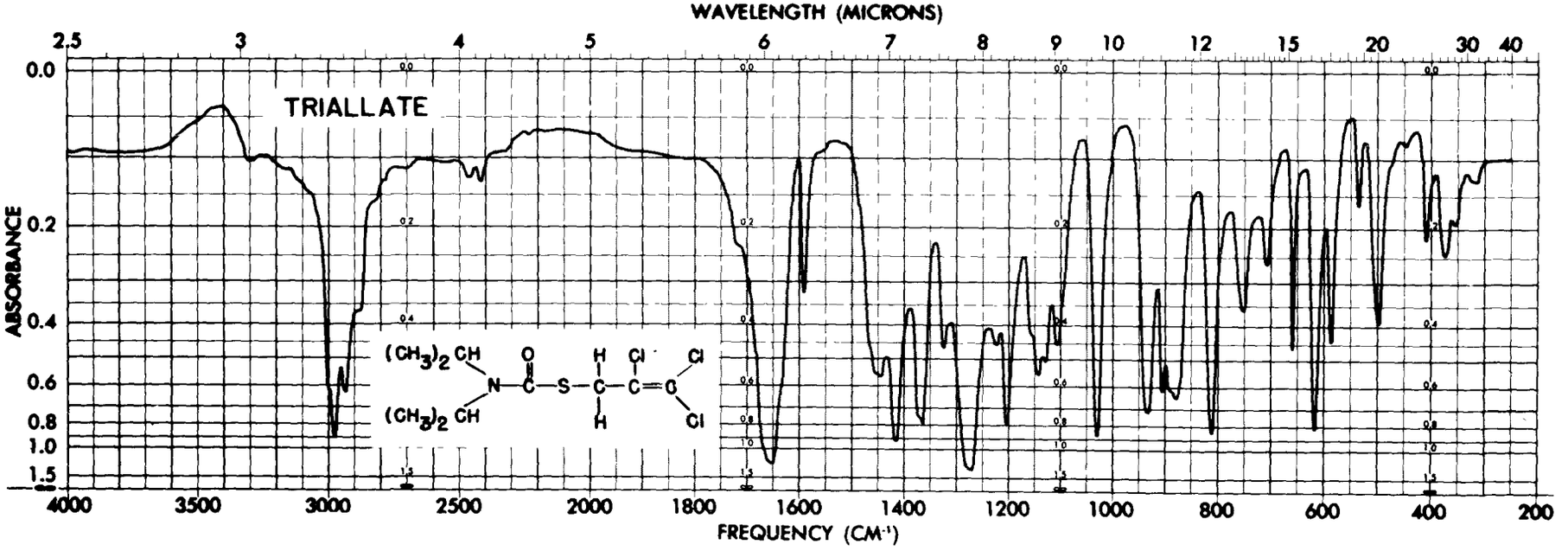

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
TERBACIL
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

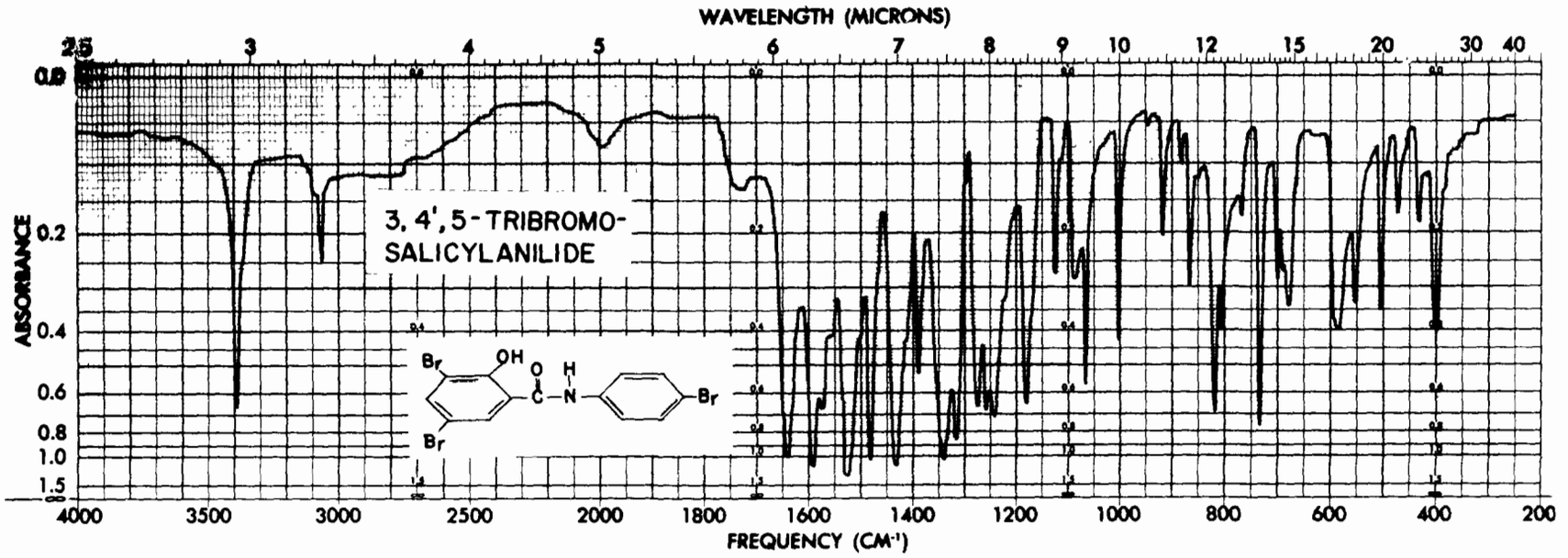

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
TERBUTOL
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

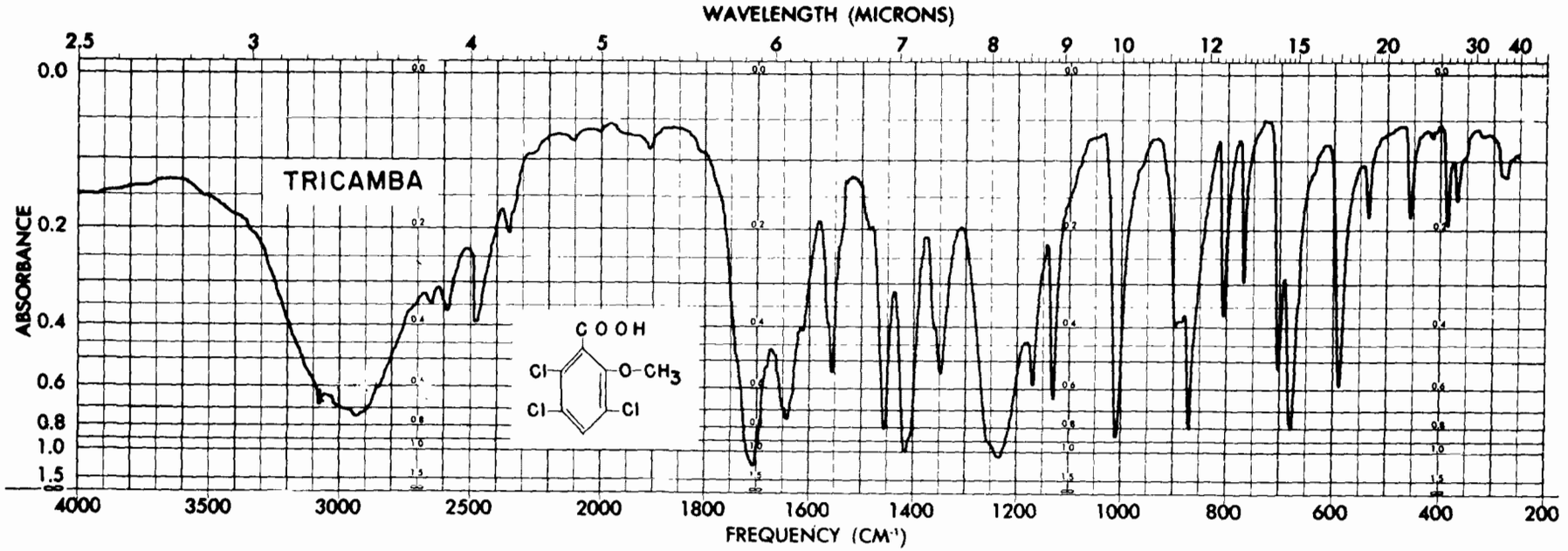

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
THIABENDAZOLE
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

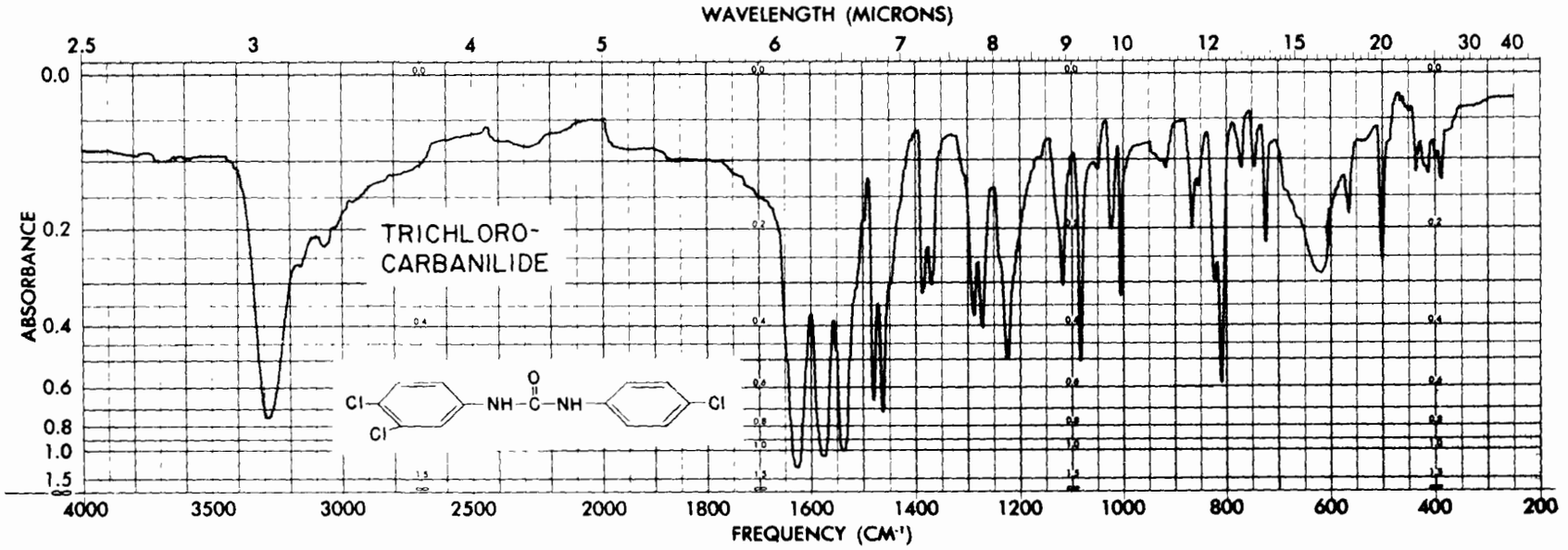

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
THIRAM
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

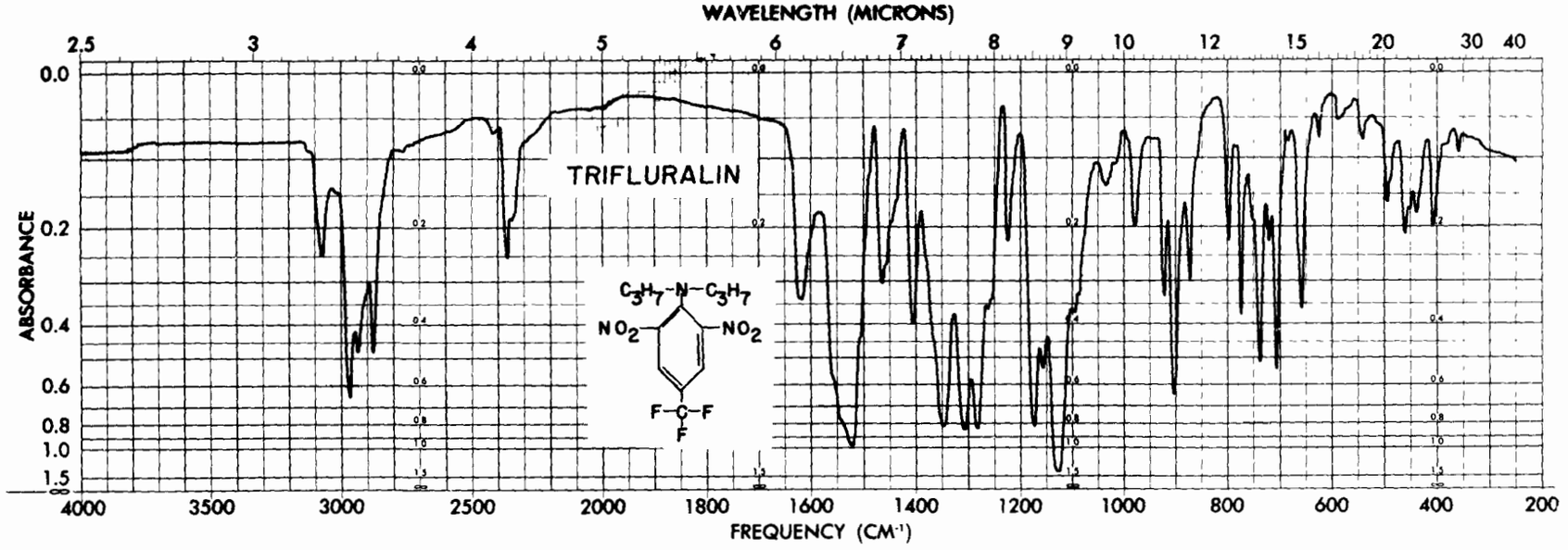

TORAK
ABSORBANCE
FREQUENCY (CM⁻¹)
WAVELENGTH (MICRONS)
2.5 3 4 5 6 7 8 9 10 12 15 20 30 40
0.0 0.2 0.4 0.6 0.8 1.0 1.5
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 200

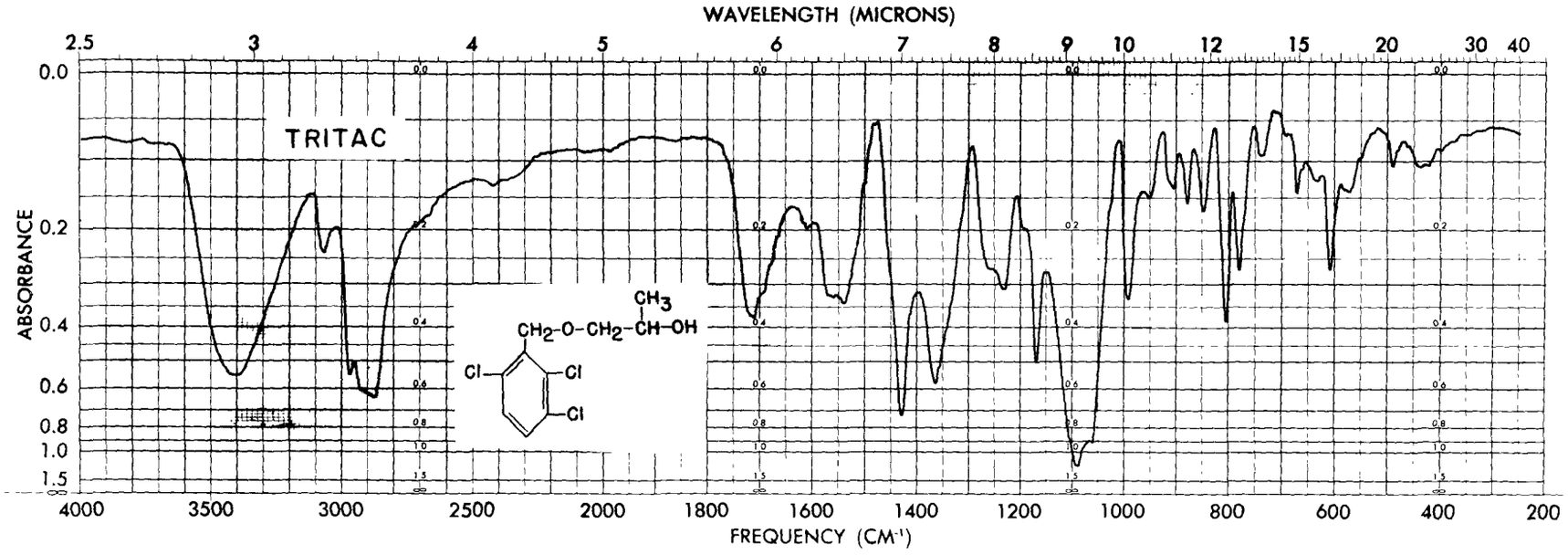

TRIALLATE
ABSORBANCE
FREQUENCY (CM⁻¹)
2.5 3 4 5 6 7 8 9 10 12 15 20 30 40
0.0 0.2 0.4 0.6 0.8 1.0 1.5
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 200

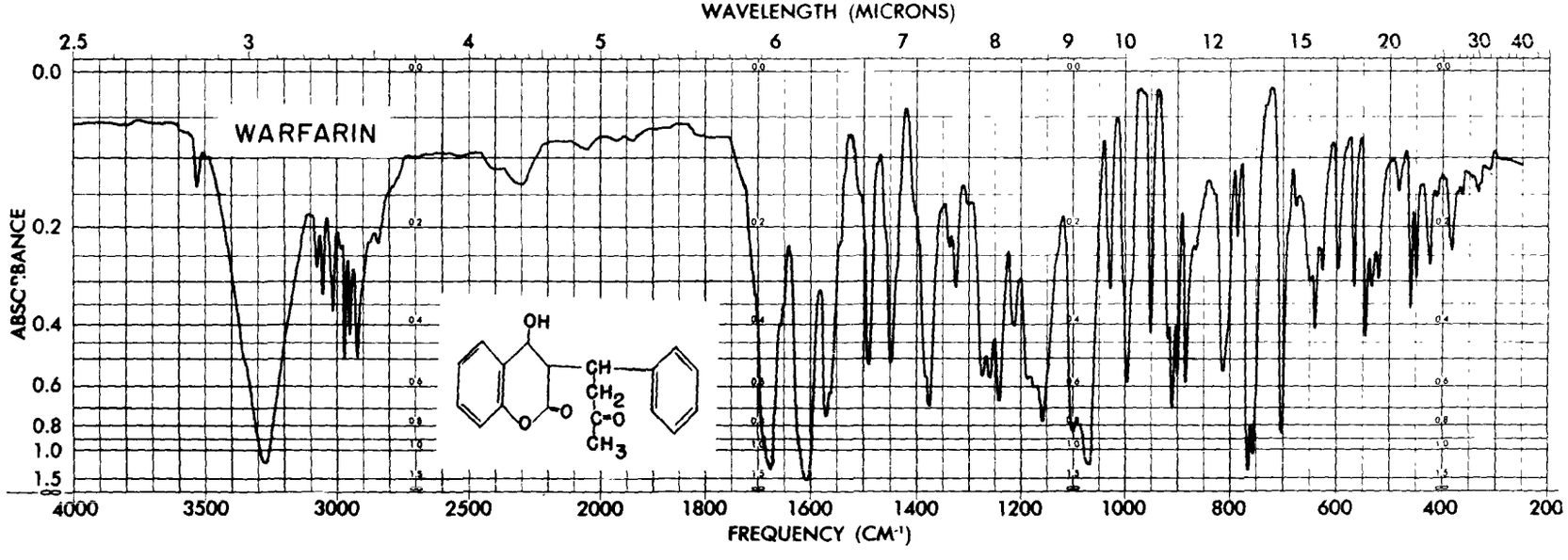

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
3, 4', 5 - TRIBROMO-
SALICYLANILIDE
Br
OH
O
H
C
N
Br
Br
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

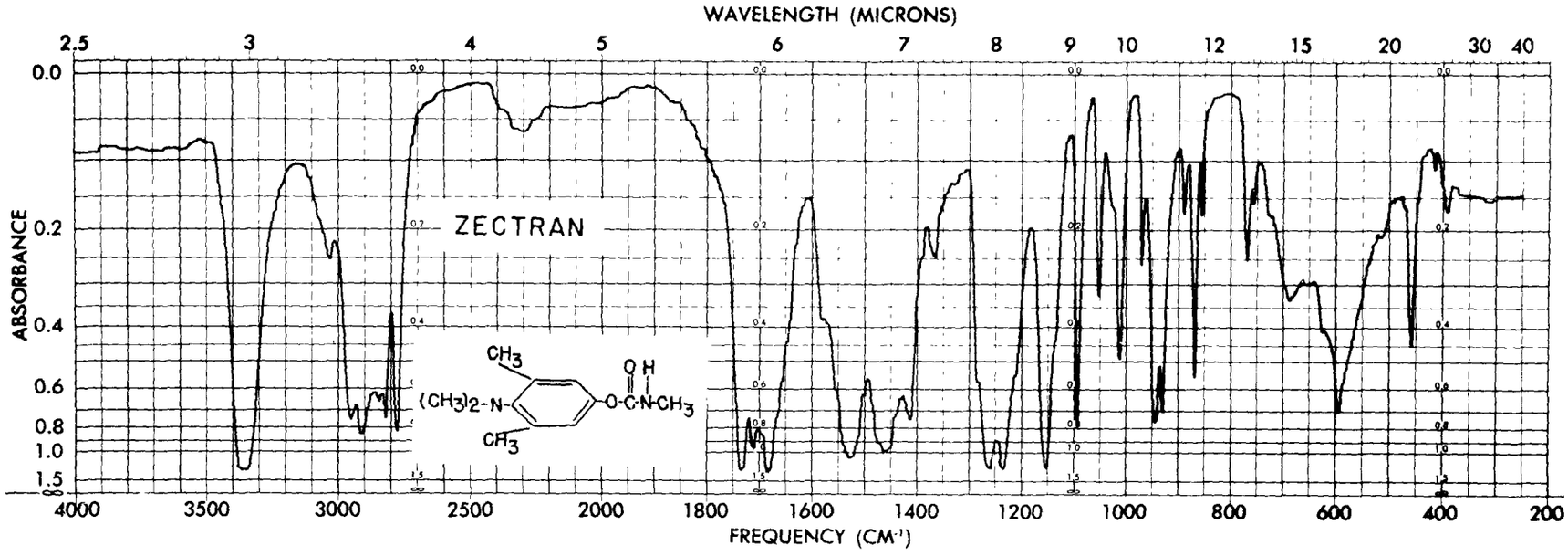

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
TRICAMBA
COOH
Cl
O-CH3
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

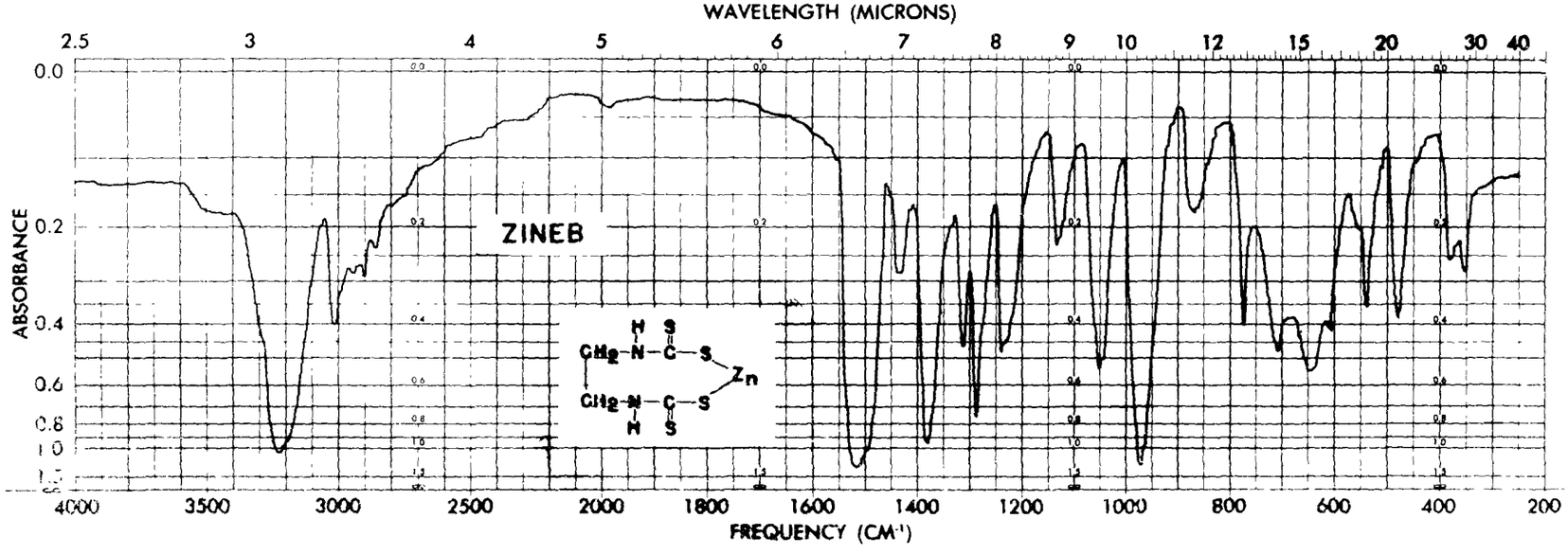

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
TRICHLORO-
CARBANILIDE
Cl
Cl
NH
C
O
NH
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

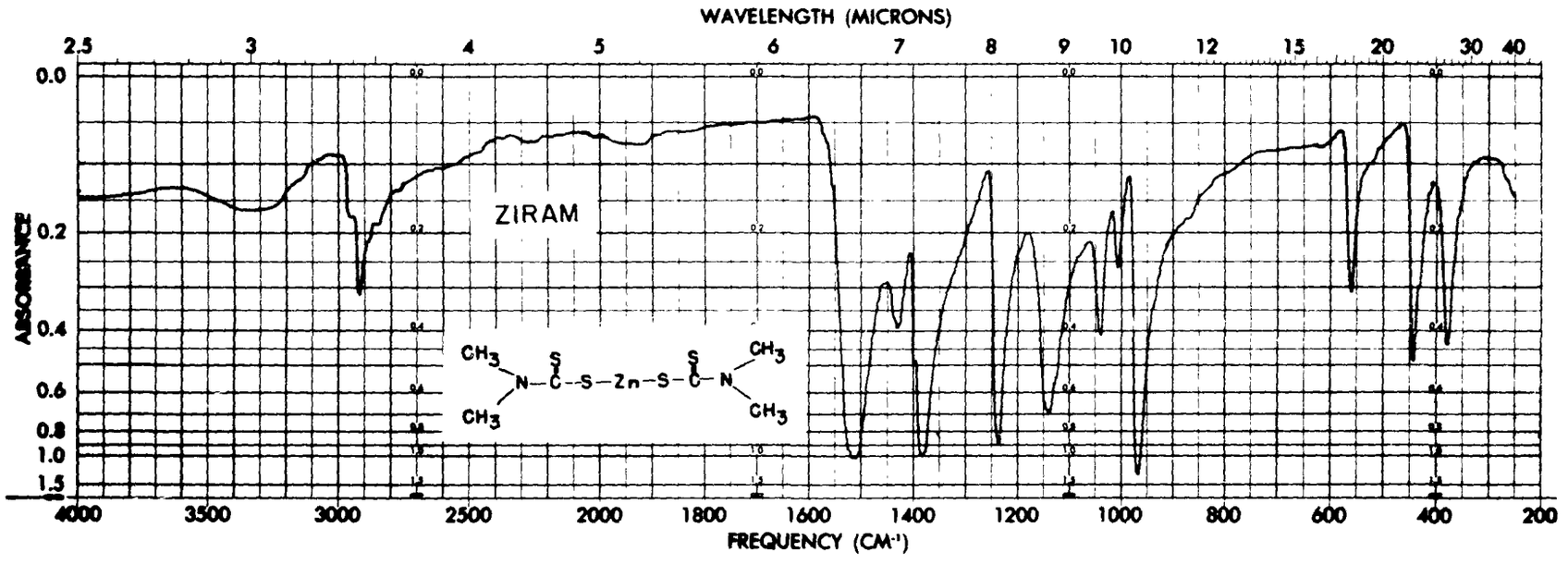

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
TRIFLURALIN
C3H7-N-C3H7
NO2
NO2
F-C-F
F
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
TRITAC
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
CH3
CH2-O-CH2-CH-OH
Cl
Cl
Cl
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
WARFARIN
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
OH
CH
CH2
C=O
CH3
O
O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ZECTRAN
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
ZINEB
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.5
ZIRAM
CH3
S
S
CH3
N–C–S–Zn–S–C–N
CH3
CH3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM-1)