

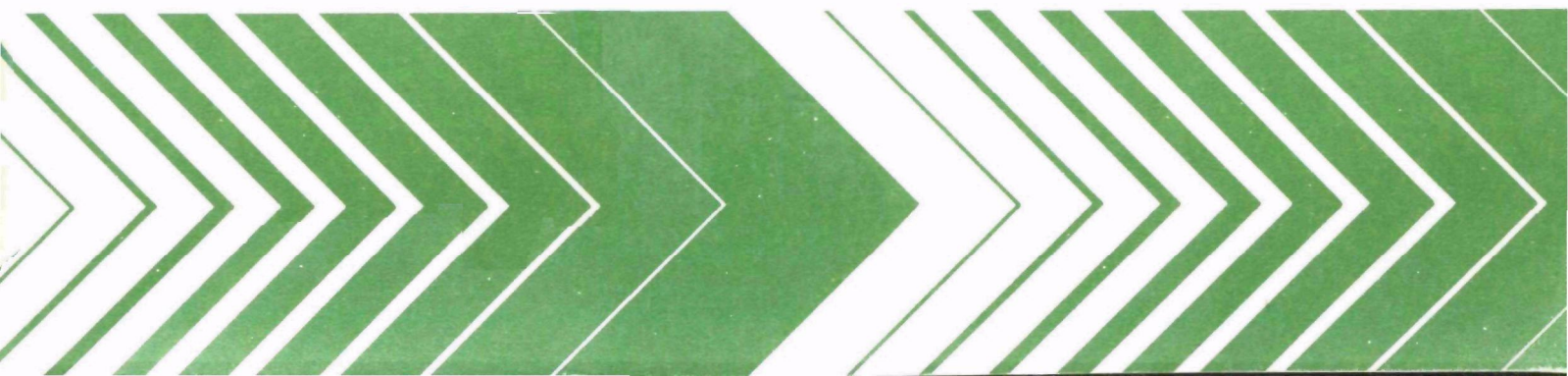
Research and Development



Polyurethane Foam as Trapping Agent for Airborne Pesticides

Analytical Method Development

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POLYURETHANE FOAM AS TRAPPING AGENT
FOR AIRBORNE PESTICIDES
Analytical Method Development

by

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FOREWORD

Environmental protection efforts are increasingly directed towards preventing adverse health and ecological effects associated with specific compounds of natural or human origin. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Environmental Systems Branch studies complexes of environmental processes that control the transport, transformation, degradation and impact of pollutants or other materials in soil and water; assesses environmental factors that affect water quality; and develops new techniques for measuring contaminants.

Pesticides transported in the air from application sites on forest and agricultural lands are receiving increased attention because of their potentially adverse health effects on humans and animals. A major problem in efforts to measure ambient air concentrations of pesticides has been the lack of an effective means of collecting samples for analysis. This report evaluates the use of polyurethane foam as a trapping agent for selected airborne pesticides.

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ABSTRACT

This research program was initiated to develop and evaluate a method for determining levels of organochlorine, organophosphorus and N-methylcarbamate insecticides in air, using polyurethane foam as the trapping agent.

A multipesticide method was developed, using 4.4 cm-diameter plugs of polyurethane foam as traps and a modified Sherma-Shafik multiresidue procedure for analysis of foam extracts. With this method, the minimum detectable air concentrations for vapors of 17 of the 18 organochlorine and organophosphorus pesticides tested was 0.1 ng/m³ or less. Six carbamate pesticides did not volatilize in sufficient amounts to allow analysis.

The experimental program consisted of measurements of efficiency of foams for trapping vapors and aerosols, tests of foam compression during air sampling, evaluations of techniques for extracting pesticide residues from the foams, evaluations of extraction solvents, comparisons of the performance of the ester and ether forms of polyurethane foam, evaluations of the steps in the Sherma-Shafik analytical procedure, evaluations of GLC columns and instrumental parameters, and tests of derivatization procedures for electron-capture gas chromatography of the N-methylcarbamates.

A 10-cm depth of foam was found to be an efficient trap for vaporized pesticides. However, there were indications that the foam may be less effective in trapping pesticides contained in airborne aerosols. Foams compressed during air sampling, necessitating continuous monitoring of flow rates for most accurate measurement of volume of air sampled.

Five-cycle Soxhlet extraction with 1:1 hexane-acetone was the best procedure for removal of pesticides from foam plugs. Excessive Soxhlet treatment produced lower recoveries of organophosphorus insecticides. Other solvents gave low recoveries or unacceptable levels of coextracted contaminants. The ester form of polyurethane gave better results than the ether form. GLC columns other than those recommended by Sherma and Shafik gave improved performance in multiresidue analysis of extracts. Carbamates (in aerosols) were best analyzed by derivatization with 0.1 ml pentafluoropropionic anhydride.

This report was submitted in fulfillment of Interagency agreement No. D6-0136 (78-D-X0449) by the Soil Nitrogen and Environmental Chemistry Laboratory (formerly the Agricultural Chemicals Management Laboratory), SEA-AR, U. S. Department of Agriculture, Beltsville, MD, under the sponsorship of the U. S. Environmental Protection Agency. This report covers the period September 30, 1976, to January 15, 1979. Owing to the time required for recruitment of personnel, work began on June 30, 1977. Work was terminated on January 15, 1979, because of the impending transfer of the principal investigator to the U. S. Environmental Protection Agency.

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SECTION 1

INTRODUCTION

Every year in the United States, millions of pounds of pesticides are applied to agricultural and forest lands, 65% by aerial application (1). During application, a significant fraction remains in the air as vapor, as particulate matter, or in aerosols. Also, some of the material that does reach the ground can later be introduced into the air as vapor by volatilization, or as adsorbate on fine particles by wind or by mechanical agricultural operations. The movement of pesticides in air is a major mode of their translocation over both short and long distances. These airborne pesticides may have epidemiological consequences for both humans and animals. As a result, the Congress has directed the EPA to establish a national system to monitor ambient air for concentrations of pesticides.

A major obstacle to the implementation of a national system is that the methods that have been used for trapping pesticides from air suffer from one or more problems. Among these are poor trapping efficiency, limited air flow, degradation of trapped pesticides, difficulty in recovery of trapped pesticide, instability of the trapping medium, and difficulty with cleanup of the recovered pesticide to permit its unambiguous quantitation.

Several of these effects do not occur with polyurethane foam (PUF). That is, PUF is not hygroscopic; since it is semi-solid, it is not entrained in air streams; it does not volatilize; and the polymer is relatively nonreactive and therefore unlikely to degrade labile pesticides. Moreover, it has been reported to perform efficiently as a trap for certain pesticides (2, 3).

The present study was designed to provide an in-depth evaluation of PUF as a trapping agent for a broad spectrum of airborne pesticides, focusing on efficiency of trapping, ease of recovery of trapped pesticides, relative performance of the ether and ester forms of PUF, and compatibility of PUF with the multipesticide analytical scheme of Sherma and Shafik (4). The latter had shown promise for use in a national monitoring system, except that the trapping procedure, air flow through a column of ethylene glycol, exhibited unacceptable shortcomings.

SECTION 2

CONCLUSIONS

The results of laboratory experiments using an airflow apparatus indicated that PUF is an efficient trap for vapors of organochlorine and organophosphorus pesticides, even when substantial amounts of air are sampled. A 10-cm depth of ester-form PUF was adequate for trapping vapors of the 18 volatile compounds tested when as much as 55 m³ of air was passed through the apparatus.

A finding having important implications for ambient monitoring was that pesticides were not trapped as well by PUF when they were sampled as airborne aerosols rather than as molecular vapors. The aerosol tests included a number of carbamate insecticides that had not volatilized in earlier airflow experiments.

During extended air sampling with plugs of PUF, the plugs compressed somewhat and air flow rates decreased. In several 24-hour airflow tests, the flow rate decrease ranged from 3 to 9%. Accurate measurement of volume of air passing through PUF plugs in ambient air sampling will require monitoring of flow rates.

Experiments showed that Soxhlet extraction was superior to both solvent elution and immersed plug compression as a technique for removal of pesticides from PUF plugs. However, excessive Soxhlet extraction should be avoided. Tests showed that extractions carried beyond five Soxhlet cycles may cause degradation and decreased recovery of the organophosphorus pesticides. The best solvent for extraction was 1:1 hexane-acetone. Less polar solvents gave low recoveries; more polar solvents coextracted interfering nonpesticidal components.

Soxhlet extracts of PUF plugs were compatible with the Sherma-Shafik multipesticide analytical procedure (4). Extracts could be analyzed, with low background levels, at concentrations down to 0.1 ng/m³ or lower for all tested pesticides except for carbophenothion, which could be measured down to 0.3 ng/m³.

No significant differences between the ester and ether forms of PUF were observed with respect to the trapping or extraction of pesticides.

In evaluations of GLC columns, improved performance was obtained by using columns other than those recommended by Sherma and Shafik (4) for analysis of

the three mixtures of pesticides resulting from their cleanup procedure. Optimum results were obtained with use of these columns: (a) 1.5% OV-17 and 1.95% OV-210 on Chromosorb W HP; (b) 3% OV-1 on Chromosorb W; and (c) 3% DC-200 on Gas Chrom Q.

Tests of the derivatization of the carbamate insecticides for analysis by electron-capture gas chromatography showed that the pentafluoropropionic anhydride (PFPA) procedure of Sherma and Shafik (4) gave the most satisfactory results, except that response was enhanced by increasing the amount of PFPA from the recommended 0.025 ml to 0.100 ml. Trifluoroacetic anhydride, 1-fluoro-2,4-dinitrobenzene and heptafluorobutyric anhydride were also tested as derivatization reagents, the first two giving unacceptable results and the last offering no improvement over PFPA.

Experiments with 2,4- and 2,6-diaminotoluene, which are products of PUF degradation, showed that their PFPA derivatives were removed during extract cleanup and, therefore, would not interfere with the quantitation of carbamate insecticides.

SECTION 3

RECOMMENDATIONS

The stability of pesticides trapped on polyurethane foam should be confirmed with respect to humidity and photochemical oxidants to evaluate suitability for use in areas of high or low humidity or high smog levels. The recommended procedure should be field tested by sampling ambient air in an urban, an industrial, and an agricultural environment.

If polyurethane foam is to be used in a multiple-site air monitoring program for pesticides, it is recommended that, to trap pesticides in both vapor and aerosol form, the column of foam be 25 cm deep and at least 4.4 cm in diameter. All of the foam should be hydrophobic and from one manufacturing lot. The foam should be thoroughly cleaned before use and be well protected from contamination at all times. All GLC columns to be used for quantitation should be from a single source to ensure uniformity in measurement of residue levels in samples collected from different sites.

Further research is necessary to confirm the penetration of polyurethane foams by aerosols and to determine the reasons and conditions for aerosol penetration. If the mechanism for this penetration is understood, it may be possible to modify the foam or sampling conditions to minimize the effect. Previous reports on sampling pesticides in air have been concerned with vapors, but aerosols may well be a major form in which pesticides occur in air. Accordingly, it will be necessary to examine trapping efficiency for aerosols in evaluations of pesticide adsorbants other than polyurethane foam, such as the reticular porous polymers.

SECTION 4

MATERIALS AND EQUIPMENT

PESTICIDES

Because one objective of the program was to evaluate the feasibility of applying the Sherma-Shafik analytical procedure to PUF extracts, the pesticides in the original paper by Sherma and Shafik (4) were selected for use in this study. All pesticides used were analytical-grade standards, obtained from commercial sources: α - and β -BHC from Applied Science Laboratories, Inc.; the remainder of the compounds from Supelco, Inc. The list of pesticides, along with chemical names and equilibrium vapor pressures as available, is shown in Table 1.

SOLVENTS

All solvents used were glass-distilled, pesticide grade, obtained from Burdick and Jackson Co.

GAS CHROMATOGRAPHS

Four gas chromatographs were used in the program: (1) a Tracor Model 222, equipped with a ^{63}Ni electron-capture detector (ECD), for analysis of organochlorine and carbamate insecticides; (2) a Tracor Model 560, with ^{63}Ni ECD, also for organochlorine analysis; (3) a second Tracor Model 222, with a flame photometric detector (FPD), for analysis of organophosphorus insecticides; and (4) a Varian Model 2100, with an alkali flame ionization detector (AFID), also for organophosphorus analysis.

GAS-LIQUID CHROMATOGRAPHY COLUMNS

Ten glass, packed GLC columns were used for pesticide analysis in the various phases of the program. Four of these were obtained from commercial sources, four were packed in our laboratory using packing material we had prepared ourselves, and the remaining two were packed in our laboratory using commercial packing material.

Of the four commercial columns, three were 180-cm long, 2-mm I.D. coiled columns for use in the Tracor 560 gas chromatograph. The packings in these were: (a) 3% OV-210 on 80- to 100-mesh Supelcoport (Supelco, Inc.); (b) 5% SE-30 on 80- to 100-mesh Supelcoport (Supelco, Inc.); and (c) 3% DC-200 on 100- to 120-mesh Gas Chrom Q (Applied Science Laboratories, Inc.). The fourth

TABLE 1. TEST PESTICIDES

Common or trade name	Vapor pressure		Chemical designation
	mm Hg	at T, °C	
Aldrin	6×10^{-6}	25	1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-4-endo,exo-5,8-dimethanonaphthalene
Aminocarb			4-dimethylamino-m-tolyl N-methylcarbamate
α -BHC			α -isomer of 1,2,3,4,5,6-hexachlorocyclohexane
β -BHC			β -isomer of 1,2,3,4,5,6-hexachlorocyclohexane
Carbaryl	$<5 \times 10^{-3}$	26	1-naphthyl N-methylcarbamate
Carbofuran			2,3-dihydro-2,2-dimethyl-7-benzofuranyl N-methylcarbamate
Carbophenothion	3.05×10^{-7}	20	O,O-diethyl-S-[[(p-chlorophenyl)thio]methyl] phosphorodithioate
p,p'-DDD			1,1-dichloro-2,2-bis(p-chlorophenyl)ethane
p,p'-DDE			1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene
o,p'-DDT			1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)ethane
p,p'-DDT	3.0×10^{-7}	25	1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane
Diazinon	8.4×10^{-5}	20	O,O-diethyl-O-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothioate
Dieldrin	1.8×10^{-7}	25	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo,exo-5,8-dimethanonaphthalene

TABLE 1. (continued)

Common or trade name	Vapor pressure		Chemical designation
	mm Hg	at T, °C	
Endrin			1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo, endo-5,8-dimethanonaphthalene
Ethion	1.5×10^{-6}	20	O,O,O',O'-tetraethyl S,S'-methylenebisphosphorodithioate
Heptachlor			1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-endo-methanoindene
Heptachlor epoxide			1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindene
2,3,5-Landrin			2,3,5-trio,etju;!jemu; N-methylcarbamate
Lindane	9.4×10^{-6}	20	γ -isomer of 1,2,3,4,5,6-hexachlorocyclohexane
Malathion	1.25×10^{-4}	20	O,O-dimethyl S-(1,2-dicarbethoxyethyl) phosphorodithionate
Methiocarb			4-methylthio-3,5-xylyl N-methylcarbamate
Methoxychlor			1,1,1-trichloro-2,2-bis(p-methoxyphenyl)ethane
Methyl parathion	9.7×10^{-6}	20	O,O-dimethyl O-p-nitrophenyl phosphorothioate
Mexacarbate			4-dimethylamino-3,5-xylyl N-methylcarbamate

TABLE 1 (continued)

	Common or trade name	Vapor pressure		Chemical designation
		mm Hg	at T, °C	
∞	Parathion	5.7×10^{-6}	20	O,O-diethyl O-p-nitrophenyl phosphorothioate
	Propoxur	1.0×10^{-2}	20	o-isopropoxyphenyl N-methylcarbamate
	Ronnel	8×10^{-2}	25	O,O-dimethyl O-(2,4,5-trichlorophenyl) phosphorothioate

commercial column was a 180-cm long, 4-mm I.D. U-tube, packed with 3% OV-1 on 80- to 100-mesh Chromosorb W (Tracor, Inc.).

To prepare packings, we used 80- to 100-mesh Chromosorb W as support material. The procedure was as follows, using SE-30 as an example: 0.50 g SE-30 was dissolved in 35 ml chloroform in a 250-ml filter flask, and 9.50 g of the support material was added. Vacuum was then applied until the solution boiled briefly. The vacuum was released and the slurry was swirled gently. Evacuation, release and swirling were repeated until all the free liquid had evaporated. The remaining slurry, which had the consistency of damp sand, was subjected to fluidized drying in a fluidizer ("HI-EFF", Applied Science Laboratories, Inc.) with nitrogen flowing through. The fluidizer was placed on a hot plate at about 100°C surface temperature until the material became free-flowing.

Packings prepared by this procedure were: (a) 5% SE-30, as above; (b) 3% OV-1, from 0.30 g OV-1, 35 ml chloroform and 9.70 g Chromosorb W; (c) 5% OV-210, from 1.021 g OV-210, 70 ml chloroform and 19.40 g Chromosorb W; and (d) another 5% OV-210, but treated with Carbowax 20M by the procedure of Ives and Giuffrida (5).

To pack columns, we poured the dry, coated support material into one end of a 180-cm long, 4-mm I.D. U-tube, while applying a vacuum to the other end and simultaneously tapping the column. The column was then conditioned by heating to 250°C for 18 hours in a flow of nitrogen. We packed columns with the four self-prepared packings and with two commercial packings: (a) 3% DC-200 on 100- to 120-mesh Gas-Chrom Q (Applied Science Laboratories, Inc.), and (b) a mixture of 1.5% OV-17 and 1.95% OV-210 on Chromosorb W HP (Supelco, Inc.).

POLYURETHANE FOAM PLUGS

Polyurethane foam, in both ester (gray) and ether (white) forms, was purchased in 5-cm-thick sheets from a commercial source, Read Plastics, Inc., Rockville, MD. Both of these foams were flexible, reticulated and hydrophobic types. Cylindrical plugs, 45-mm diameter by 5 cm thick, were cut from the sheets with a special tool mounted in a drill press. The tool was fabricated to our specifications from thin-wall stainless steel tubing in our Instrument Design Shop.

SECTION 5

EXPERIMENTAL PROGRAM AND RESULTS

INVESTIGATION OF PUF TRAPPING EFFICIENCY

Laboratory evaluations of pesticide vapor trapping efficiency by various media have generally involved the spiking of some type of source with small quantities of the pesticides to be tested; passing a given volume of air through the source and through the trapping medium in a suitable apparatus; analyzing the source, trapping medium, and chamber washings for pesticide content; and calculating trapping efficiency by a material balance (6). The factors that control the rate at which a given pesticide is volatilized in these tests include the vapor pressure of the pesticide, air temperature, airflow rate, energy of adsorption of the pesticide by the source material, and surface area of the source.

The material balance approach is valid only if the pesticides are stable during volatilization, trapping and analysis. Finding a suitable method for introducing thermally unstable pesticides with very low vapor pressures into air in such a system is a major experimental obstacle. Because of the latter restriction, we conducted experiments on PUF trapping efficiency not only with pesticides as molecular vapors, but also as components of aerosols.

First Vapor Trapping Experiment

One microgram of each of 16 pesticides was applied to a glass-fiber filter mounted in an all-glass apparatus, and two ester-form PUF plugs, 5 cm deep and 45 mm in diameter, were placed in series in the apparatus as traps. Air was drawn through the source and plugs for 22 hours at an average flow rate of $2.52 \text{ m}^3/\text{hr}$, a total volume of 55.4 m^3 . At the end of that time, the plugs were extracted individually by Soxhlet extraction with 1:1 hexane-acetone, and the source was extracted by washing with acetone. The extracts were concentrated, separated into pesticide groups by silica-gel column chromatography according to Sherma and Shafik (4), and quantitated by GLC. The analytical results are listed in Table 2.

The results showed that the N-methylcarbamates (carbofuran, carbaryl, methiocarb) did not volatilize from the source, that a 5-cm depth of PUF was insufficient to trap the more volatile compounds quantitatively, and that some degradative loss of parathion and methyl parathion apparently occurred. The remainder of the compounds were quantitatively volatilized and trapped.

Second Vapor Trapping Experiment

To aid pesticide volatilization and concurrently reduce chemical degradation, a trapping experiment was conducted at an elevated temperature and with decreased volume of air flow. Glass wool (1.65 g) was placed in a 44-mm-I.D.

TABLE 2. PUF^a TRAPPING EFFICIENCY FOR 1- μ g
DOSES OF PESTICIDES IN 55 M³ OF AIR

Compound	Residues, % of applied pesticides			
	Remaining on source	On first PUF plug	On second PUF plug	Total recovered
Aldrin	0	98	23	121
p,p'-DDE	0	100	0	100
p,p'-DDD	0	84	0	84
p,p'-DDT	3	98	17	118
Lindane	0	69	3	72
Heptachlor	0	71	33	104
Heptachlor epoxide	0	74	0	74
Dieldrin	0	100	0	100
Methoxychlor	42	45	0	87
Methyl parathion	0	70	0	70
Parathion	0	75	0	75
Diazinon	4	64	24	92
Malathion	29	64	0	93
Carbofuran	100	0	0	100
Carbaryl	100	0	0	100
Methiocarb	91	0	0	91

^a Ester-form polyurethane

glass tube and held in place with a brass screen. To this, 1 ml of hexane solution containing 1 µg of each of 24 pesticides was applied slowly. After evaporation of the hexane, two 5-cm, ester-form PUF plugs were placed in the tube, and the tube was wrapped with heating tape. Air was drawn through the apparatus for 2 hours at 4.3 m³/hr. The temperature in the chamber was 45°C during the experiment. The plugs (analyzed together) and the wool were then subjected to 5-cycle Soxhlet extraction with 1:1 hexane-acetone. The extracts were concentrated, chromatographed on silica gel, and quantitated by GLC. The analytical results are listed in Table 3.

Except for α-BHC, the organochlorine insecticides were quantitatively trapped on the plugs. Certain of the organophosphorus compounds did not volatilize completely, but the portions that did volatilize were quantitatively trapped. The carbamates again did not volatilize from the source to any appreciable extent. Attempts to detect the carbamates on the plugs were confounded by GLC interference in the form of a large injection peak. The low recovery of mexacarbate, a carbamate, may have been caused by oxidation or thermal breakdown on the source.

TABLE 3. ESTER-FORM PUF TRAPPING EFFICIENCY AT 45°C^a

Compound	Residues, % of applied pesticides		
	On source	On plugs	Total
α-BHC	0	76	76
Aldrin	0	98	98
p,p'-DDE	0	100	100
o,p'-DDT	0	110	110
p,p'-DDD	0	92	92
p,p'-DDT	0	86	86
Lindane	0	93	93
β-BHC	0	102	102
Heptachlor epoxide	0	88	88
Dieldrin	0	101	101
Endrin	0	95	95
Methyl parathion	0	113	113

TABLE 3 (continued)

Compound	Residues, % of applied pesticides		Total
	On source	On plugs	
Ronnel	0	119	119
Parathion	0	106	106
Ethion	0	118	118
Carbophenothion	36	45	81
Diazinon	112	0	112
Malathion	10	91	101
Propoxur	94	-	94
Carbaryl	93	-	93
Carbofuran	89	-	89
Aminocarb	87	-	87
Methiocarb	100	-	100
Mexacarbate	57	-	57

^a 8.6 m³ of air passed through system

Third Vapor Trapping Experiment

A further experiment on vapor trapping was conducted under intensified conditions. Chamber temperature was increased again, to 52°C, and air was passed through the apparatus for 8 hours at 3.88 m³/hr, a total volume of 31 m³. The air was prefiltered through two ester-form PUF plugs before entry into the sampling chamber. Two similar plugs were again used as traps. The source and plugs were extracted, chromatographed and quantitated as before, and the results are listed in Table 4.

Total recoveries of all organochlorine and organophosphorus pesticides were quantitative or nearly so, showing that a 10-cm depth of PUF is an efficient trap for these compounds. For the most part, the carbamates again remained on the source. However, the small amounts of carbofuran and methiocarb

TABLE 4. ESTER-FORM PUF TRAPPING EFFICIENCY AT 52°C^a

Compound	Residues, % of applied pesticides		Total
	On source	On plugs	
α -BHC	0	92	92
Aldrin	0	106	106
p,p'-DDE	0	99	99
o,p'-DDT	0	101	101
p,p'-DDD	0	88	88
p,p'-DDT	2	104	106
Lindane	0	95	95
β -BHC	5	98	103
Heptachlor epoxide	0	88	88
Dieldrin	0	83	83
Endrin	3	98	101
Methyl parathion	0	95	95
Ronnel	5	102	107
Parathion	0	88	88
Ethion	0	96	96
Carbophenothion	0	82	82
Diazinon	5	90	95
Malathion	3	90	93
Propoxur	82	10	92
Carbaryl	78	0	78

TABLE 4 (continued)

TABLE 4 (continued)

Compound	Residues, % of applied pesticides		Total
	On source	On plugs	
Carbofuran	88	8	96
Aminocarb	68	5	73
Methiocarb	91	3	94
Mexacarbate	62	2	64

^a 31.0 m³ of air passed through system

that did evaporate were apparently trapped essentially quantitatively, suggesting that PUF is also a suitable trapping agent for vapors of these carbamates.

Aerosol Generation

Since we had not been able to volatilize the carbamate insecticides in amounts sufficient to allow PUF evaluation, several experiments were performed with pesticide solutions injected into air as aerosols. To do this, a test chamber was fabricated from aluminum sheet. The chamber and associated equipment are illustrated in Figure 1^a and a closeup of the aerosol generating assembly is shown in Figure 2. The pesticide solutions were contained in the graduated glass chamber and the aerosols were generated by aspiration with a stream of nitrogen through the vertical nozzle. The aerosol spray at the bottom aperture of the test chamber moved upward, along with air flowing up through the chamber and with PUF plugs mounted in a glass holder at the top of the chamber to trap the flowing aerosols. A major shortcoming of this apparatus was that the sample air could not be prefiltered to remove contaminants.

First Aerosol Trapping Experiment

The first two tests of aerosol trapping were conducted with an experimental aerosol bomb in lieu of the aerosol generator of Figure 2. In the first test, the bomb was loaded with a hexane solution containing 5 µg of each of 24 pesticides, plus about 100 ml of Freon 12, and was then screw-jack mounted on its side for spraying upward into the test chamber. The assembly was placed outdoors, at 24°C air temperature and 80% relative humidity. One 5-cm-thick ester-form PUF plug was installed as the trap. Five-second bursts of aerosol were sprayed into the chamber every 15 seconds, for about 15 minutes. The Freon gas was vented for an additional 15 minutes without

aerosol formation, then air was passed continuously through the system for one hour. Total air flow (1.5 hours) was 8.5 m³. The chamber was washed down with 300 ml acetone, the bomb residues were recovered by washing with acetone, and the plug was Soxhlet-extracted as usual. Each of the three extract solutions was concentrated, separated into three fractions on a silica gel column, and quantitated by GLC. The results are listed in Table 5.

With the exception of certain of the carbamates, recoveries of pesticides from the system were low, so that the effectiveness of the PUF trap could not be adequately judged. Substantial amounts of material remained in the bomb, and there were residues on the chamber walls for all but the most volatile compounds. In general, recoveries were poorest for the organophosphorus compounds, best for the carbamates. Results for the carbamates suggested that ester-form PUF may be an effective trap for these pesticides when in airborne aerosols. Volatilization and inefficient trapping of vapors of the most volatile compounds may have contributed to the poor material balance in this experiment, as suggested by the particularly low recovery for α -BHC. Loss of a liquid chromatographic fraction (Fraction I) during analysis may also have

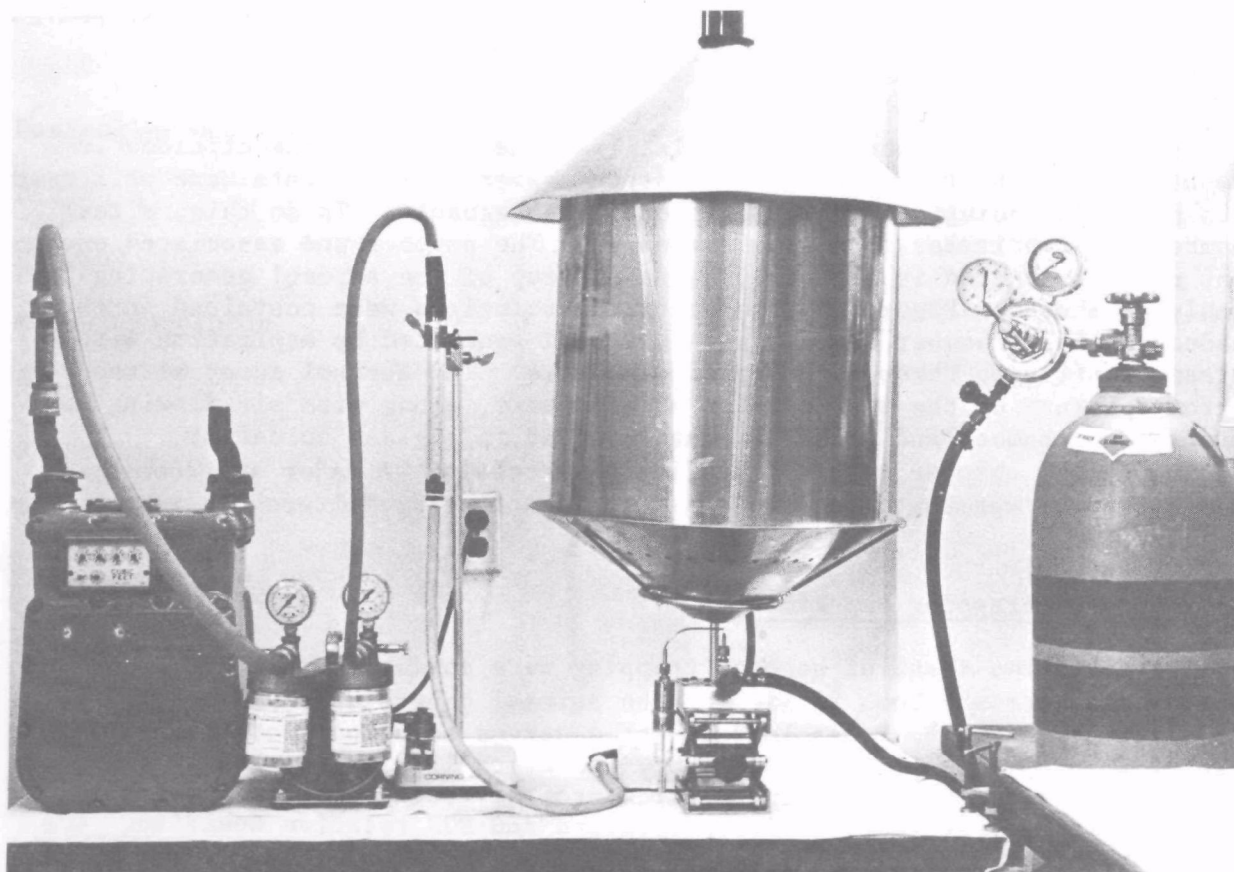


Figure 1. Apparatus for aerosol trapping experiments

contributed to this. Other factors that may have decreased pesticide recovery include oxidation, hydrolysis, and degradative reactions catalyzed by the aluminum surface of the test chamber. If there had been no volatilization nor degradation during the experiment, all the pesticides should have had a constant ratio of bomb:plug:chamber-wash residues. It is obvious that they did not.

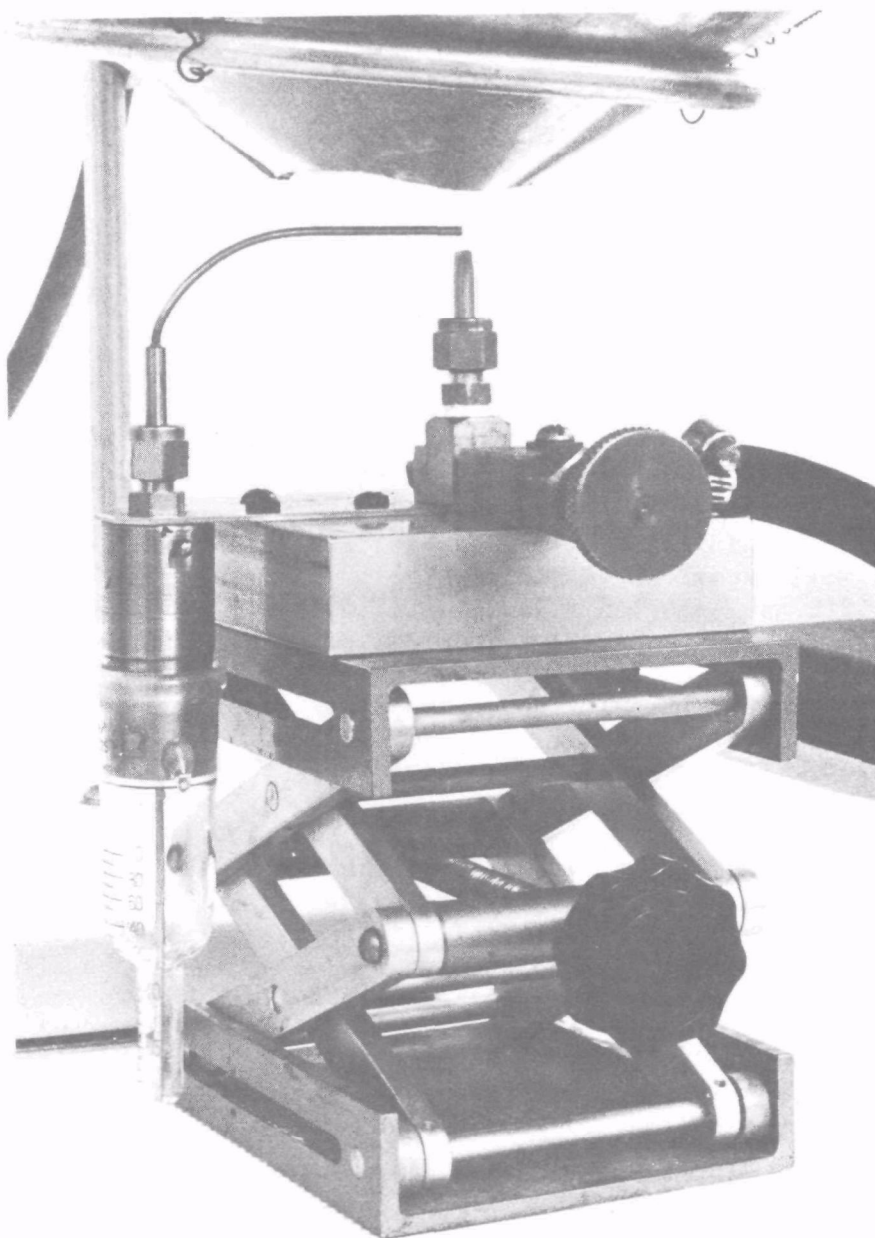


Figure 2. Closeup of aerosol generator

TABLE 5. THE TRAPPING OF PESTICIDE AEROSOLS BY A
5-CM ESTER-FORM PUF PLUG^a

Compound	Residues, % of applied pesticides			
	In bomb	In chamber washings	In PUF trap	Total
α -BHC	9.0	-	24.8	≥ 33.8
Aldrin	17.8	-	39.7	≥ 57.5
p,p'-DDE	19.8	-	29.4	≥ 49.2
o,p'-DDT	24.6	-	32.0	≥ 56.6
p,p'-DDD	18.6	-	25.7	≥ 44.3
p,p'-DDT	45.7	-	43.9	≥ 89.6
Lindane	12.0	5.4	46.2	63.6
β -BHC	18.5	3.7	40.0	62.2
Heptachlor epoxide	13.6	10.6	33.8	58.0
Dieldrin	14.3	7.4	28.3	50.0
Endrin	20.7	23.3	43.5	87.5
Methyl parathion	15.2	4.9	27.4	47.5
Ronnel	13.0	4.3	32.9	50.2
Parathion	16.3	4.2	27.3	47.8
Ethion	15.1	1.9	24.8	41.8
Carbophenothion	6.3	1.2	17.2	24.7
Diazinon	8.9	2.8	13.2	24.9
Malathion	1.9	0.6	2.5	5.0
Propoxur	18.0	20.0	25.0	63.0

TABLE 5 (continued)

TABLE 5 (continued)

Compound	Residues, % of applied pesticides			
	In bomb	In chamber washings	In PUF trap	Total
Carbaryl	17.0	2.4	25.0	44.4
Carbofuran	27.0	19.6	57.0	103.6
Aminocarb	-	21.2	87.0	108.2
Methiocarb	14.5	4.4	22.0	40.9
Mexacarbate	34.5	8.0	76.0	118.5

^a 8.5 m³ of air passed through system

Second Aerosol Trapping Experiment

The preceding experiment was repeated, except that two ether-form (rather than ester form) PUF plugs were placed in series as traps, flow rate was 4.82 m³/hr, temperature was 25°C, and relative humidity was 35%. The analytical results are listed in Table 6.

Carbofuran and aminocarb could not be quantitated because of a large interfering peak in the chromatograms, possibly a result of a contaminant introduced during filling of the aerosol bomb. In general, total recoveries of the remaining pesticides were low. Substantial amounts of all pesticides were trapped on the second plug, strongly suggesting that at least part of the poor recoveries was caused by passage of a portion of the aerosols through both plugs. This is in contrast to the results with molecular vapors, which were adequately trapped on two plugs (Tables 2, 3 and 4). The ratio of residue levels on the second plug to those on the first was relatively constant (last column, Table 6), suggesting that pesticide degradation was not responsible for the low residue levels on the first plug. These levels were generally somewhat lower than those found on the single plug of the previous experiment (Table 5), which may be a result of the use of ether-form rather than ester-form PUF, or may have been caused by the lower relative humidity in the second experiment.

Third Aerosol Trapping Experiment

Following the experiment above, two additional tests were conducted on the N-methylcarbamate insecticides alone, one outdoors and one with the apparatus contained in a large environmental chamber. In these, the bomb used in the

TABLE 6. THE TRAPPING OF PESTICIDE AEROSOLS BY TWO
5-CM ETHER-FORM PUF PLUGS^a

Compound	Residues, % of applied pesticides					Residue ratio on plugs: 2/1
	In bomb	In chamber washings	On first plug	On second plug	Total	
α -BHC	10.5	1.0	17.1	6.4	35.0	0.37
Aldrin	17.0	2.2	26.8	11.7	57.7	0.44
p,p'-DDE	15.2	3.7	21.3	14.2	54.4	0.67
o,p'-DDT	19.3	5.3	24.1	16.5	65.2	0.68
p,p'-DDD	16.0	4.2	21.7	14.6	56.5	0.67
p,p'-DDT	23.6	6.7	27.8	18.9	77.0	0.68
Lindane	20.6	1.9	36.5	12.9	71.9	0.35
β -BHC	11.1	14.4	34.6	26.7	86.8	0.77
Heptachlor epoxide	13.0	18.4	34.5	25.7	91.6	0.74
Dieldrin	10.2	13.5	30.4	19.7	73.8	0.65
Endrin	14.8	24.2	47.5	29.8	116.3	0.63
Methyl parathion	15.2	5.0	27.5	16.8	64.5	0.61
Ronnel	13.0	4.3	33.0	19.4	69.7	0.59
Parathion	16.2	4.2	27.4	18.9	66.7	0.69
Ethion	15.1	1.8	24.8	15.7	57.4	0.63
Carbophenothion	6.3	1.2	17.2	11.7	36.4	0.68
Diazinon	7.0	2.4	9.8	5.6	24.8	0.57
Malathion	15.3	3.9	23.8	15.4	58.4	0.65

TABLE 6 (continued)

TABLE 6. (continued)

Compound	Residues, % of applied pesticides					Residue ratio on plugs: 2/1
	In bomb	In chamber washings	On first plug	On second plug	Total	
Propoxur	15.7	6.2	28.0	11.0	60.9	0.39
Carbaryl	12.8	2.4	24.0	15.2	54.4	0.63
Carbofuran	-	-	-	-	-	-
Aminocarb	-	-	-	-	-	-
Methiocarb	12.0	3.6	18.5	11.5	45.6	0.62
Mexacarbate	10.0	20.0	26.5	9.0	65.5	0.34

^a 7.2 m³ of air passed through system

first two aerosol experiments was replaced with the aerosol generator (Figure 2). Neither experiment yielded usable results, owing to contamination of chromatograms that prevented quantitation of the carbamates.

A successful experiment was then performed, with the apparatus moved to a second environmental chamber, using a mixture of organochlorine and organophosphorus pesticides. Three high-flow ester-form PUF plugs were used in series as traps. Ten ml of hexane containing 5 µg of each of the 18 compounds was aspirated into the chamber by a stream of nitrogen, and washed into the air stream in the chamber with 3 x 15 ml hexane. The conditions were: 29°C, 75% R.H., and 2.81 m³/hr flow rate. The pesticides were introduced into the chamber in about 15 minutes and the air sampling was continued for 30 minutes, so that total air volume sampled was 2.1 m³. Extracts of the various substrates were concentrated, separated by silica-gel liquid chromatography, and quantitated by GLC. Results are shown in Table 7.

Large losses of material occurred throughout this experiment. The first PUF plug generally had the highest residue levels, but there were measurable quantities of all the pesticides on the second and third plugs. The presence of residues on the third plug after passage of only 2.1 m³ of air contrasts sharply with the quantitative trapping of molecular vapors by two ester-form PUF plugs (10 cm) after passage of 55 m³ of air (Table 2). This again implies that PUF, at least under certain conditions, may not trap aerosols as readily as vapors.

TABLE 7. THE TRAPPING OF PESTICIDE AEROSOLS BY THREE
5-CM ESTER-FORM PUF PLUGS^a

Compound	Residues, % of applied pesticides				
	In chamber washings	On first plug	On second plug	On third plug	Total
α -BHC	0.8	19.3	0.5	0.6	21.2
Aldrin	1.4	24.6	1.0	0.7	27.7
p,p'-DDE	10.4	10.5	2.0	2.5	25.3
o,p'-DDT	13.7	8.2	2.7	2.9	27.6
p,p'-DDD	10.0	4.8	2.4	2.9	20.1
p,p'-DDT	13.7	4.8	3.3	3.4	25.2
Lindane	3.0	30.2	1.5	2.0	36.7
β -BHC	7.3	16.7	1.2	2.3	27.5
Heptachlor epoxide	10.0	15.4	2.5	3.4	31.3
Dieldrin	17.4	14.2	2.1	5.6	39.3
Endrin	14.3	13.3	1.7	2.7	32.0
Methyl parathion	7.1	13.1	22.1	2.4	44.7
Ronnel	5.5	17.0	12.2	18.5	53.2
Parathion	10.8	9.3	1.3	3.1	24.5
Ethion	9.6	3.8	2.3	3.9	19.6
Carbophenothion	30.2	4.4	2.2	4.4	41.2
Diazinon	15.4	18.5	20.8	2.2	56.9
Malathion	16.2	7.4	1.7	3.9	29.2

^a 2.1 m³ of air passed through system

Fourth Aerosol Trapping Experiment

To compare directly the performance of the two forms of PUF, a replicate of the previous experiment was run, with the exception that ether-form, rather than ester-form, plugs were used. The conditions were: 29°C, 75% R.H., and 2.88 m³/hr flow rate. The analytical results are listed in Table 8.

Poor recoveries again occurred. The degree of trapping of the organo-chlorine insecticides agreed well with that of the previous experiment, whereas trapping of some of the organophosphorus compounds was somewhat less efficient. In general, the two forms of PUF apparently do not differ greatly in their ability to trap pesticides in aerosols.

TABLE 8. THE TRAPPING OF PESTICIDE AEROSOLS BY THREE
5-CM ETHER-FORM PUF PLUGS^a

Compound	Residues, % of applied pesticides				
	In chamber washings	On first plug	On second plug	On third plug	Total
α-BHC	0.4	16.0	n.d.	0.2	16.6
Aldrin	1.5	28.5	0.4	0.3	30.7
p,p'-DDE	13.8	12.8	1.1	0.9	28.6
o,p'-DDT	16.7	9.3	1.7	1.4	29.1
p,p'-DDD	13.7	4.0	1.3	0.9	19.9
p,p'-DDT	13.9	5.3	2.2	1.9	23.3
Lindane	4.7	27.7	0.4	0.4	33.2
β-BHC	8.7	16.3	0.6	0.2	25.8
Heptachlor epoxide	18.2	14.1	0.8	0.6	33.7
Dieldrin	24.8	12.4	1.7	1.6	40.5
Endrin	23.4	12.4	3.4	1.4	40.6
Methyl parathion	11.4	9.8	0.8	0.7	22.7

Table 8 (continued)

TABLE 8 (continued)

Compound	Residues, % of applied pesticides				
	In chamber washings	On first plug	On second plug	On third plug	Total
Ronnel	10.5	16.2	0.6	0.7	28.0
Parathion	14.4	6.5	0.7	0.8	22.4
Ethion	13.5	3.3	1.3	1.3	19.4
Carbophenothion	16.6	3.6	1.6	1.4	23.2
Diazinon	37.1	12.8	0.6	0.5	51.0
Malathion	30.2	5.5	0.8	0.8	37.3

^a 2.2 m³ of air passed through system

Fifth Aerosol Trapping Experiment

Because pesticide recoveries were consistently poor in the aerosol tests conducted in the large aluminum test chamber, a smaller glass-chamber apparatus was fabricated in this Laboratory by Mr. H. P. Freeman. This was a modified Rappaport-Weinstock apparatus, consisting of a 44-mm ID glass tube with a glass cup on the bottom, a stainless-steel 1.6-mm OD tube connecting an exterior sample solution reservoir to a nitrogen-gas-driven aerosol generator located above the cup, and space at the top of the tubular chamber for five 5-cm-thick PUF plugs. Dry nitrogen gas was introduced under slight pressure through a tubulation in the center of the bottom cup and a vacuum pump was used to equalize pressure in the chamber. This apparatus allowed the generation and trapping of aerosols without exposure to air, so that oxidation, hydrolysis, or contamination from ambient vapors or aerosols could not occur.

In a three-hour experiment with this apparatus at a nitrogen flow rate of 3.43 m³/hr, the trapping of eight organochlorine and five organophosphorus insecticides by five ester-form plugs in series (25 cm of foam) was studied. The plugs were extracted and analyzed individually and the results for the organochlorines are listed in Table 9. Results for the organophosphorus compounds are not tabulated because extracts for all but the first plugs were lost.

TABLE 9. THE TRAPPING OF PESTICIDE AEROSOLS BY FIVE
5-CM ESTER-FORM PUF PLUGS^a

Compound	Residues, % of applied pesticides						
	In chamber washings	On plug No.					Total
		1	2	3	4	5	
Aldrin	nd	102.9	2.8	1.8	1.4	1.0	109.9
p,p'-DDE	3.6	81.6	2.7	1.9	1.0	2.2	93.0
o,p'-DDT	5.1	92.8	3.8	2.7	2.9	2.1	109.4
p,p'-DDD	7.1	65.7	nd	nd	nd	2.2	75.0
p,p'-DDT	9.7	70.6	5.6	4.2	3.6	3.9	97.6
Heptachlor epoxide	nd	95.7	1.7	1.3	1.0	1.4	101.1
Dieldrin	nd	87.3	4.9	3.6	2.0	4.2	102.0
Endrin	nd	83.6	4.8	3.0	1.5	2.6	95.5

^a 10.3 m³ of air passed through system

Trapping of all the organochlorine pesticides was almost quantitative on the first plug, but there were detectable residues on all the plugs. This indicates that under these conditions small amounts of the pesticide aerosols penetrated the first plug and were trapped on later plugs. In this experiment, 25 cm of ester-form PUF was sufficient to trap organochlorine aerosols essentially quantitatively. There were substantial but less than quantitative amounts (60 - 75%) of the organophosphorus pesticides trapped on the first plug; presumably, succeeding plugs would also have contained measurable residues of these compounds.

Summary and Analysis of Pesticide Trapping Experiments

A number of conclusions may be drawn from the PUF trapping experiments (Tables 2-9). It is apparent that a 10-cm depth of foam is an efficient trap for vapors of organochlorine and organophosphorus pesticides. Trapping of all the test pesticides from ca. 10 m³ of air, and of many of them from as much as 55 m³ of air, was essentially quantitative. The ester form of PUF was somewhat, but not significantly, superior to the ether form in its trapping efficiency. The N-methylcarbamate insecticides were extremely difficult to

vaporize, but the small amounts that did vaporize were apparently efficiently trapped on PUF.

When the pesticides were injected into the air as aerosols, there were indications that PUF trapping ability was substantially lower than with molecular vapors. Although most of the residues were found on the first plug, measurable amounts of all the test pesticides occurred on backup plugs, even when as many as 5 plugs (25-cm total depth of PUF) were placed in series to trap the aerosols. The pattern, high residue levels on first plug and much lower levels on succeeding plugs, is consistent with three possible interpretations, but the early termination of the experimental program did not allow disclosure of which was operative. The possibilities are: (a) most of the generated aerosols had vaporized by the time they reached the trapping plugs, so that vapors were trapped on the first plug and aerosols, less efficiently trapped, passed through; (b) hexane solvent carried into the aerosols desorbed small amounts of the pesticides as it passed through the plugs; or (c) plugs were contaminated before the experiments with low levels of the pesticides not removed in earlier experiments with the same plugs, or adsorbed from laboratory air.

One possible reason for poor trapping efficiency of aerosols by PUF is electrostatic repulsion. Polymers such as PUF tend to have high dielectric constants, thus can acquire significant electrostatic charges. Moreover, droplets disrupted from an organic liquid such as hexane by atomization acquire charges, and the charge to mass ratio increases as the solvent evaporates (7). If the charges on the droplet and PUF surfaces were the same, electrostatic repulsion would result and trapping efficiency would consequently diminish. Humidity in air tends to dissipate electrostatic charges, so that the charge effect would be accentuated under conditions of low humidity.

The low recoveries of pesticides in the large-chamber aerosol experiments and the differences in recoveries between compounds may have been caused by any of a number of physical and chemical processes. Among the latter are oxidation, hydrolysis, rearrangement, and catalytic degradation. These are especially important for the organophosphorus pesticides. Hydrolysis would cause a total loss from chromatograms obtained with the flame photometric detector (FPD), since the hydrolysis products are nonvolatile phosphate acids. Oxidation and rearrangement can give volatile products that would not have the same GLC retention times as the parent organophosphorus molecules. For example, it has been shown that the oxidation product and the rearrangement product of parathion (paraoxon and S-ethyl parathion, respectively) have shorter retention times than the parent molecule on 3% OV-1, and that the three compounds are separable (8). Examination of the FPD chromatograms in some of the experiments did in fact show a number of new, small, short-retention-time GLC peaks. That these chemical transformations were quite important to pesticide recovery was illustrated by the high recoveries in the one experiment conducted under conditions in which they could not occur (Table 9).

Among the physical processes that may have contributed to losses are imperfect injection of aerosol into the chamber, loss of droplets through chamber apertures, imperfect washing of residues off chamber walls, and aerosol passage through all the plugs because of poor adsorptivity, as discussed above. The contribution of each of these processes to losses or differences in recovery is unknown.

EVALUATION OF PESTICIDE EXTRACTION METHODS

Comparison of Three Extraction Techniques

Considerable exploratory work in analytical methodology was conducted throughout our laboratory program, looking to development of the optimum method for use of PUF as a trapping agent in a national airborne pesticide monitoring program. An early phase of this involved a search for the best technique for extracting a wide variety of pesticides from PUF plugs. Three replicate experiments were performed, in which extractions of the 24 test pesticides by Soxhlet treatment, mechanical squeezing, and simple elution were compared. In each experiment, six ester-form PUF plugs were spiked directly with all 24 compounds in hexane at 1 μ g of each compound per plug. The hexane was allowed to evaporate, then two of the plugs were Soxhlet-extracted with 250 ml of 1:1 hexane-acetone for five Soxhlet cycles; two were extracted by squeezing each plug five times with a metal plunger in 50 ml 1:1 hexane-acetone and repeating this four times with fresh solvent, for a total of 250 ml of extract solution; and the remaining two were extracted by passing 250 ml of 1:1 hexane-acetone through each plug at a rate of about 4 ml/min. All extract solutions were concentrated, separated into fractions by liquid chromatography according to Sherma and Shafik (4), and analyzed by GLC. Results of the experiments are summarized in Table 10.

Several samples were lost during the many analytical manipulations involved, but clear-cut findings were nevertheless obtained. For both the organochlorine and organophosphorus insecticides, recoveries were little different among the three techniques, but Soxhlet extraction gave the most consistent results for classes of compounds and, at least for the organochlorines, showed the least variation in replicate determinations of individual compounds. Results by the squeezing and the elution techniques were not appreciably different from each other with respect to both extent and precision of pesticide recovery. The very high and variable recovery of the early-eluting α -BHC by all methods reflects the difficulty in quantitating on a sharply sloped baseline. Results for the carbamates showed that recoveries by the Soxhlet technique were not only distinctly higher than by the other techniques, but were also the most consistent for the class. Variations in recoveries of individual compounds, although large, were no greater than those obtained by squeezing or elution.

Cumulative results for all 24 pesticides (last line, Table 10) indicated that 5-cycle Soxhlet extraction with 1:1 hexane-acetone gave the highest and most consistent recoveries, and it was consequently selected as the method of choice in the other phases of the experimental program. The limitations to 5

cycles and the selection of 1:1 hexane-acetone as the preferred solvent were based on additional exploratory work described in detail in the following sections.

TABLE 10. COMPARISON OF THREE TECHNIQUES FOR EXTRACTION OF PESTICIDES FROM PUF PLUGS^a

Compound	% Recovery by					
	Soxhlet extraction		Mechanical squeezing		Elution	
	Mean ^b	Standard deviation	Mean ^b	Standard deviation	Mean ^b	Standard deviation
α -BHC	123.0	35.1	128.3	23.3	128.9	27.6
Aldrin	96.3 ^c	8.1	108.5	10.1	105.4	18.6
p,p'-DDE	106.1 ^c	9.9	104.9	14.2	101.1	15.3
o,p'-DDT	95.6 ^c	10.6	100.2	12.9	96.3	9.7
p,p'-DDD	96.7 ^c	4.2	131.5	23.4	124.0	26.8
p,p'-DDT	93.9 ^c	8.5	107.9	17.8	105.9	16.1
Lindane	82.0	5.7	86.3	10.2	86.9	8.2
β -BHC	85.0	18.9	76.7 ^e	14.1	73.4 ^d	9.9
Hept. epox.	89.4	10.2	85.4 ^e	22.7	73.5 ^d	16.6
Dieldrin	99.2	7.1	94.0 ^e	11.7	95.2 ^d	12.6
Endrin	94.6	15.3	84.6 ^e	9.6	96.5 ^d	11.0

Organochlorines	96.5	11.0	101.4	17.2	98.8	17.6

Me parathion	85.3	24.2	84.6 ^c	9.6	79.1	13.0
Ronnel	90.3	6.2	73.2 ^c	2.8	68.8	8.8

Table 10 (continued)

TABLE 10 (continued)

Compound	% Recovery by					
	Soxhlet extraction		Mechanical squeezing		Elution	
	Mean ^b	Standard deviation	Mean ^b	Standard deviation	Mean ^b	Standard deviation
Parathion	76.6	18.9	89.2 ^c	5.0	91.4	7.8
Ethion	99.8	8.7	91.0 ^c	4.2	96.8	11.2
Carbophenothion	99.1	5.3	99.8 ^c	7.2	102.5	15.9
Diazinon	91.1 ^d	6.9	89.4 ^d	4.6	91.9 ^d	7.1
Malathion	95.5 ^d	5.0	79.6 ^d	2.6	87.6 ^d	10.3

Organophosphates	91.1	8.2	86.7	8.6	88.3	11.3

Propoxur	91.9 ^d	13.0	80.8 ^d	19.4	77.3 ^d	24.0
Carbaryl	97.8 ^d	20.5	56.6 ^d	11.8	66.7 ^d	26.0
Carbofuran	81.9 ^d	26.3	73.4 ^d	11.9	70.3 ^d	28.6
Aminocarb	85.3 ^d	10.5	53.9 ^d	19.4	89.0 ^d	22.9
Methiocarb	102.5 ^d	3.3	88.5 ^d	10.3	73.8 ^d	18.9
Mexacarbate	93.1 ^d	25.1	36.9 ^d	16.0	63.1 ^d	28.1

Carbamates	92.1	7.6	65.0	19.3	73.4	9.2

All pesticides	93.8	9.4	88.0	21.3	89.4	17.2

^a Ester-form polyurethane^b Six replicates, unless otherwise specified^c Five replicates^d Four replicates^e Three replicates

Development of the Soxhlet Procedure

Because certain of the organophosphorus pesticides may degrade under prolonged high-temperature conditions such as those encountered in Soxhlet extraction, systematic study was made to determine the optimum number of Soxhlet cycles for extraction of these compounds from PUF plugs. Twelve ester-form plugs were precleaned by Soxhlet extraction with acetone for 850 cycles, then each plug was spiked with a hexane solution containing 1 µg of each of the 7 test organophosphorus pesticides. The plugs were then dried and placed individually in Soxhlet extractors. All plugs were extracted with 280 ml of 1:1 hexane-acetone, but the extractions were stopped after different numbers of Soxhlet cycles ranging from 1 through 12. The extracts were evaporated in Kuderna-Danish flasks with five drops of paraffin oil keeper solution, dissolved in 1 ml acetone, and quantitated on a 3% OV-1 column with flame photometric detector. Recoveries are listed in Table 11.

Extraction of all the test compounds proceeded very rapidly, reaching quantitative level in only 2 cycles. At 3 cycles, recoveries were not only quantitative, but also consistent for the class of compounds. Recoveries only for the class remained essentially quantitative up to 9 cycles, but the variability increased with increased cycling, a reflection of decreasing recoveries of parathion and methyl parathion. The data were subjected to least-squares regression analysis, with the postulation that change in recovery is a first-order process with respect to time, and thus with respect to number of extraction cycles. The operative relation is:

$$\ln y = a + b x$$

where y is the percent recovery, x is the number of extraction cycles, b is the slope of the regression line, and a is the natural logarithm of the intercept of the line. The coefficients of this equation are shown in Table 12, along with correlation coefficients, r. The regression analysis statistically confirmed the observation that parathion and methyl parathion were being lost with prolonged Soxhlet extraction, as illustrated by the values of the slopes of the regression lines. The negative values for parathion and methyl parathion are significant at the 95% confidence level.

In view of these results, Soxhlet extraction for from 3 to 7 cycles appeared to be the optimum range of duration of treatment, and 5 cycles was consequently selected as the technique used in other phases of our investigations. Five cycles would not produce significant loss of the labile organophosphorus pesticides, while assuring quantitative recovery of other organophosphorus compounds, carbamates, and organochlorine pesticide residues on the PUF plugs.

Choice of Extraction Solvent

A large number of pure solvents and combinations of solvents can be used for the extraction of pesticide residues from PUF. However, to keep the work within practical bounds, it was necessary to choose a small number of likely candidates for testing. The solvents had to be commercially available in

TABLE 11. THE EFFECT OF NUMBER OF SOXHLET EXTRACTION
CYCLES ON RECOVERIES OF ORGANOPHOSPHORUS
PESTICIDES FROM POLYURETHANE FOAM PLUGS

Compound	% recovery at Soxhlet cycle No.										
	1	2	3	4	5	7	8	9	10	11	12
Diazinon	90	105	98	97	110	103	103	109	91	108	97
Me parathion	83	95	100	85	98	95	90	95	75	86	78
Ronnel	90	102	99	97	109	106	105	104	97	105	101
Malathion	89	105	99	101	100	107	107	105	99	104	101
Parathion	86	95	95	91	94	96	84	95	77	84	83
Ethion	90	108	100	97	100	91	99	97	101	100	97
Carbophenothion	88	103	100	100	102	99	98	102	100	99	103
Average	88	102	99	95	102	100	98	101	91	98	94
Std. deviation	2.6	5.0	1.8	5.6	5.8	6.0	8.5	5.4	11.0	9.4	9.8

TABLE 12. REGRESSION AND CORRELATION COEFFICIENTS
OF SOXHLET EXTRACTION DATA IN TABLE 11.

Compound	Coefficients		
	a	b	r
Diazinon	4.6377(103.3) ^a	-0.0019	-0.107
Methyl parathion	4.6240(101.9)	-0.0185	-0.661*
Ronnel	4.6220(101.7)	+0.0010	+0.095
Malathion	4.6269(102.3)	+0.0007	+0.084
Parathion	4.6022(99.7)	-0.0157	-0.701*
Ethion	4.6250(102.0)	-0.0040	-0.353
Carbophenothion	4.6151(101.0)	-0.0006	-0.120

^a Numbers in parentheses are antilogs of a, and are intercepts expressed as % pesticide recovery

adequate purity for pesticide residue analysis, not be unduly hazardous, be inert to the pesticides, be readily distilled and evaporated, and be reasonably priced. Alcohols, ethers and aromatic solvents were rejected because they could not meet one or more of these criteria. Hexane and acetone, by contrast, were selected for study because they not only met the criteria, but also had a history of use as pesticide extractants. Moreover, they differed greatly with respect to polarity, so that they provided needed contrast in dissolving power. Hexane, being relatively nonpolar, is a less powerful solvent than the more polar acetone. Tests were conducted with pesticide-grade hexane, pesticide-grade acetone, and a 1:1 mixture of the two. In the interests of time, experiments were limited to extractions of the seven test organophosphorus insecticides from ester-form PUF plugs, circumventing the need for the liquid chromatographic separation step of the Sherma-Shafik procedure.

In the first experiment, six ester-form PUF plugs were precleaned by individual Soxhlet extraction with hexane for 17 hours at about 5 cycles per hour, then were dried by drawing PUF-filtered air through for about an hour. Three of the plugs were each spiked with 1 ml of hexane containing 0.1 µg of each of the seven OP pesticides, and the other three were spiked with 1 ml of hexane containing 1.0 µg of each pesticide. The plugs were placed individually in size E Soxhlet extractors (Kontes Glass Co.) and left open for 15 min. to evaporate the hexane. The extractors were then fitted to 300-ml boiling flasks and 250 ml of hexane, acetone, or 1:1 hexane-acetone was poured through the plugs. Temperatures of the Soxhlet heaters were adjusted to give

solvent distillation rates of about 20 minutes per extraction cycle. After five cycles, each solvent was cooled to about 35°C and poured into a Kuderna-Danish (K-D) flask fitted with a 15-ml receiver tube. A boiling chip and 5 drops of a 1% paraffin oil-in-hexane keeper solution were added to each flask, Snyder columns were fitted to the flasks, and the flasks were heated gently in a steam bath until solvent loss through the Snyder columns stopped. The flasks were removed from the steam bath and, after cooling, about 5 ml of residual solution remained in each receiver. This was evaporated with gentle heating in a stream of nitrogen to 1 ml. The solutions were quantitated with the alkali-flame ionization detector, using a 3% OV-1, 180-cm column at 200°C. The elution times for the organophosphorus compounds, as determined with individual standards, were: diazinon, 2.4; methyl parathion, 3.1; ronnel, 3.5; malathion, 3.85; parathion, 4.15; ethion, 9.8; and carbophenothion, 11.1 minutes.

The final concentrates obtained from the acetone and 1:1 hexane-acetone extractions were yellow oils that yielded chromatograms so contaminated that quantitation of the early peaks of interest was not possible. By contrast, the hexane extracts were colorless and yielded acceptable chromatograms. Results with hexane are shown in Table 13. Recoveries of 1 µg of the test compounds were generally high and consistent, whereas those at the 0.1 µg level were considerably lower and more variable. Above-quantitative recoveries of 0.1 µg of malathion and ethion were produced by background interferences.

The contaminated extracts obtained with acetone and hexane-acetone in the above experiment were evidence that hexane-precleaning of the PUF plugs was not adequate except for further extraction with hexane. Consequently, the experiment was repeated with plugs that had been subjected to more intensive pretreatment. Six ester-form PUF plugs were individually Soxhlet-extracted with acetone for 170 hours at about 5 cycles per hour. During this treatment, the foam plugs swelled somewhat, showing that the more polar acetone penetrated the polyurethane matrix as well as passing through the open channels of the PUF. This swelling did not interfere with the subsequent analytical process. The cleaned plugs were dried by drawing PUF-prefiltered air through the plugs for 1 hour, during which time the plugs shrank to their original dimensions. The procedure of the previous experiment was repeated, and yielded colorless extracts and usable chromatograms. Thus, initial plug cleaning by Soxhlet extraction with acetone for 850 cycles was adequate, whereas Soxhlet extraction with hexane for 85 cycles was not. The results of the repeat experiment are tabulated in Table 14.

The superiority of 1:1 hexane-acetone as a pesticide extractant for PUF was apparent in this experiment. At the 1-µg spike level, recoveries of all the test compounds were essentially quantitative with the mixed solvent, whereas those with acetone were somewhat more variable and those with hexane were not only more variable, but also substantially less than quantitative. At the 0.1-µg level, recoveries with all the solvents were lower and quite variable, but the mixed solvent again was best. These results led us to use 1:1 hexane-acetone as the solvent of choice in the other phases of our experimental program.

TABLE 13. RECOVERY OF ORGANOPHOSPHORUS INSECTICIDES FROM
SPIKED PUF PLUGS BY SOXHLET EXTRACTION WITH HEXANE

Compound	Percent recovery at	
	1 µg per plug	0.1 µg per plug
Diazinon	115	86
Methyl parathion	85	60
Ronnel	102	66
Malathion	99	155
Parathion	88	57
Ethion	92	120
Carbophenothion	91	101
Average	96.0	92.1
Standard deviation	10.3	36.0

Performance of the Developed Method With PUF Extract Blanks

Having identified the most suitable extraction technique, duration of extraction, and solvent, we conducted a systematic study of the method of choice, 5-cycle Soxhlet extraction with 1:1 hexane-acetone, to determine whether the procedure would yield coextractives from PUF that would interfere with analysis of any of the 24 test pesticides. Each of the three fractions resulting from the silica-gel liquid-chromatographic cleanup step of the Sherma-Shafik analytical method (4) was examined. Of the 24 compounds, 6 organochlorines occur in Fraction I, 5 organochlorines and 5 organophosphates in Fraction II, and 2 organophosphates and the 6 carbamates in Fraction III. Specific compounds are indicated in the chromatograms that follow. The chromatograms of PUF blank extracts and of extracts spiked with appropriate pesticide standard solutions can be used not only to illustrate the presence or absence of coextracted interferences to pesticide detection and quantitation, but also to evaluate the minimum detectability of each pesticide.

Six ester-form PUF plugs were Soxhlet-extracted with acetone for 98 hours at about 5 cycles per hour (490 cycles). To remove acetone, the solvent was decanted while the plugs were squeezed with a metal plunger. Then, clean

TABLE 14. RECOVERY OF ORGANOPHOSPHORUS INSECTICIDES FROM SPIKED PUF PLUGS BY SOXHLET EXTRACTION WITH THREE SOLVENTS

Compound	Percent recovery at					
	1 μ g per plug			0.1 μ g per plug		
	Hexane	Hex-Acet	Acetone	Hexane	Hex-Acet	Acetone
Diazinon	98	103	110	105	91	128
Me parathion	76	95	93	51	82	37
Ronnel	82	98	102	72	65	85
Malathion	80	101	95	90	121	105
Parathion	79	96	94	38	73	65
Ethion	83	100	98	82	111	81
Carbophenothion	68	97	101	55	95	89
Average	80.9	98.6	99.0	70.4	91.1	84.3
Std deviation	9.1	2.9	5.9	23.7	20.0	28.8

300-ml receiver flasks containing 280 ml 1:1 hexane-acetone were fitted to the Soxhlets without removing the plugs, and extraction was conducted for 5 cycles. The extract solutions were evaporated to dryness with 5 drops of keeper solution, taken up in 0.5 ml hexane, and chromatographed on silica gel. The resulting fractions were analyzed by GLC, spiked with appropriate pesticide standard solutions, and analyzed again by GLC under the same conditions.

The chromatograms for Fraction I, both blank and with spike, are presented in Figure 3. Analysis was by ^{63}Ni electron-capture gas chromatography (ECGC) on a 1.5% OV-17/1.95% OV-210 column. The spike solution contained 0.1 μ g of each of the 6 organochlorine insecticides normally found in Fraction I, plus 0.1 μ g of lindane. The latter was included because it was occasionally found in Fraction I as well as in Fraction II, its normal location. Comparison of the two chromatograms in Figure 3 shows that Soxhlet extraction of these plugs with acetone for about 490 cycles constituted adequate treatment for precleaning the plugs. No significant interferences to the quantitation of the organochlorine compounds appear in Fraction I. Each of the peaks in Figure 3B represents 4×10^{-11} grams of the appropriate pesticide.

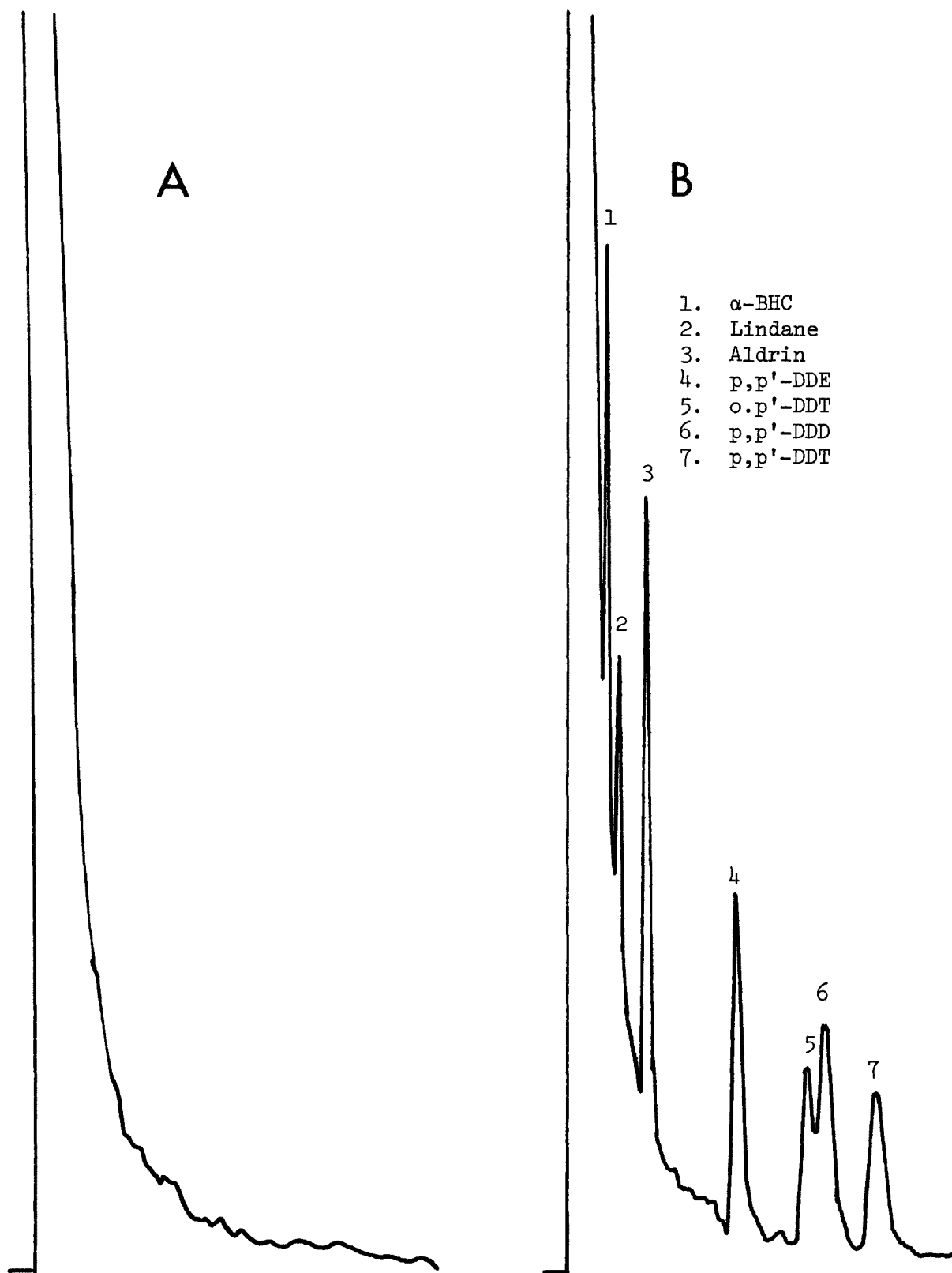


Figure 3. Fraction I chromatograms. A. PUF blank; B. Spiked blank

Because both organochlorine and organophosphorus pesticides occur in Fraction II, PUF blanks were chromatographed by both electron-capture and flame-photometric GLC. Chromatograms typical of the six samples of each that were run are presented in Figure 4. In Figure 4A, the column was 1.5% OV-17/1.95% OV-210, and temperatures of inlet, column, and ^{63}Ni -detector were 250°, 205°, and 325°C, respectively. Injection volume was 4 μl from 15 ml of final extract. The three small peaks that are shown at retention times of 1.3, 1.8, and 3.7 minutes appeared in the chromatograms of all six samples at about the same level. There was also a large peak, not illustrated, at about 23 minutes. This peak did not occur in solvent blanks, but did appear in all plug extracts, with some variation in peak height. In figure 4B, the column was 3% OV-1 and 5 μl of a 1-ml extract was injected. There were no detectable peaks after the injection peak.

Two representative blank extracts were spiked with standard solutions containing the five organochlorine and five organophosphorus pesticides that elute in liquid-chromatography Fraction II. Spiked-blank solution volumes were adjusted to the original volumes of the blank extracts, then one solution was analyzed by ECGC and the other by FPD-GC. The electron-capture chromatogram is reproduced in Figure 5 and the flame-photometric chromatogram in Figure 6.

In Figure 5, each peak represents 0.27 ng of a pesticide. The first of the small peaks in the blank (Figure 4A) appears as a small shoulder at the leading-edge base of the lindane peak, the second occurs between the peaks for β -BHC and ronnel, and the third is seen between the peaks for ronnel and methyl parathion. The large late peak, designated peak A, is illustrated in this chromatogram. Although none of the background peaks interfere with the peaks of interest, the large late peak does make it necessary to delay further injections on the column until the peak has cleared the detector. In Figure 6, each of the peaks represents about 5 ng of the designated organophosphorus pesticide. No interferences with quantitation are evident.

A fraction III PUF blank eluate off the silica-gel column was evaporated to 0.5 ml, and 10 μl of this solution was analyzed by flame-photometric GLC. In the chromatogram, reproduced in Figure 7A, there are two small, early peaks. A standard solution containing diazinon and malathion, which would normally appear in Fraction III, was added to the blank solution, the volume was adjusted, and 10 μl of this solution was injected into the GC, with the result depicted in Figure 7B. The first large peak represents 5 ng of diazinon and the second, 10 ng of malathion. Neither of the background peaks interfered with the pesticide peaks.

The remaining five Fraction III blanks were evaporated with keeper solution and derivatized with pentafluoropropionic anhydride (PFPA) according to the method developed for the carbamate insecticides, as described in a later section of this report. Electron-capture GC of the derivatized blanks generally showed a relatively broad injection peak and three small, early peaks. One of the chromatograms, representing injection of 0.6 μl out of 5 ml of solution onto a 3% DC-200 column, is shown in Figure 8. This sample, as may be seen, produced several somewhat larger peaks as well as a large, late peak,

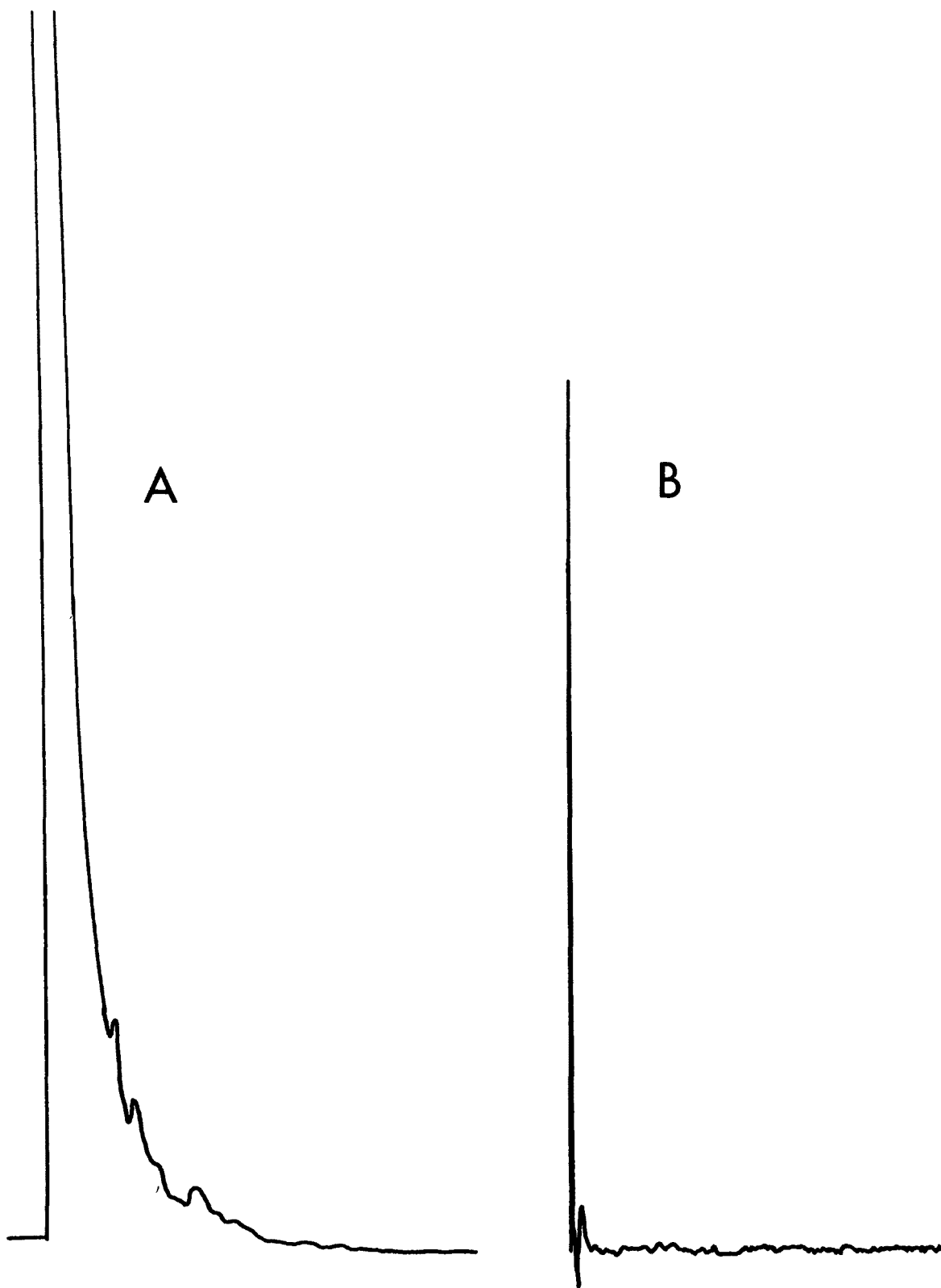


Figure 4. Fraction II PUF blanks. A. Electron-capture chromatogram.
B. Flame photometric chromatogram

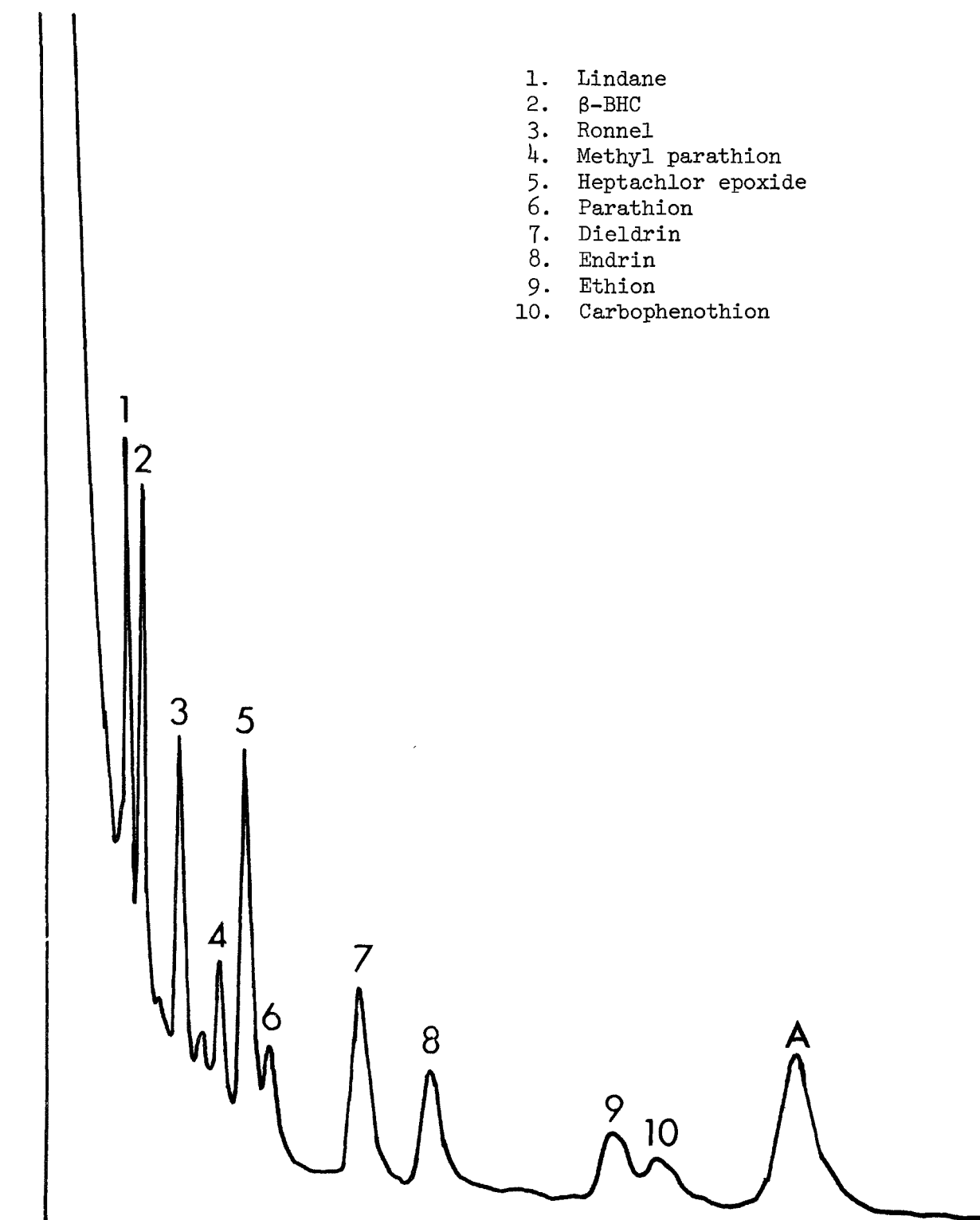


Figure 5. Fraction II spiked blank---electron-capture

1. Methyl parathion
2. Ronnel
3. Parathion
4. Ethion
5. Carbophenothion

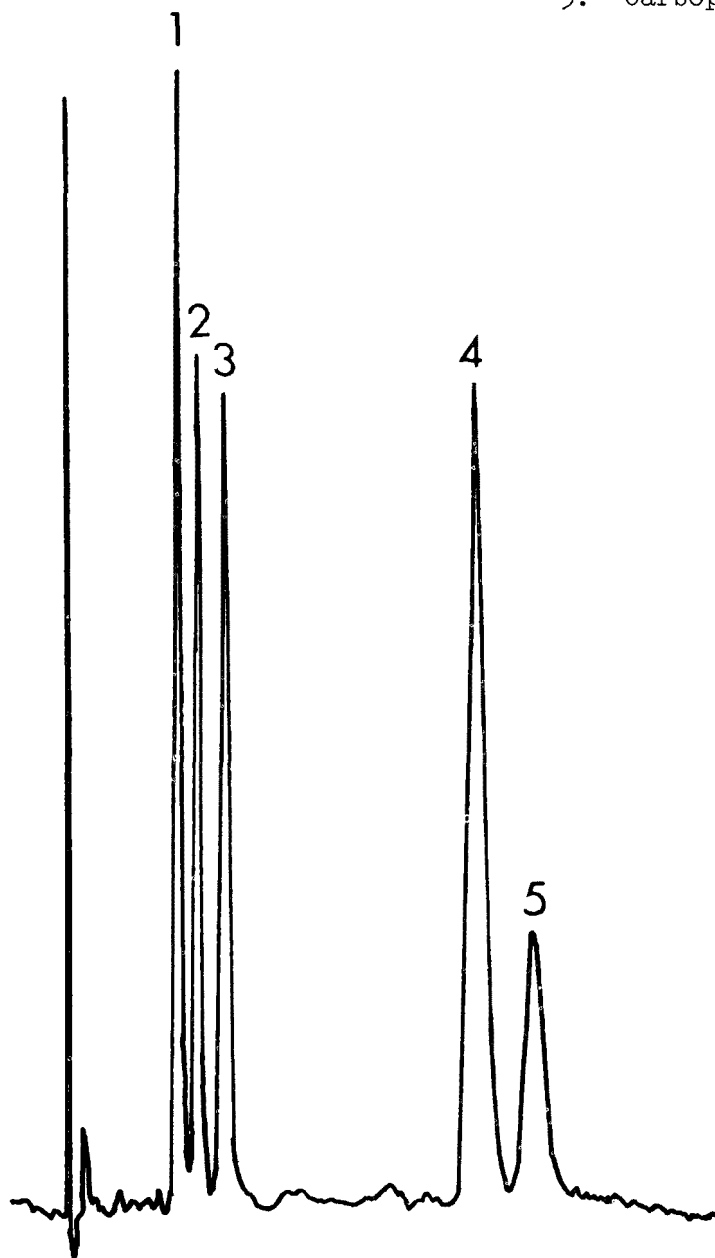


Figure 6. Fraction II spiked blank--flame photometer

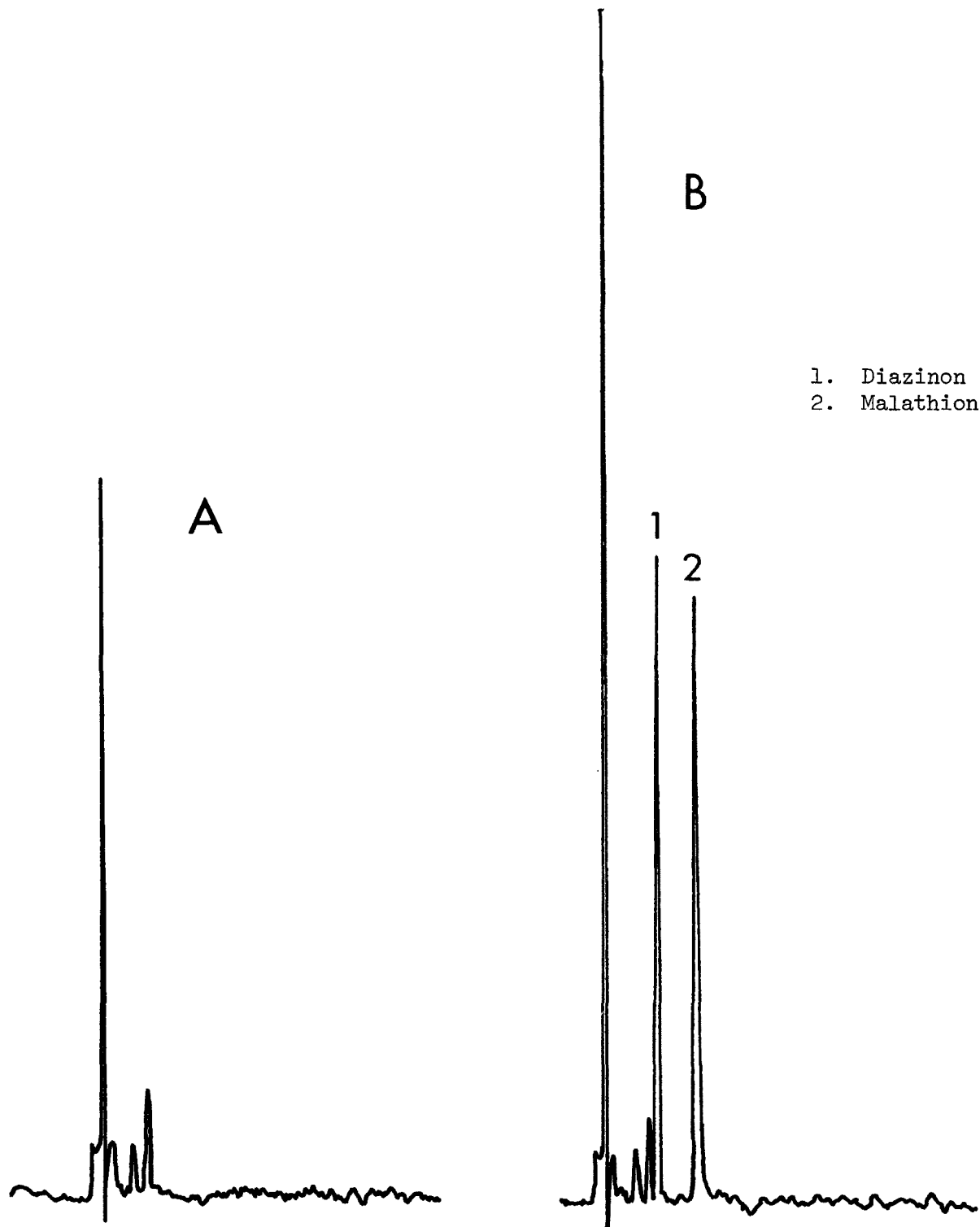


Figure 7. Fraction III chromatograms. A. PUF blank;
B. OP-spiked blank

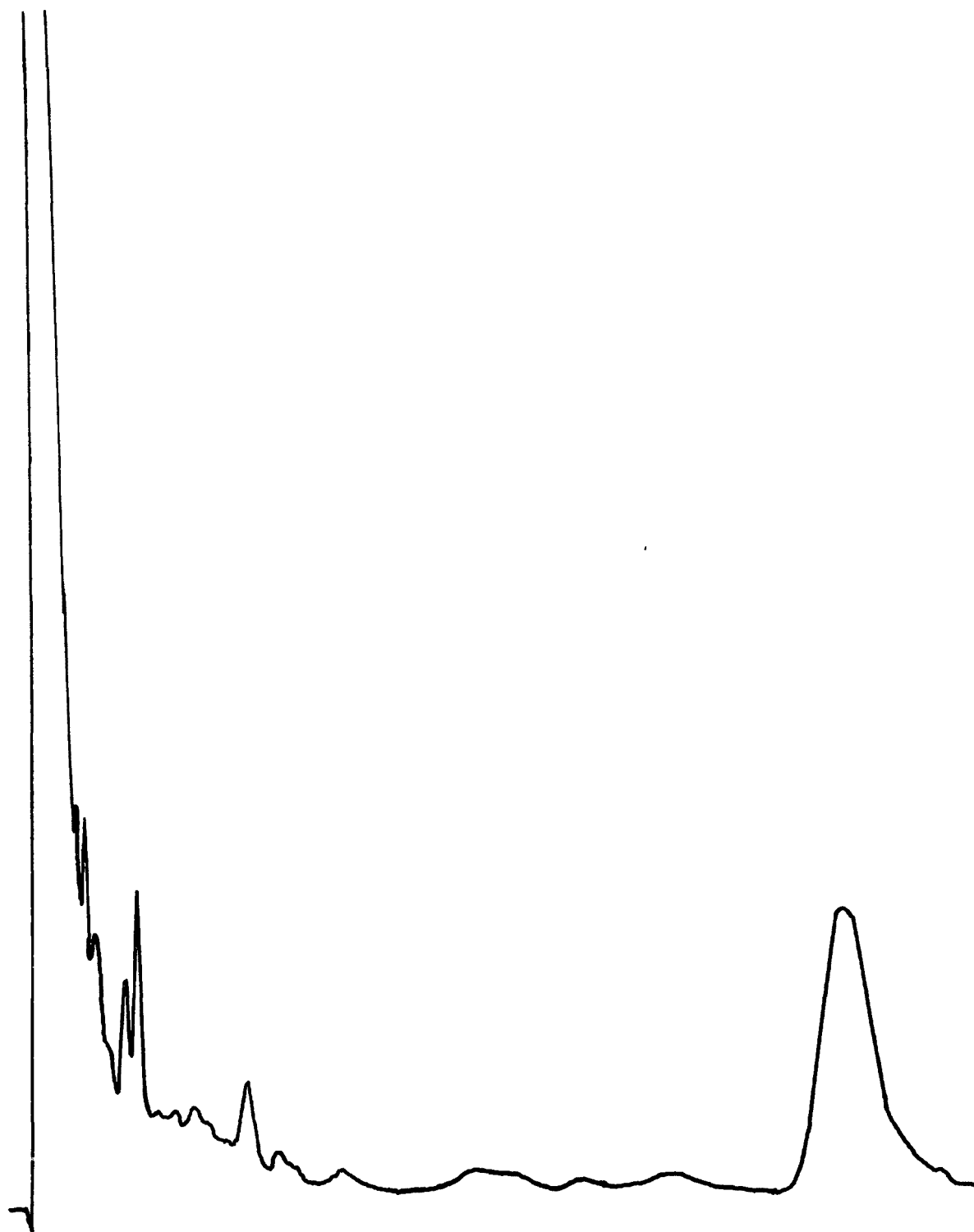


Figure 8. Electron-capture chromatogram of PUF blank extract derivatized with PFPA

and may be considered as a worst case. A standard solution containing the 8 compounds normally found in Fraction III - 6 carbamates and 2 organophosphates - was also derivatized with PFPA and subjected to ECGC on a 3% DC-200 column. The chromatogram, representing an injection of 120 pg of each carbamate, is shown in Figure 9. The two organophosphorus compounds produced only one peak, sufficiently removed that it did not interfere with the carbamate peaks. To estimate the possible extent of interference arising from the PUF background, the derivatized standard of Figure 9 and the derivatized blank of Figure 8 were simultaneously applied to the column at the same injection volumes as before. The chromatogram produced is shown in Figure 10. The large, late peak does not interfere with any of the carbamate peaks, but at least two of the small peaks do interfere. Comparison of peak heights for the standard and spiked blank shows that the peak sizes of aminocarb and mexacarbate were affected by the PUF blank. The aminocarb peak height was increased about 48%, and that of mexacarbate about 63%, relative to the peak heights in the standard. Such interferences, though random, do occur, and would have greatest effect at very low carbamate levels. Consequently, false positive results could be obtained unless identities of the peaks were confirmed by independent means.

In sum, our experiments show that, when the best analytical methodology is used, polyurethane foam does not interfere with the quantitation of even very low levels of airborne organochlorine and organophosphorus insecticides, but that some interference with certain of the N-methylcarbamates may possibly occur.

COMPARISON OF ESTER AND ETHER FORMS OF PUF

Experiments were conducted to ascertain whether the extractability of the test pesticides from the two types of PUF differed significantly. In tests of recoveries from pesticide aerosols, the ester form had yielded slightly, but not significantly, superior results (Tables 7 and 8), which may have reflected differences in extractability.

Four ether-form PUF plugs were spiked with all 24 pesticides, two at 1.0 μg of each compound per plug, and two at 0.1 μg per plug. In addition, two ester-form plugs were spiked at the 0.1- μg level. The six plugs were extracted with 1:1 hexane-acetone for five Soxhlet cycles and the extracts were evaporated with five drops of keeper solution, put through liquid chromatography on silica gel, and quantitated by GLC. The results for the 0.1- μg spikes are recorded in Table 15 and those for the 1.0- μg spikes in Table 16. In the latter table, the results obtained earlier with ester-form plugs are shown for comparison.

Although average recoveries of all pesticides showed no significant differences between the two forms of PUF at both spike levels, close examination of the data reveals clear trends that indicate that extractability of pesticides from ester-form PUF is superior to that from ether-form material. For example, in Table 15, recoveries of 10 of the 24 compounds from ester-form PUF were in the optimum range between 90 and 100%, whereas recoveries of only 3 compounds were in that range with ether-form PUF.

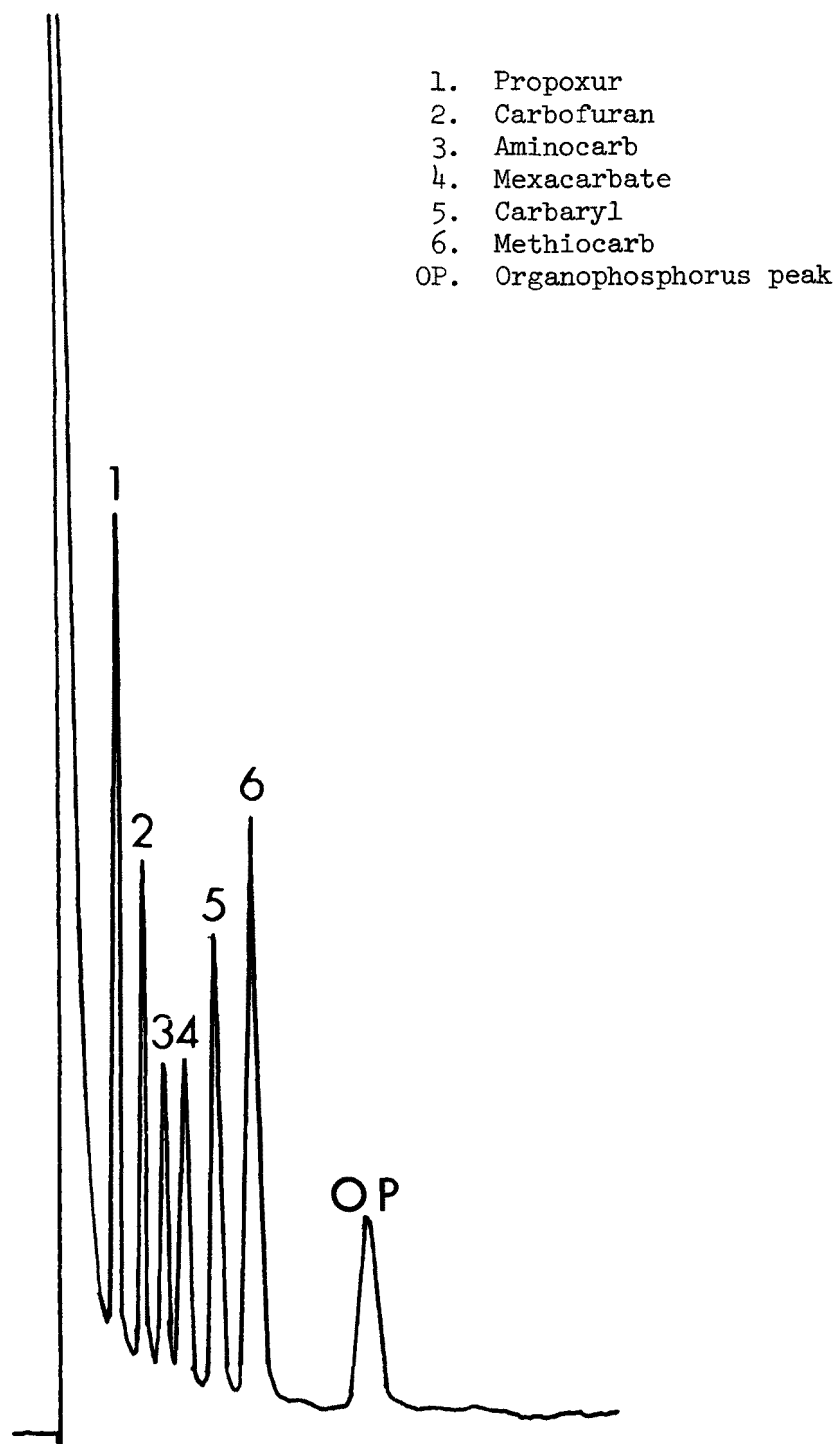


Figure 9. ECGC chromatogram of Fraction III standard solution derivatized with PFPA

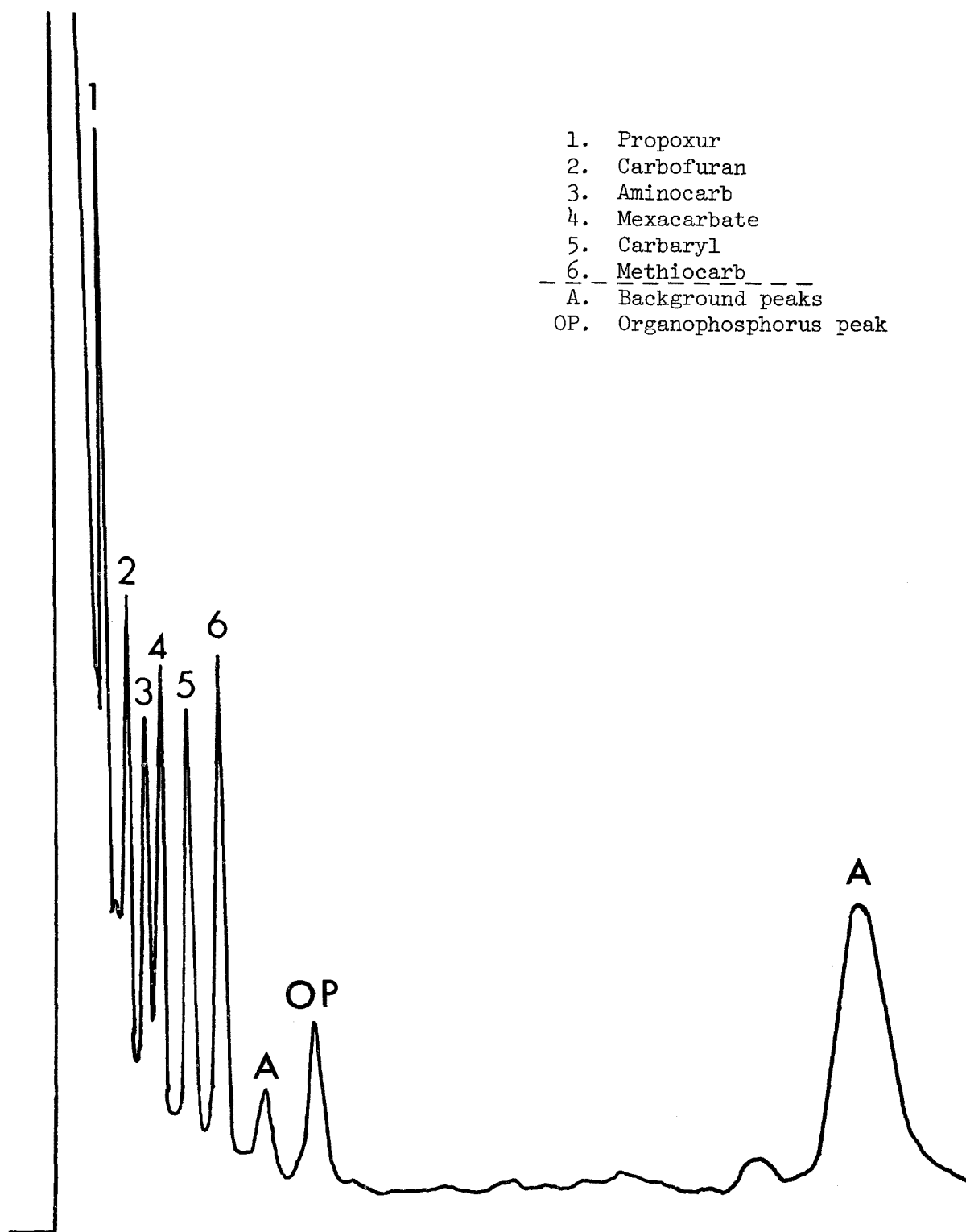


Figure 10. ECGC chromatogram of combined PUF blank and Fraction III standard, PFPA-derivatized

TABLE 15. RECOVERIES OF PESTICIDE SPIKES (0.1 μ G PER COMPOUND)
FROM ESTER- AND ETHER-FORM PUF PLUGS BY SOXHLET EXTRACTION^a

Compound	Pesticide recoveries, %					
	Ester-form PUF			Ether-form PUF		
	Repl. 1	Repl. 2	Avg.	Repl. 1	Repl. 2	Avg
α -BHC	84.0	104.4	94.2	145.1	76.5	110.8
Aldrin	86.9	99.1	93.0	163.4	86.6	125.0
p,p'-DDE	93.0	105.4	99.2	187.7	94.3	141.0
o,p'-DDT	100.0	116.3	108.2	190.0	102.3	146.2
p,p'-DDD	87.4	99.8	93.6	187.5	86.9	137.2
p,p'-DDT	109.7	130.5	120.1	201.0	118.4	159.7
Lindane	97.3	68.3	82.8	88.5	84.7	86.6
β -BHC	87.8	89.3	88.6	84.6	87.7	86.2
Hept. epox.	82.4	77.6	80.0	76.2	79.1	77.7
Dieldrin	86.0	86.6	86.3	83.5	83.3	83.4
Endrin	57.9	79.7	68.8	70.1	82.0	76.1
Me parathion	88.2	74.6	81.4	87.5	78.8	83.2
Ronnel	94.9	87.1	91.0	100.0	96.2	98.1
Parathion	97.2	83.3	90.3	86.6	74.7	80.7
Ethion	94.8	96.8	95.8	88.9	105.6	97.3
Carbophenothion	77.3	80.0	78.7	88.9	105.3	97.1
Diazinon	94.4	63.6	79.0	-	83.7	83.7
Malathion	104.8	91.9	98.4	-	85.5	85.5
Propoxur	80.0	110.0	95.0	187.5	165.0	176.3

TABLE 15 (continued)

TABLE 15 (continued)

Compound	Pesticide recoveries, %					
	Ester-form PUF			Ether-form PUF		
	Repl. 1	Repl. 2	Avg.	Repl. 1	Repl. 2	Avg
Carbaryl	175.0	177.0	176.0	32.5	125.0	78.8
Carbofuran	20.0	150.0	85.0	80.0	45.0	62.5
Aminocarb	432.0	680.0	556.0	350.0	412.0	381.0
Methiocarb	135.0	247.0	191.0	73.0	175.0	124.0
Mexacarbate	210.0	151.0	180.5	233.0	262.0	247.5
Average			121.4			121.9
Std. deviation			98.2			69.1

^a 5 cycles, with 1:1 hexane-acetone

TABLE 16. RECOVERIES OF PESTICIDE SPIKES (1.0 µG PER COMPOUND)
FROM ESTER- AND ETHER-FORM PUF PLUGS BY SOXHLET EXTRACTION^a

Compound	Pesticide recoveries, %			
	Ester-form PUF ^b	Ether-form PUF		
		Repl. 1	Repl. 2	Avg
α-BHC	123.0	176.6	160.6	168.6
Aldrin	96.3	91.5	77.8	84.7
p,p'-DDE	106.1	92.0	76.0	84.0
o,p'-DDT	95.6	93.3	78.6	86.0
p,p'-DDD	96.7	84.7	75.0	79.9

TABLE 16 (continued)

TABLE 16 (continued)

Compound	Pesticide recoveries, %			
	Ester-form PUF ^b	Ether-form PUF		
		Repl. 1	Repl. 2	Avg
p,p'-DDT	93.9	94.3	79.8	87.1
Lindane	82.0	67.8	69.8	68.8
β-BHC	85.0	99.8	93.9	96.9
Hept. epox.	89.4	76.4	71.6	74.0
Dieldrin	99.2	101.1	89.6	95.4
Endrin	94.6	83.5	86.4	85.0
Me parathion	85.3	77.8	72.9	75.4
Ronnel	90.3	78.0	71.8	74.9
Parathion	76.6	80.7	74.9	77.8
Ethion	99.8	97.1	88.9	93.0
Carbophenothion	99.1	86.2	80.1	83.2
Diazinon	91.1	80.3	80.4	80.4
Malathion	95.5	90.9	89.5	90.2
Propoxur	91.9	97.5	81.6	89.6
Carbaryl	97.8	101.0	88.3	94.7
Carbofuran	81.9	97.0	94.0	95.5
Aminocarb	85.3	88.0	136.0	112.0
Methiocarb	102.5	100.0	85.0	92.5
Mexacarbate	93.1	100.0	128.0	114.0
Average	93.8			91.0
Std. deviation	9.4			19.8

^a 5 cycles, with 1:1 hexane-acetone^b Averages, from Table 10

Similarly, of the 24 compounds in Table 16, 20 gave recoveries closer to 100% with ester- than with ether-form material, and 14 of the 24 were closer in Table 15. If the data for aminocarb and mexacarbate, which were shown in the previous section to be interfered with by underlying background peaks, are deleted, the average deviations from 100% recovery at the 1.0- μ g level are 8.6 ± 1.5 and $17.3 \pm 3.0\%$ for the ester and ether forms, respectively. We therefore judge ester-form PUF to be the superior material for an air monitoring program.

EVALUATION OF GLC COLUMNS AND PROCEDURES

One of the most important factors in the quantitation of pesticides by gas-liquid chromatography is the performance of the columns used. The coating of the liquid on the support material and the packing of the coated solid into the columns are critical factors and are subject to considerable variability. The quality of a column is manifest in the chromatograms obtained with it as to its ability to separate the compounds to be analyzed, the sharpness of the peaks, and the relation of peak height to quantity of compound. On a poorly prepared column, closely eluting peaks will be poorly separated and will exhibit tailing. On a properly prepared column, the calibration curve, the graph of peak height vs. quantity of injected material, will be a straight line that ends at the origin. When reactive compounds such as the organophosphorus and carbamate pesticides are chromatographed on a poorly prepared column, the calibration graphs curve upward and may not pass through the origin. The usual cause for this phenomenon is retention and degradation of the compounds on uncoated support material.

We examined the quality of the columns that had been purchased or prepared for use in this study, particularly seeking comparable or even improved performance in comparison to that reported by Sherma and Shafik in the original publication of the general analytical method (4). These authors used a 5% OV-210 column for the organochlorine insecticides in liquid-chromatography Fractions I and II (except that a 5% SE-30 column was used for dieldrin), a 5% OV-210 Carbowax-treated column for the organophosphates in Fractions II and III, and a 5% SE-30 column for the carbamates in Fraction III.

A 5% OV-210 column prepared in this laboratory was tested with the six organochlorine pesticides found in Fraction I plus lindane, which is also sometimes found in Fraction I. The conditions were 180°C column temperature and 60 ml/min carrier gas flow rate, as specified by Sherma and Shafik. In the chromatogram, the seven peaks were completely resolved except for slight overlap between p,p'-DDD and p,p'-DDT. The chromatogram was very similar to that of Figure 2 in the Sherma-Shafik paper, and will not be repeated here. For comparison, a mixed column, 1.5% OV-17/1.95% OV-210, was also tested with the same mixture of pesticides, but at 200°C column temperature and 36 ml/min carrier gas flow rate. The chromatogram is presented in Figure 11. The retention times of the compounds relative to aldrin are: α -BHC, 0.48; lindane, 0.63; aldrin, 1.00; p,p'-DDE, 2.29; o,p'-DDT, 3.24; p,p'-DDD, 3.52; and p,p'-DDT, 4.28. As may be seen, the o,p'-DDT and p,p'-DDD peaks do overlap somewhat, but the peaks are adequately separated for quantitation of all seven compounds, and the overlap is no greater than the p,p'-DDD and

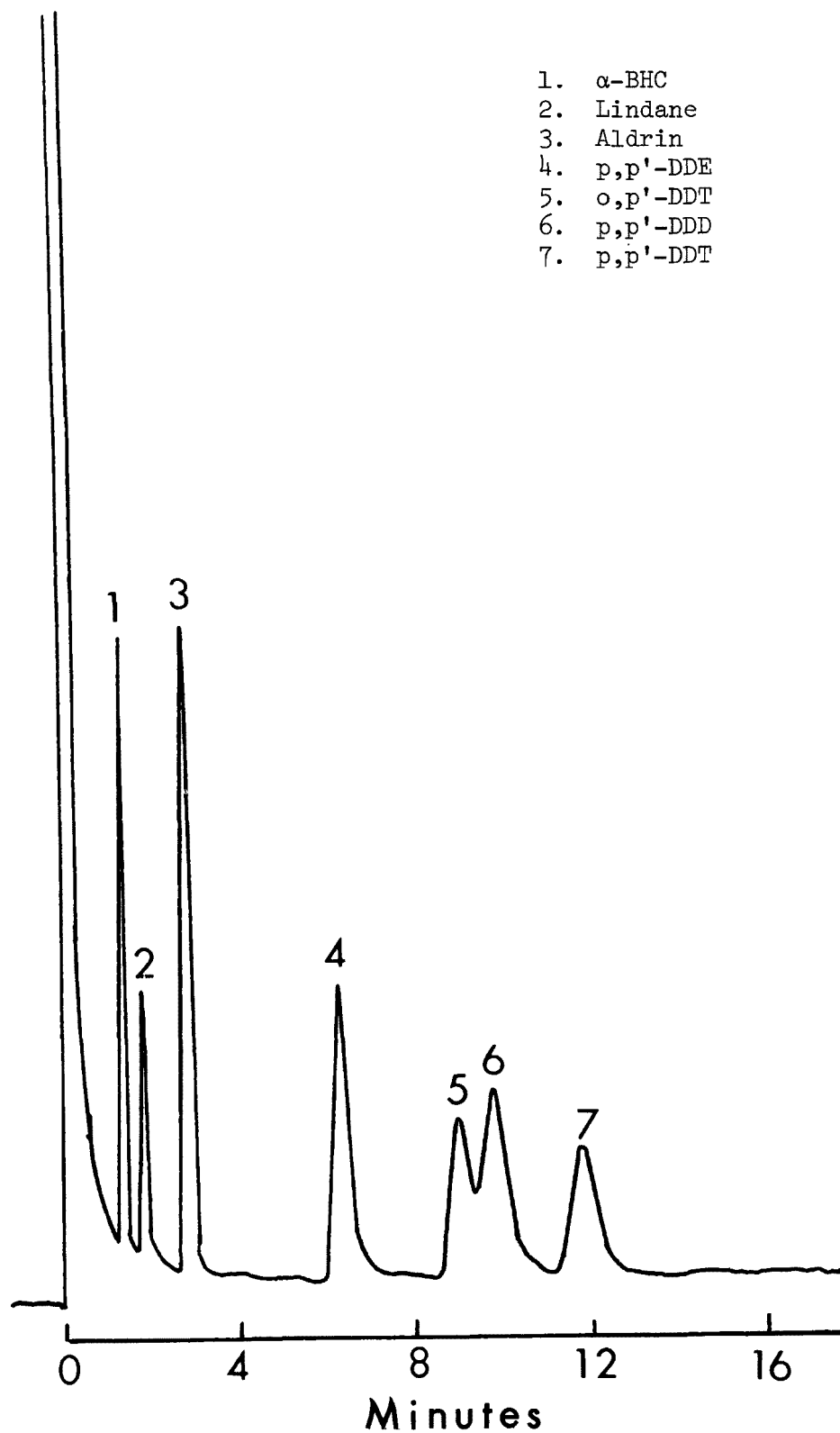


Figure 11. ECGC chromatogram of 0.2 ng each of Fraction I organochlorine insecticides, obtained with a 1.5% OV-17/1.95% OV-210 column.

p,p'-DDT overlap on the 5% OV-210 column reported by Sherma and Shafik. The most significant difference in the chromatograms for the two columns is the shift of the p,p'-DDD peak away from the p,p'-DDT peak and toward the o,p'-DDT peak. Figure 11 indicates that a mixed 1.5% OV-17/1.95% OV-210 column can be a suitable alternative to a 5% OV-210 column for the analysis of liquid-chromatography Fraction I.

A major advantage of the mixed OV-17/OV-210 column over a 5% OV-210 is that the former can separate all 10 compounds found in Fraction II, whereas the latter does not adequately separate dieldrin and methyl parathion, as illustrated in Table III of Sherma and Shafik. Figure 12 is an electron-capture chromatogram for all five organochlorine and five organophosphorus compounds that occur in Fraction II. The retention times of the compounds relative to that of aldrin are: lindane, 0.63; β -BHC, 0.72; ronnel, 0.99; methyl parathion, 1.29; heptachlor epoxide, 1.53; parathion, 1.71; dieldrin, 2.37; endrin, 2.91; ethion, 4.35; and carbophenothion, 4.68. This chromatogram suggests that, at relatively high concentrations, it may be possible to quantitate the organophosphorus compounds by electron-capture detection at the same time that the organochlorine compounds are analyzed.

The 5% OV-210 column treated with Carbowax 20M, recommended by Sherma and Shafik, was tested for ability to separate the five organophosphorus pesticides in Fraction II and the two in Fraction III. All pesticides within a fraction were adequately separated and the peak shapes were reasonably symmetrical. However, if all seven pesticides are applied to this column, malathion and methyl parathion overlap, as shown in Figure 13. To obtain this chromatogram, all seven pesticides at 5 ng per compound were injected simultaneously, column temperature was 180°C, and flame photometric detection was used. In a comparative test of a 3% OV-1 column with the seven organophosphorus pesticides at 5 ng per compound, it was found that the peaks were all separated. A typical chromatogram with this column, showing differences in order of elution as well as improved resolution, is illustrated in Figure 14. Calibration graphs were linear and the line passed through the origin. Figure 15 is a calibration graph for diazinon and is typical of the graphs for the organophosphorus compounds, although the others all had lower slopes. The 3% OV-1 column was used almost exclusively for the quantitation of organophosphorus compounds in the other phases of our experimental program because tests could be run with all seven compounds without the necessity for prior separation by liquid chromatography.

The SE-30 column prepared in this laboratory did not perform as well as that used by Sherma and Shafik for analysis of the N-methylcarbamates (4, Fig. 7). As an illustration of our results, Figure 16 is a chromatogram of the seven test carbamates, at 600 pg per compound, derivatized with PFPA and using the Sherma-Shafik GLC conditions, 195°C column temperature and 70 ml/min carrier gas flow rate. As may be seen, carbofuran and aminocarb were not well separated. Separation was improved slightly by decreasing the column temperature to 165°C, as illustrated in Figure 17. By temperature programming from 165°C to 195°C at 10°C/min. after a 5-minute hold at 165°C, the peak heights for carbaryl and methiocarb were improved, as illustrated in Figure 18. However, the separation of carbofuran and aminocarb was no better under these conditions.

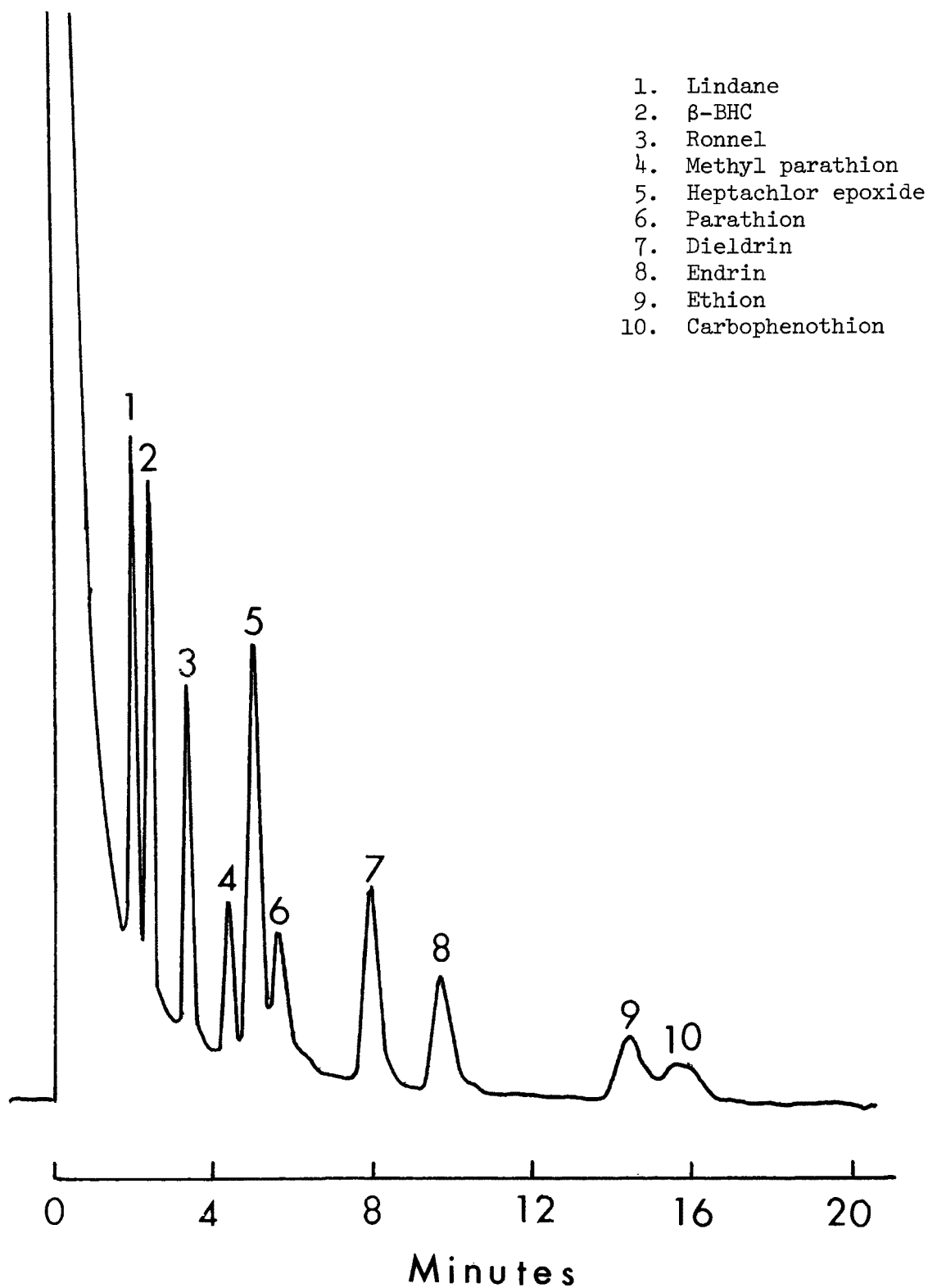


Figure 12. ECGC chromatogram of 0.4 ng each of Fraction II insecticides, obtained with a 1.5% OV-17/1.95% OV-210 column.

1. Diazinon
2. Ronnel
3. Malathion plus
Methyl parathion
4. Parathion
5. Carbophenothion
6. Ethion

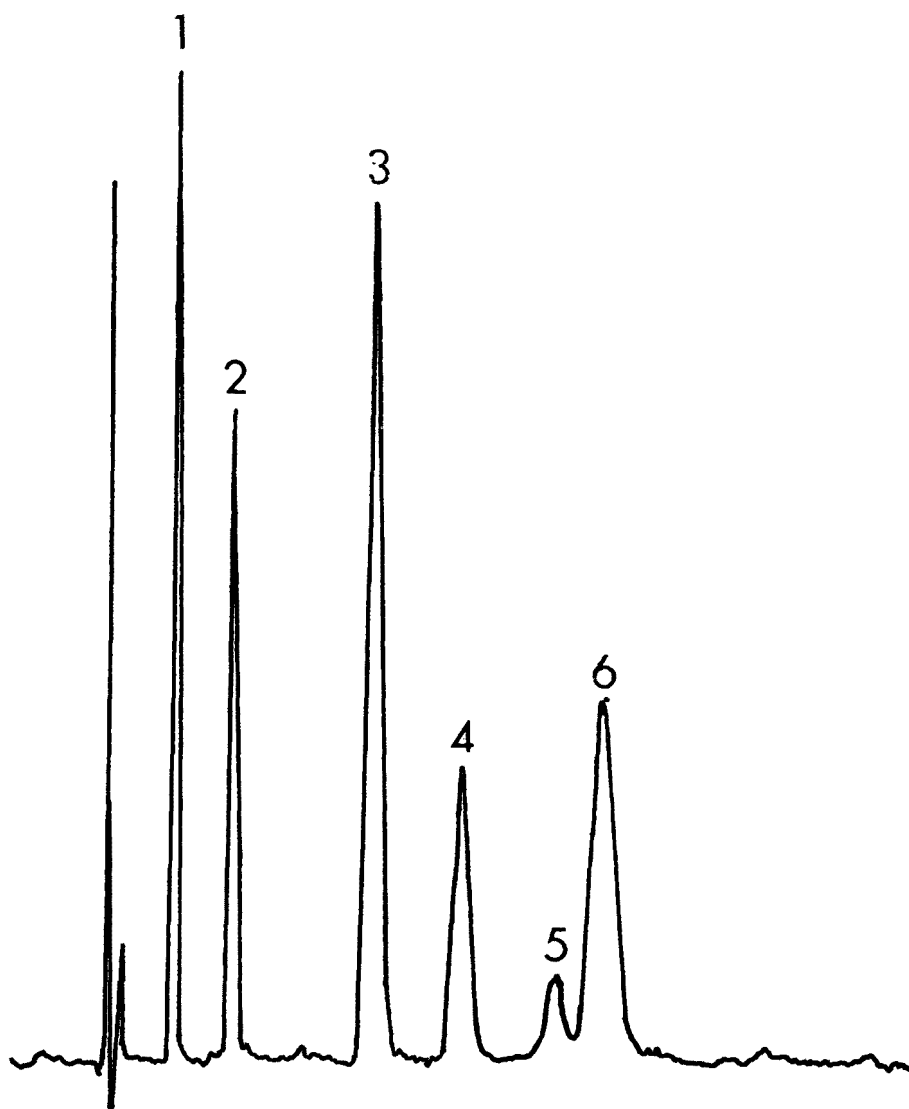


Figure 13. Flame-photometric chromatogram of 5 ng each of the test organophosphorus insecticides, obtained with a 5% OV-210/Carbowax column

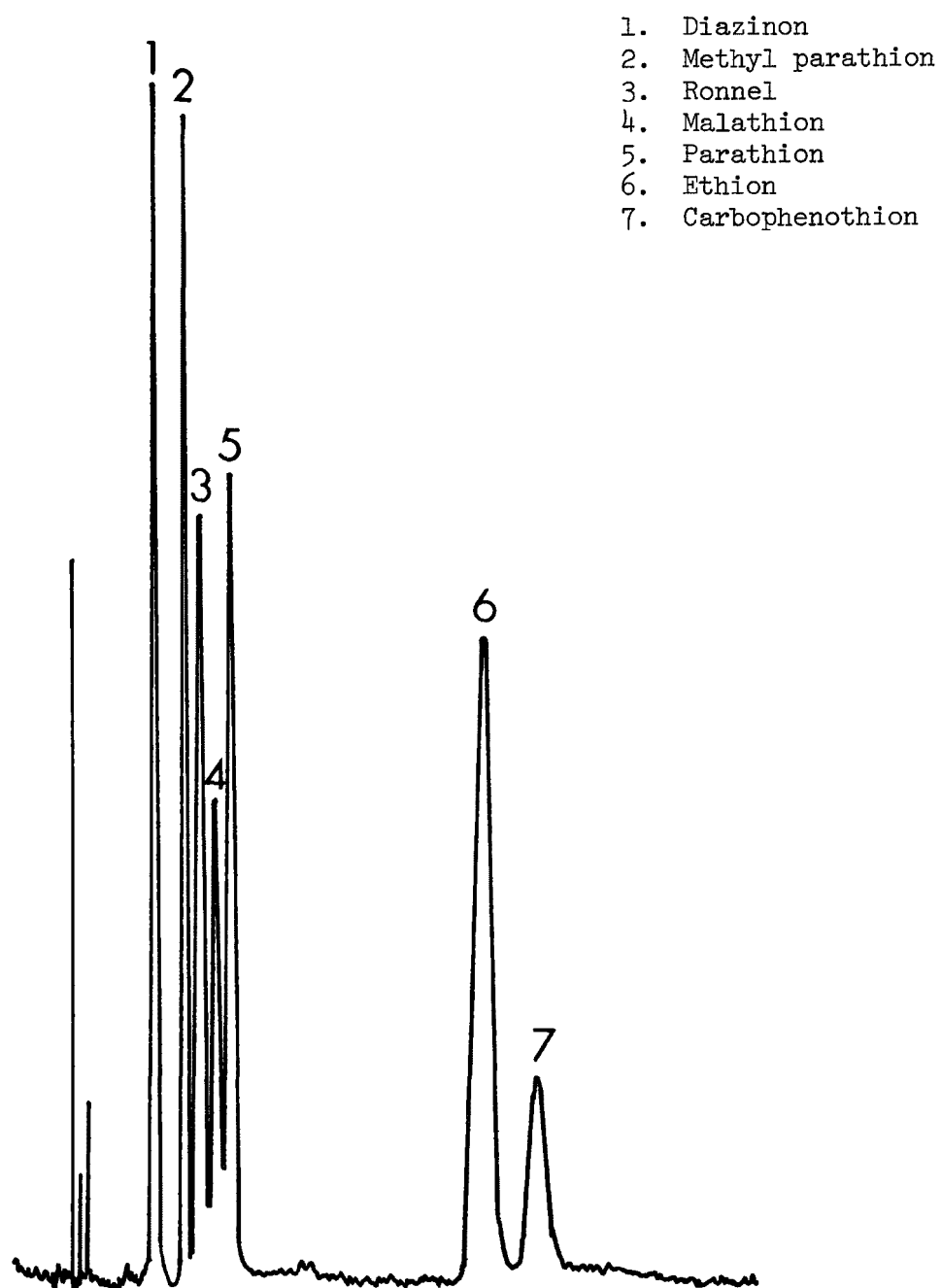


Figure 14. Flame-photometric chromatogram of 5 ng each of the test organophosphorus insecticides, obtained with a 3% OV-1 column

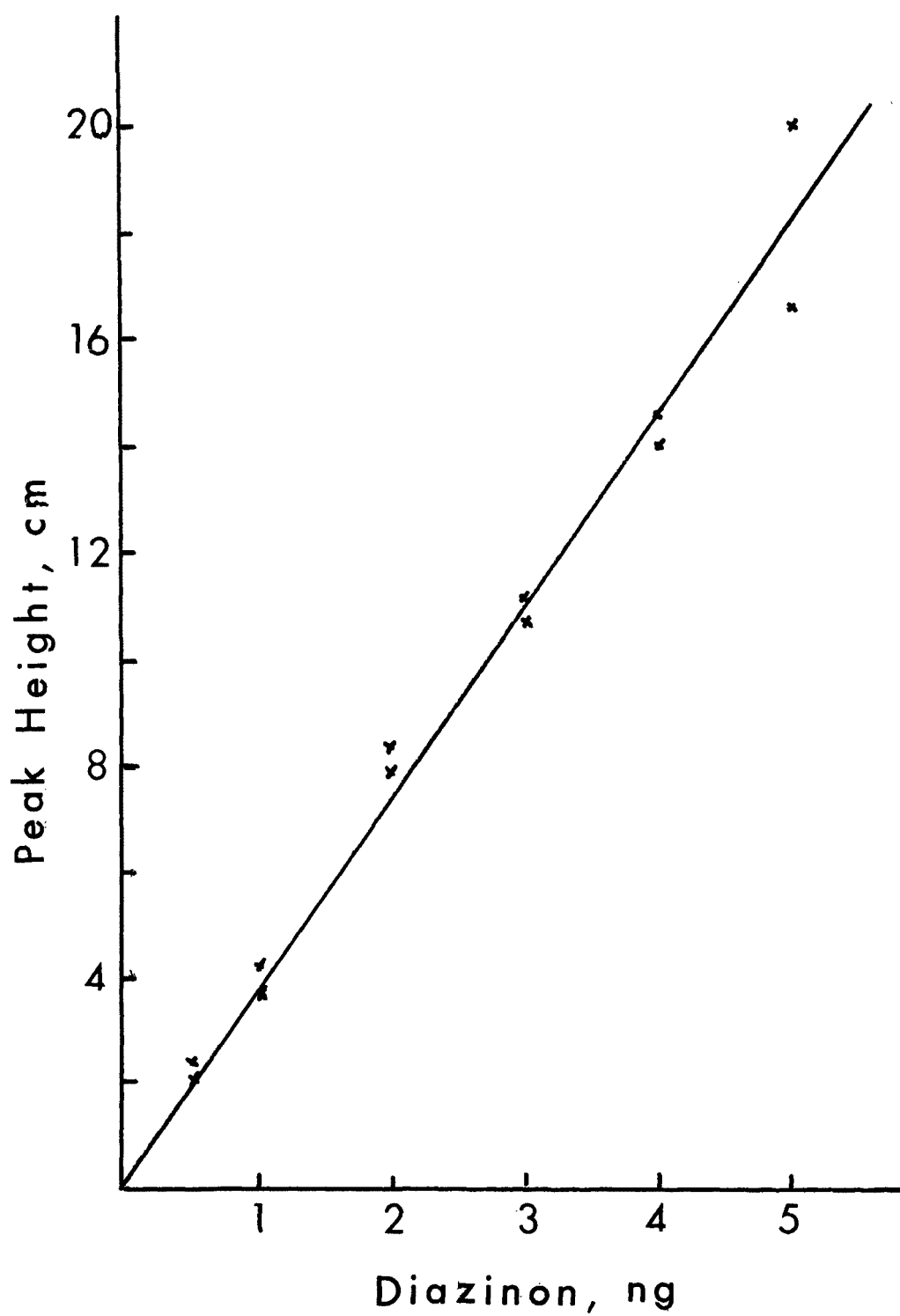


Figure 15. Calibration graph for diazinon

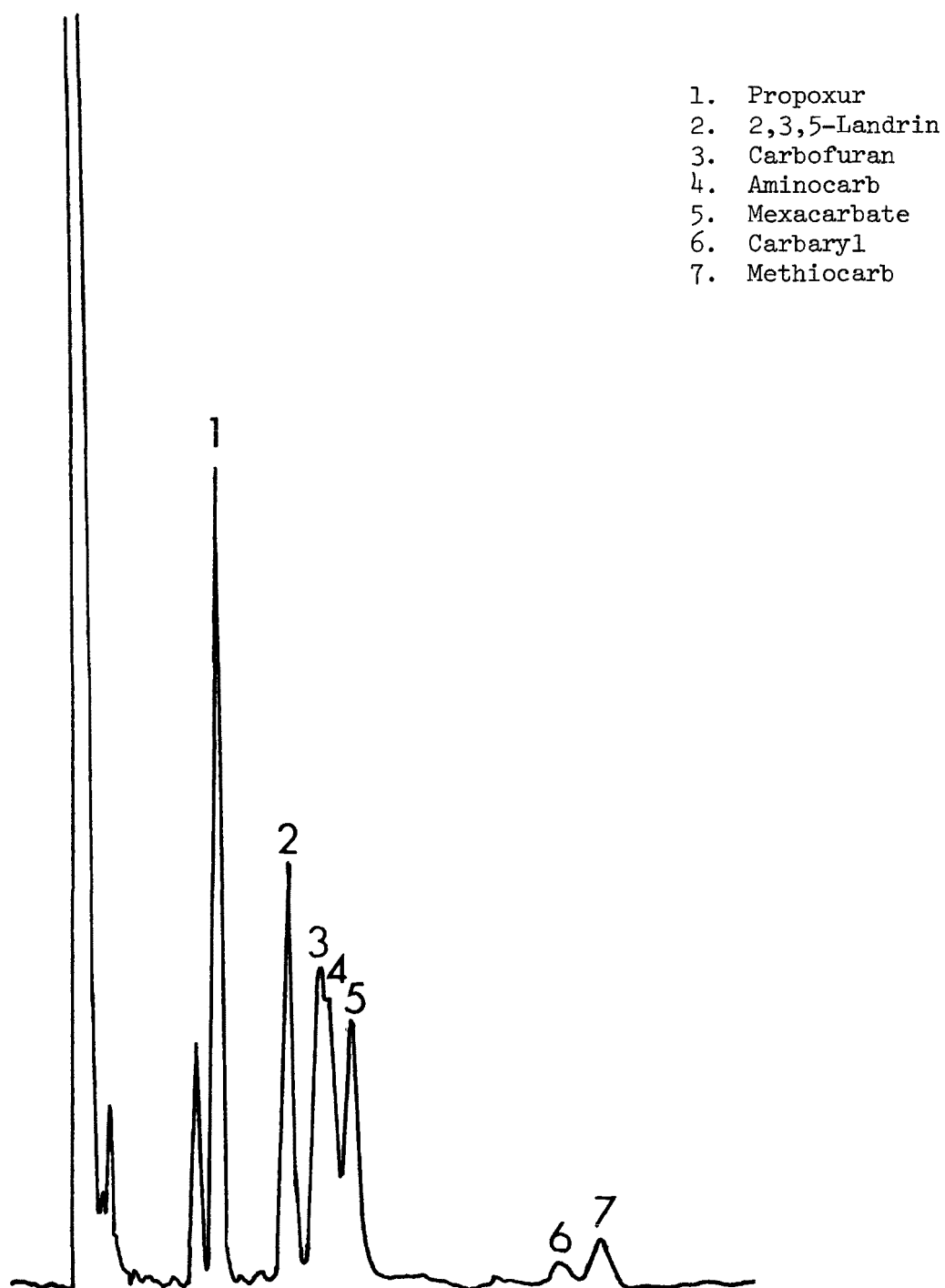


Figure 16. Electron-capture chromatogram of N-methylcarbamate insecticides, obtained with a 5% SE-30 column at 195°C

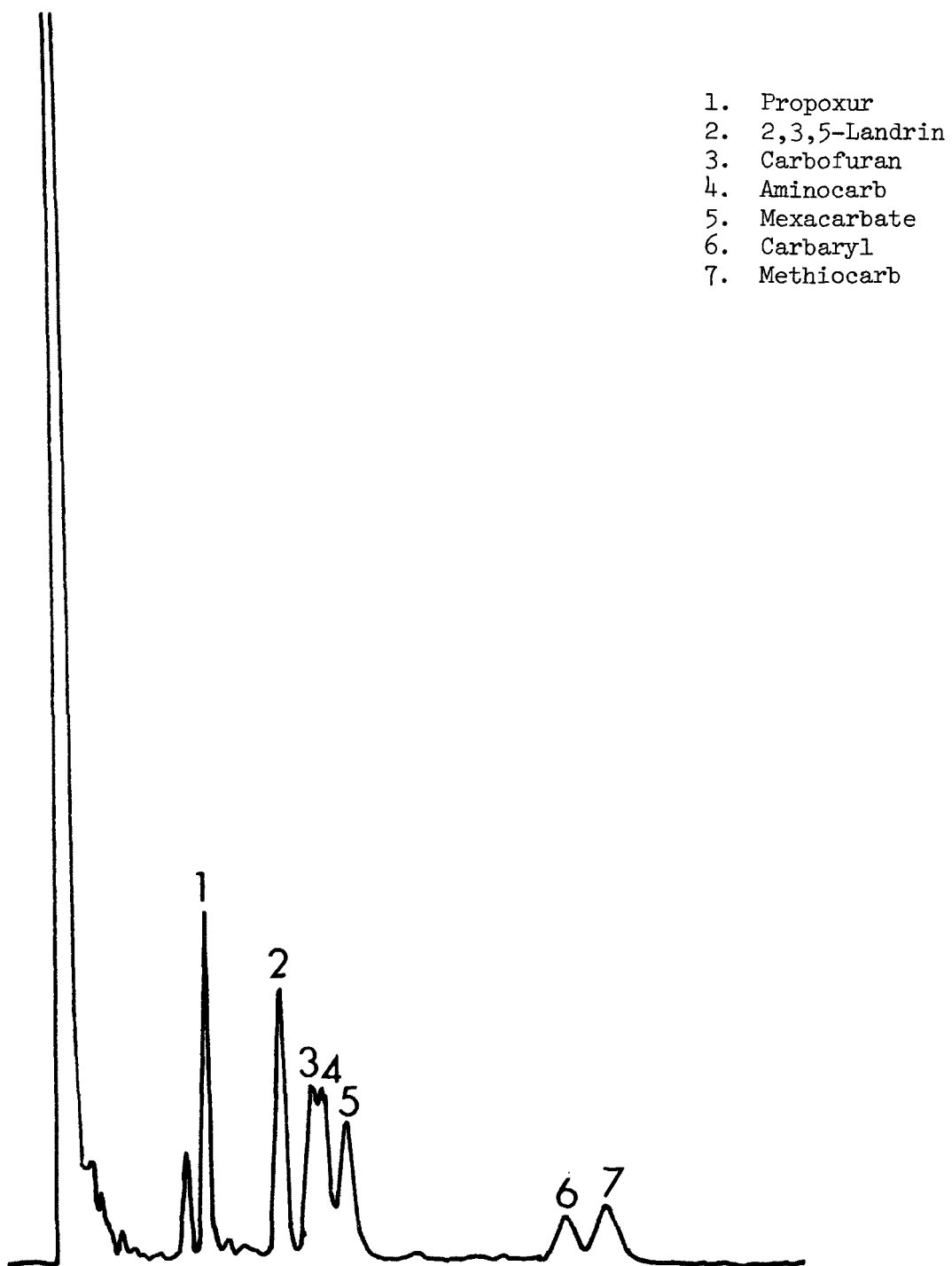


Figure 17. Electron-capture chromatogram of N-methylcarbamate insecticides, obtained with a 5% SE-30 column at 165°C

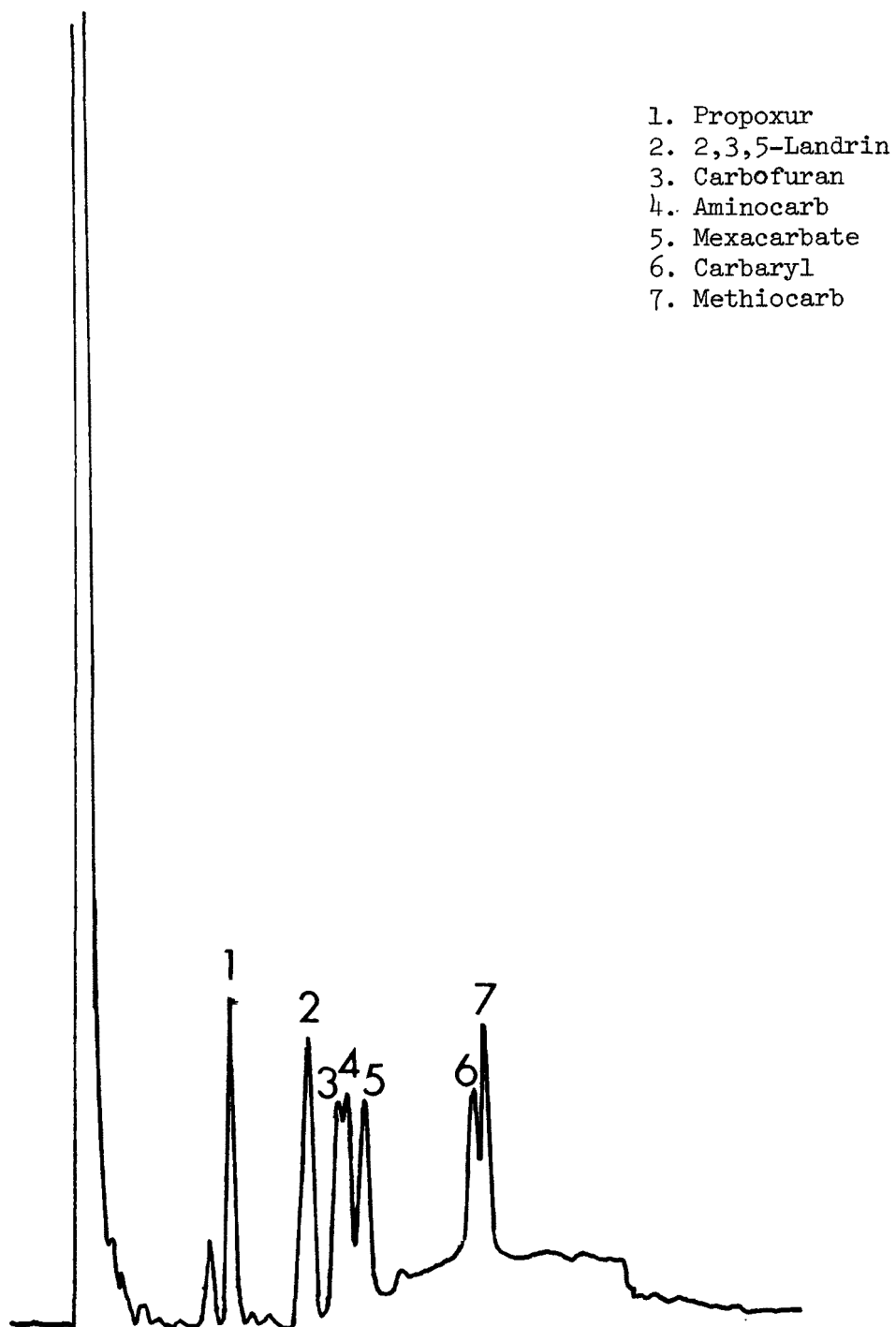


Figure 18. Electron-capture chromatogram of N-methylcarbamate insecticides, obtained by temperature programming as described in text

In surveying the columns available in this laboratory, we found that a 3% DC-200 column gave excellent response with the pentafluoropropionate derivatives of the carbamates. This is illustrated in Figure 19, which represents an injection of 400 pg of each compound. The peak height for propoxur was about double that found for PFP-propoxur at 600 pg with SE-30 column (Figure 16). However, the peaks for 2,3,5-Landrin and carbofuran were not separated. In a later experiment, 20 pg of each of the compounds in liquid-chromatography Fraction III except 2,3,5-Landrin (that is, diazinon, malathion and the remaining six carbamates) were treated with PFPA and applied to the 3% DC-200 column. The chromatogram is reproduced in Figure 20. Both of the organophosphorus compounds elute after the PFP-carbamates and the latter are well separated, with excellent sensitivity with respect to noise level. Calibration graphs for the six carbamates are presented in Figure 21. All six graphs are linear and pass through the origin, indicating that compound degradation on the DC-200 column is not a problem.

In the Sherma-Shafik procedure, diazinon and carbaryl elute together from the SE-30 column, and at some levels of diazinon this compound must be removed by an acid wash before carbaryl can be quantitated. By contrast, diazinon does not interfere on the DC-200 column. Since 2,3,5-Landrin is a minor constituent of Landrin and, moreover, production of the latter has been discontinued by the manufacturer, 2,3,5-Landrin was omitted in the other phases of our studies so that the superior DC-200 column could be used for the quantitation of the carbamates.

To summarize, we have found GLC columns that exhibit advantages in performance over those recommended by Sherma and Shafik for quantitation of each of the classes of test pesticides. Our selections include a 1.5% OV-17/1.95% OV-210 mixed column for organochlorine insecticide analyses, a 3% OV-1 column for the organophosphorus compounds, and a 3% DC-200 column for the N-methylcarbamates. The use of alternate columns is also beneficial in that retention times on more than one column can provide evidence with respect to confirmation of identity of individual pesticides.

EFFECT OF FOAM STRUCTURE ON AIR FLOW RATES

In the vapor trapping experiments described earlier, the PUF plugs appeared to compress somewhat during air sampling and the flow rate seemed to diminish with time. Six experiments were performed to confirm this effect, to determine the relationship of flow rate to sampling time, and to determine if the change in flow rate was directly related to the porosity of the foam. High-flow (low pressure drop), 45-mm PUF plugs were tested in three of the experiments, medium-flow plugs in the other three.

For each experiment, a single plug was placed in a glass sampling holder and air was drawn through the plug by vacuum pump. The pressure across the plug was measured with a diaphragm vacuum gauge, and the flow rate was measured with a rotameter. Readings were taken periodically over a 24-hour period.

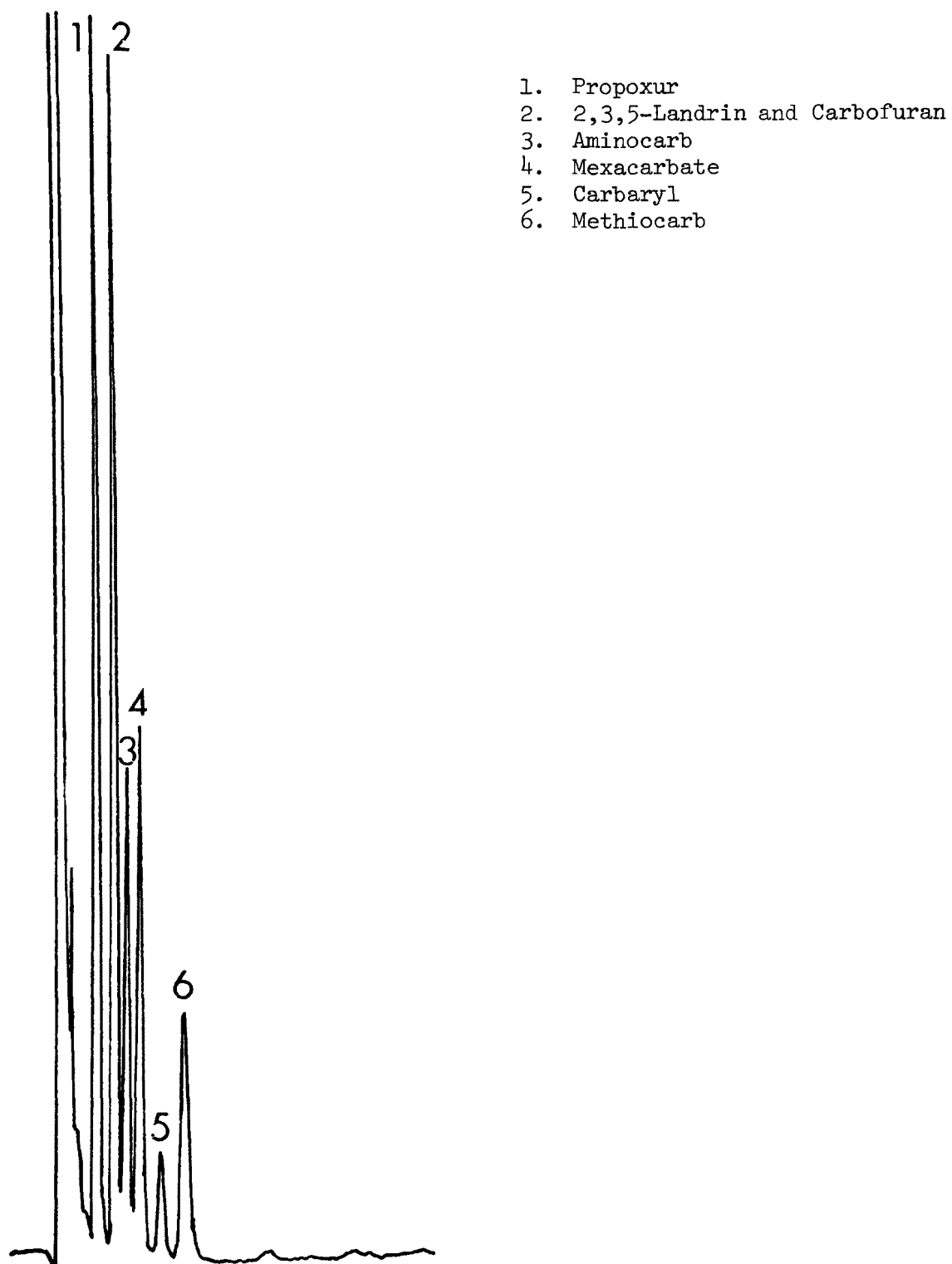


Figure 19. Electron-capture chromatogram of 400 pg each of N-methylcarbamates, obtained on a 3% DC-200 column

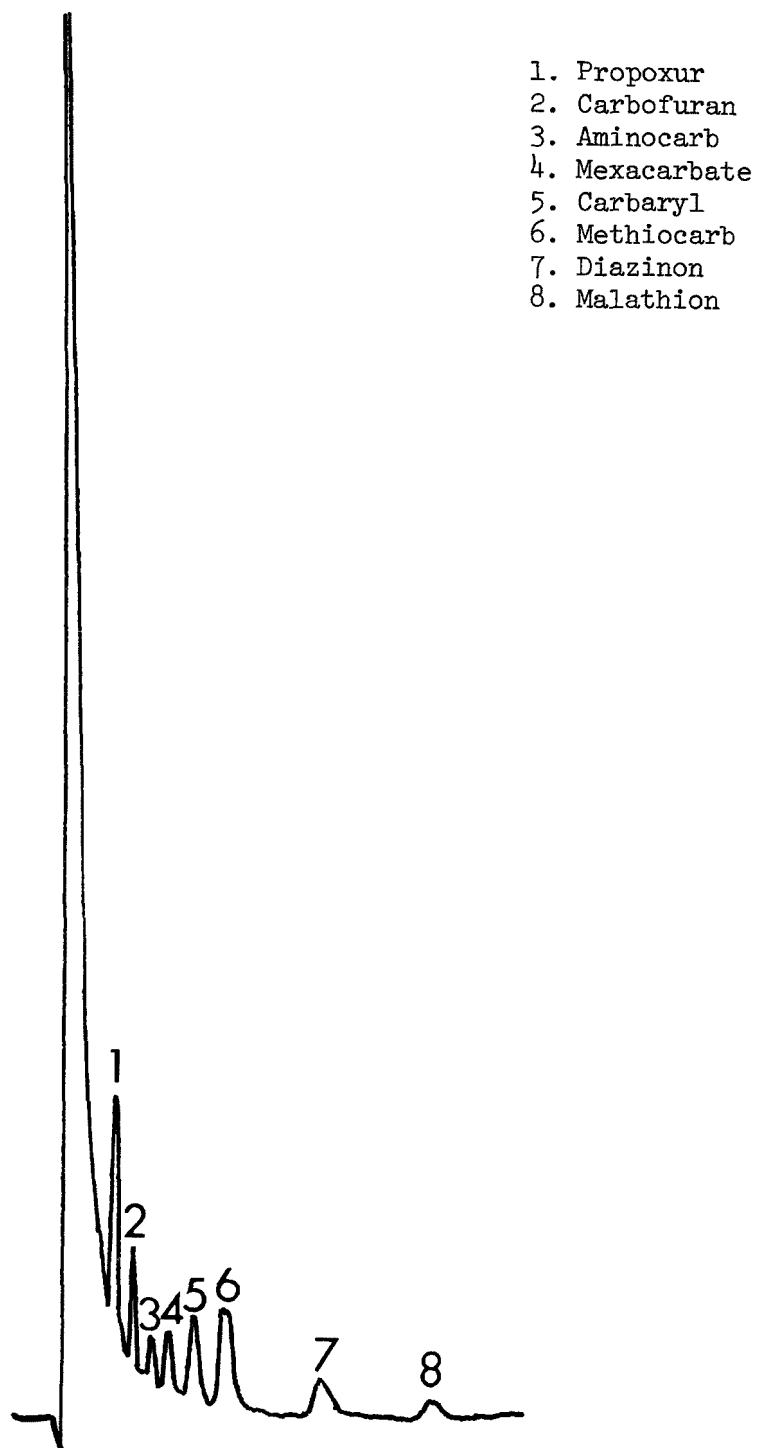


Figure 20. Electron-capture chromatogram of 20 pg each of Fraction III pesticides, obtained on a 3% DC-200 column

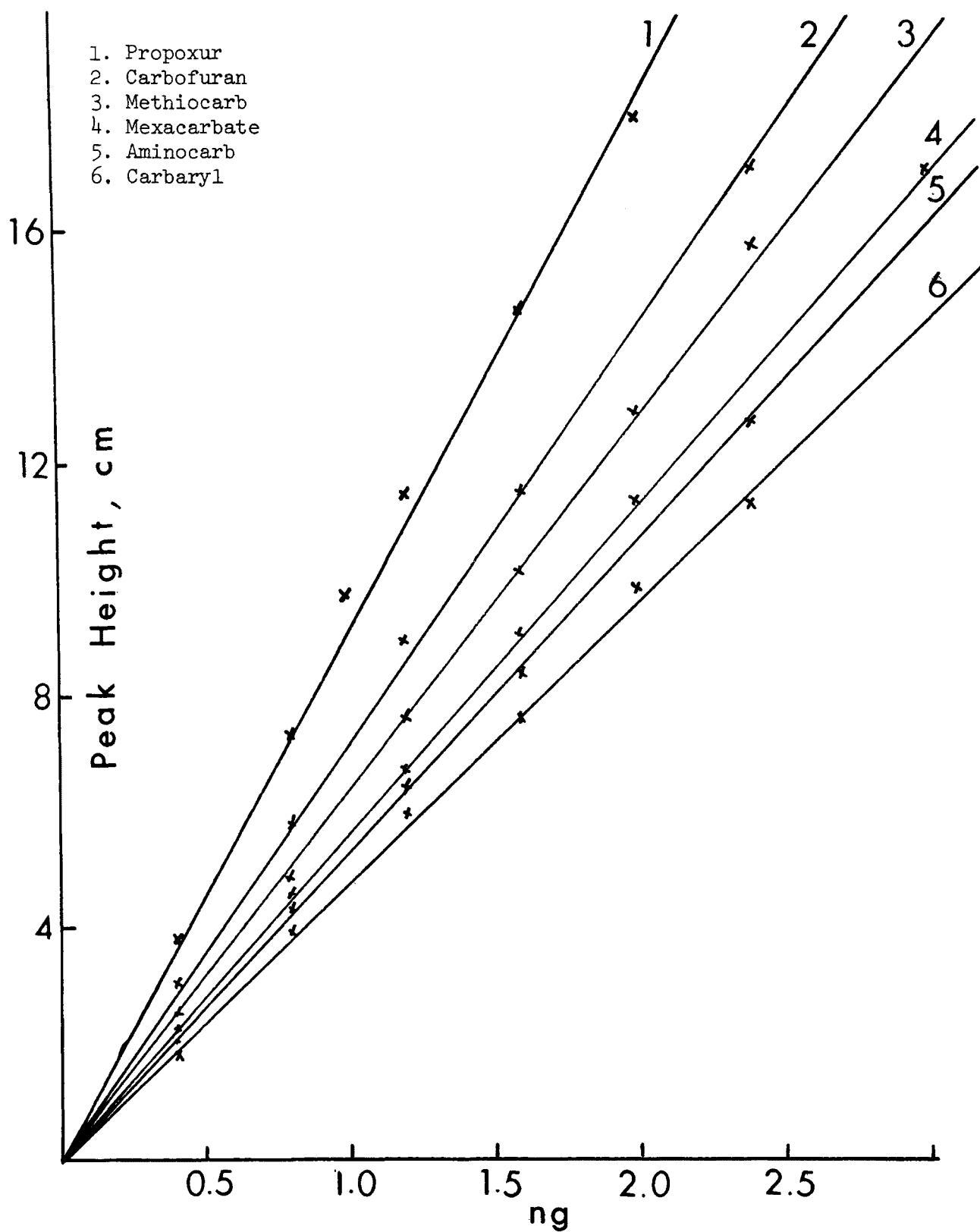


Figure 21. Calibration graphs of N-methylcarbamate insecticides, obtained on a 3% DC-200 column

With all plugs, flow rates decreased with time and the pressure across the plugs increased slightly with time. The flow rates decreased relatively rapidly at the start of the experiments and asymptotically approached the final flow rates. The decrease in flow rate ranged from 3.2 to 9.0% of the initial value, and no relationship was apparent between porosity of the plug and degree of decrease in the flow rate. The change in flow rate with time for a typical experiment is presented in Table 17. The plug in this experiment was rated as high-flow, and the total decrease in flow rate was 8.6% of the initial value.

Quantitation of the pesticide residue levels in air depends on the accuracy of the flow rate measurement as well as on the analytical procedures. These experiments indicate that, for maximum accuracy in quantitation of pesticides in air with PUF foam, the flow rate should be monitored continuously during the sampling.

TABLE 17. CHANGE IN AIR FLOW RATE WITH TIME OF AIR
PASSAGE THROUGH A PUF PLUG

Hours of air flow	Air flow rate, m ³ /hr
0	5.22
0.1	5.18
0.5	5.04
1.5	4.99
2.5	4.92
3.5	4.88
4.5	4.88
6.5	4.84
23.5	4.77
24.5	4.77

ANALYSIS OF N-METHYLCARBAMATE INSECTICIDES

Evaluation of Carbamate Derivatization Procedures

Several problems exist in the GLC determinations of N-methylcarbamates. These compounds generally have low vapor pressures, so that GLC retention

times are long; they are thermally unstable and decompose in the GLC column under common gas chromatographic conditions; and their sensitivities to detection by electron-capture and other detectors is not high. The Sherma-Shafik procedure (4) attempts to solve all these problems by derivatization of the N-methylcarbamates with pentafluoropropionic anhydride (PFPA) according to the method of Shafik *et al.* (9). In this procedure, the nitrogen-bound proton of the carbamate is replaced by a pentafluoropropionyl (PFP) moiety. The resulting PFP-carbamate compounds are more volatile and more stable than the parent carbamates and also have five fluorine atoms to enhance electron-capture detection. Several other derivatization procedures have also been used to facilitate quantitation of carbamates. For example, the phenolic moieties liberated from the carbamates have been derivatized by 1-fluoro-2,4-dinitrobenzene (FDNB) (10). This method has been used on soil residues in this laboratory with excellent results (11). Parent N-methylcarbamates can also be derivatized with trifluoroacetic anhydride (TFAA) and heptafluorobutyric anhydride (HFBA) in reactions similar to that for PFPA. We performed a number of experiments to determine which method was best for analysis of the seven test N-methylcarbamate insecticides, and to optimize the analytical conditions.

Effect of PFPA Concentrations on GLC Peak Heights--

The procedure of Shafik *et al.* (9) specifies that the carbamates in 2 ml isooctane should be reacted with 0.025 ml PFPA, with one drop of pyridine as catalyst. After one hour at room temperature, the reaction is stopped by addition of 3 ml phosphate buffer. Three ml isooctane and 0.05 ml acetonitrile are added and the aqueous layer is aspirated with a pipet. The organic layer is washed three times with 2 ml water, with the wash removed each time by aspiration, and is then dried by addition of 0.5 g sodium sulfate. An experiment was conducted using this procedure, partly for familiarization but also to examine the effect of increasing the amount of PFPA reagent. Pyridine was redistilled (12, p. 175), and phosphate buffer was prepared as specified by Sherma and Shafik (4). A standard solution of the seven carbamates and the two organophosphorus insecticides that elute in liquid-chromatography Fraction III was prepared in hexane at 1 µg/ml per compound. One drop of keeper solution and 1.00 ml of this standard were placed into each of seven 15-ml Kuderna-Danish receiver tubes. The contents of each tube were evaporated at 50°C in a water bath by a stream of nitrogen gas. The Shafik *et al.* procedure was then followed, except that 0.025, 0.05, 0.10, 0.15, 0.20, 0.25 or 0.30 ml PFPA was added to a tube. The derivatized carbamates were analyzed by electron-capture GLC on a 5% SE-30 column (the superiority of the 3% DC-200 column had not yet been discovered). Figure 22 shows the chromatogram, representative of the seven chromatograms, for the standard treated with 0.10 ml PFPA. The relatively poor resolution of peaks, previously shown for the 5% SE-30 column (Figure 16), was apparent. However, the organophosphorus components of the standard solution did not interfere with the carbamate peaks.

The height of each peak in each of the seven chromatograms was measured and is recorded in Table 18. Changes in the amount of PFPA used in the reaction did not affect the peak heights of the individual carbamates equally. Peak heights increased for all the compounds as the quantity of PFPA

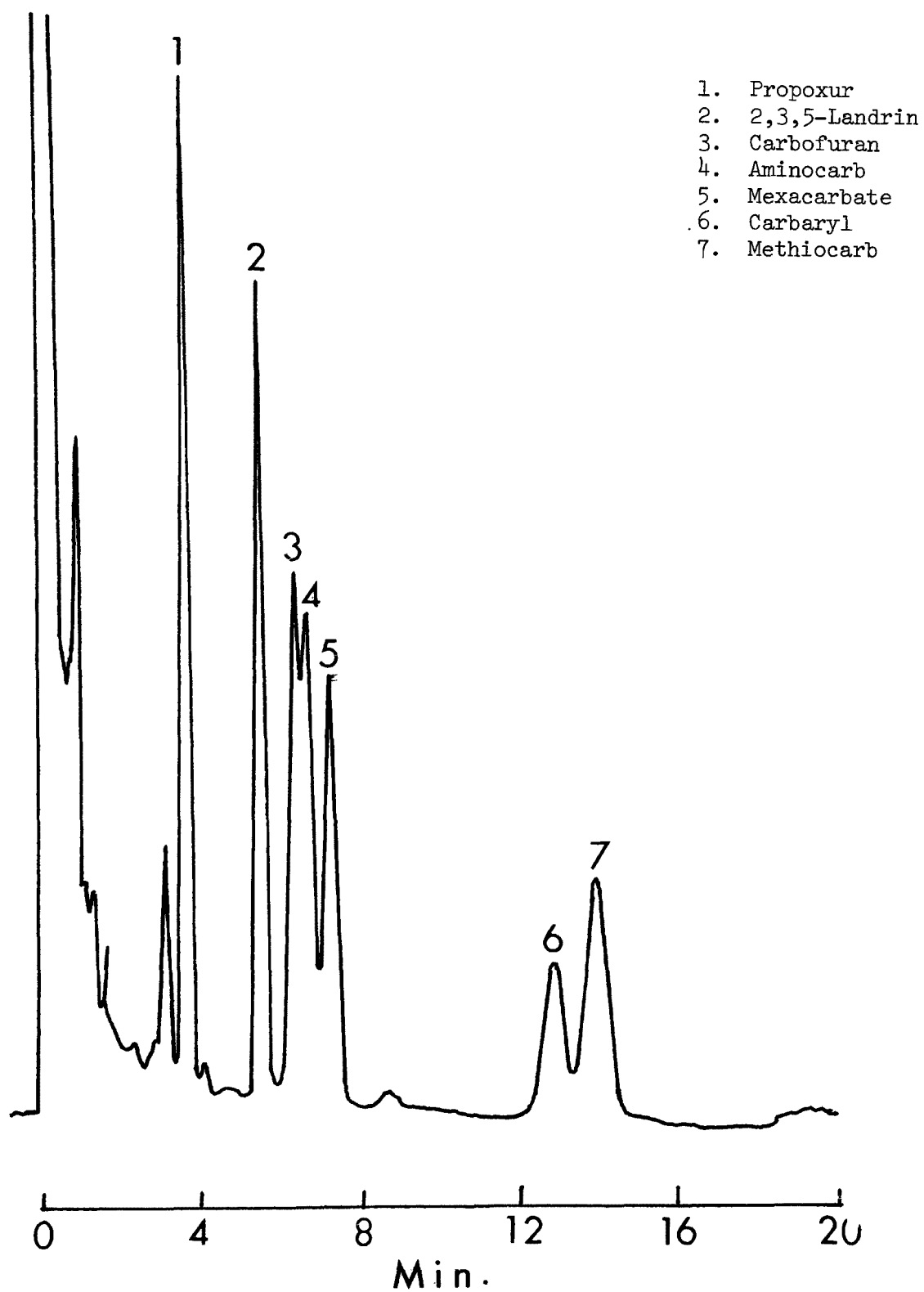


Figure 22. Electron-capture chromatogram of 400 pg each of the N-methylcarbamates, reacted with 0.1 ml PFPA

TABLE 18. THE EFFECT OF CONCENTRATION OF PFPA REAGENT
ON GLC PEAK HEIGHTS OF CARBAMATE INSECTICIDES

Compound	Peak heights, mm						
	PFPA volume added, ml						
	0.025	0.05	0.10	0.15	0.20	0.25	0.30
Propoxur	46	52	80	91	88	95	92
2,3,5-Landrin	46	50	74	77	78	80	74
Carbofuran	30	33	46	49	52	54	50
Aminocarb	48	36	54	36	36	31	-
Mexacarbate	33	38	43	35	27	27	26
Carbaryl	3	3	8	8	18	20	20
Methiocarb	6	9	15	19	22	23	19

was increased up to about 0.10 ml, but the increase was much more modest for aminocarb and mexacarbate than for the other compounds. Moreover, the aminocarb and mexacarbate peaks decreased in size as the amount of PFPA exceeded 0.1 ml, whereas the other peaks leveled off or continued to increase. At the highest levels of PFPA, the carbofuran peak tended to obscure the aminocarb peak. The data indicated that an increase of the PFPA from 0.025 ml up to 0.10 ml in the Shafik et al. procedure would be beneficial.

Evaluation of a TFAA-derivative Procedure--

Seiber (13) demonstrated that temperature and solvent polarity strongly affect rates of N-methylcarbamate derivatization by perfluoroacyl anhydrides. When the reaction is performed in polar solvents, shorter reaction times and/or lower temperatures may be used to effect complete derivatization. Greenhalgh et al. (14) reported that methiocarb could be trifluoroacetylated in 15 minutes at 100°C in ethyl acetate. We therefore performed an experiment to compare results from the Greenhalgh et al. procedure with those from the Shafik et al. method.

A 1-ml aliquot of each 1-ppm carbamate standard solution was placed into a screw-cap vial, one drop of keeper solution was added, and the solvent was evaporated at 50°C in a stream of nitrogen. Ethyl acetate (2 ml) and 0.20 ml TFAA were added and the vial was capped. After two hours, the vial was opened, excess reagent and solvent were evaporated in a stream of

nitrogen, and 1 ml ethyl acetate was added. This solution was analyzed by GLC as in the Sherma-Shafik procedure.

The injection peak was very large and tailed badly. Moreover, the derivative peaks were relatively small, had short retention times, and were not well separated. TFAA, and perhaps ethyl-TFA (if formed from ethyl acetate by transesterification), may not be totally removed in the evaporation step; if not, they would produce a large injection peak such as that observed. Greenhalgh et al. used flame-photometric detection in the sulfur mode for analysis of methiocarb. In that system, neither TFAA nor ethyl-TFA would interfere. The Greenhalgh et al. procedure did not give acceptable results with electron-capture detection and was consequently abandoned.

Comparison of PFFA With HFBA for N-Methylcarbamate Derivatization--

Seiber (13) reported that TFA, PFP and HFB derivatives of several N-methylcarbamates had similar stabilities and rates of formation. However, the electron-capture response increased two-fold for carbaryl and five-fold for carbofuran from the TFA to HFB derivatives. We conducted an experiment to determine if the HFB derivatives would offer higher electron-capture response and/or better separation of GLC peaks than the PFP derivatives.

One ml of the Fraction III standard solution and one drop of keeper solution were placed in a 4-dram screw-cap vial and evaporated in a stream of nitrogen at 50°C. Benzene (4 ml) was added and the vial was sonicated for 2 minutes to dissolve the pesticides. After addition of 0.10 ml HFBA, the vial was sealed with a teflon-lined cap and heated at 100°C for 2 hr. The solution was diluted with 4 ml hexane and washed three times with 5-ml portions of water. It was then dried with sodium sulfate and concentrated to 5.0 ml with a stream of nitrogen. This solution was analyzed by GLC on a 3% SE-30 column, resulting in the chromatogram shown in Figure 23. In the figure, each peak represents approximately 200 pg of the designated carbamate. Although the retention times here were longer and the residue levels lower by half, a comparison of Figure 23 with Figure 22 shows that the response with this HFBA procedure was no better than that with the Shafik PFFA procedure. There was also no advantage in terms of effort or analysis time.

The same Fraction III standard was also derivatized with 0.10 ml HFBA by the Shafik et al. procedure detailed above. The derivatized solution was analyzed on the 3% DC-200 column at 165°C column temperature. At the 200-pg residue level, six sharp and well-separated peaks were obtained for the seven carbamates. Derivatization of each carbamate individually with HFBA showed that 2,3,5-Landrin and carbofuran had such close retention times that they would appear as one peak when both compounds were present. The six-peak chromatogram of the HFB-carbamates was therefore essentially identical to that obtained with the PFP-carbamates on the same column (Figure 19).

A standard solution containing only the six test carbamates, without 2,3,5-Landrin, was prepared at 1 µg/ml per compound. One ml of this solution was derivatized with 0.10 ml HFBA by the Shafik et al. procedure and analyzed on a 3% DC-200 column. The chromatogram is presented in Figure 24. A comparison of this figure with the corresponding chromatogram for the

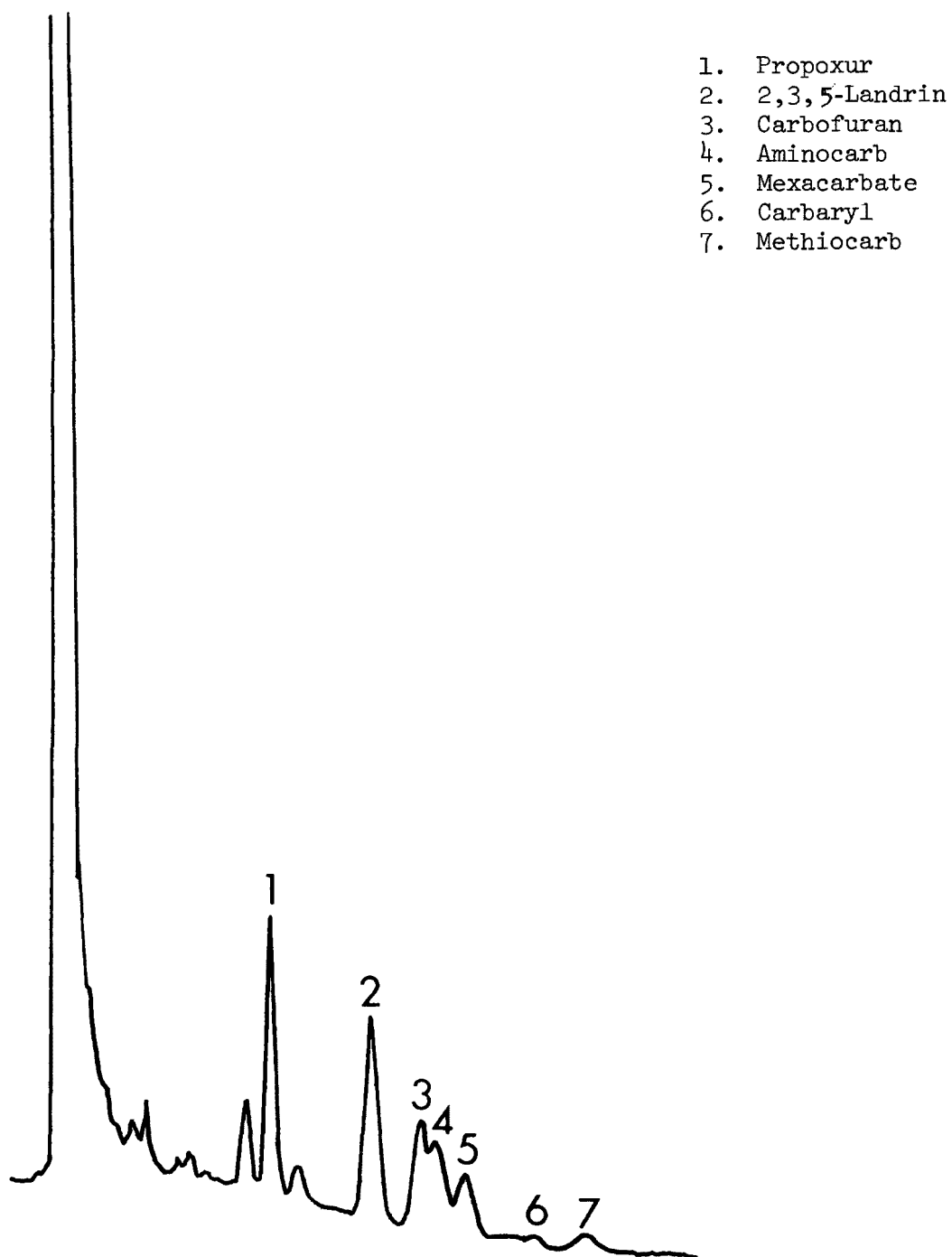


Figure 23. Electron-capture chromatogram of 200 pg each of the N-methylcarbamates, reacted with 0.1 ml HFBA

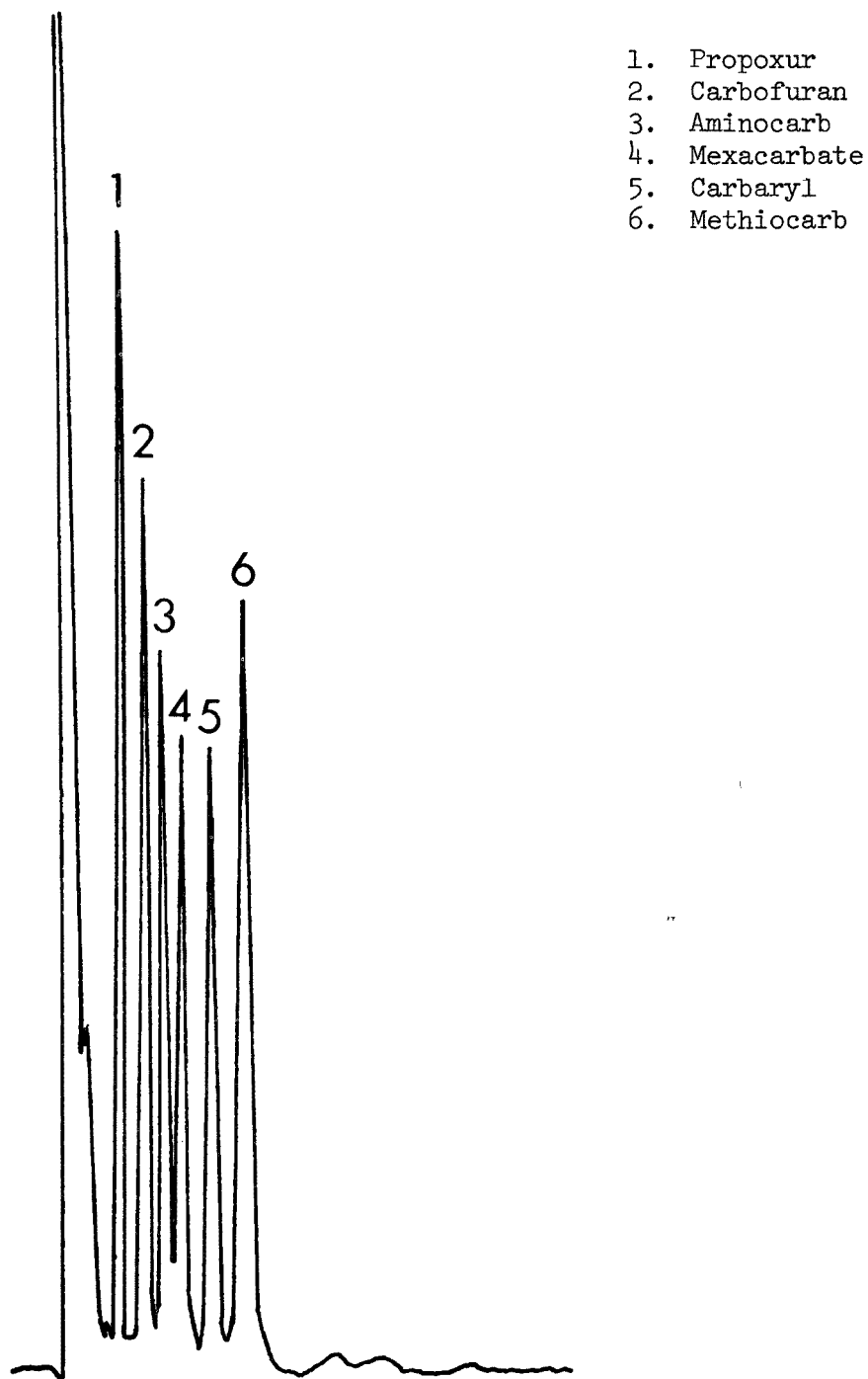


Figure 24. Electron-capture chromatogram of six HFB-carbamate derivatives, obtained on a 3% DC-200 column

PFP-carbamates (not shown) demonstrates that there is little difference in retention times or peak heights between HFB-carbamates and PFP-carbamates. Our experiments have shown that HFBA can be regarded as a substitute for, but apparently not an improvement on, PFPA in the Shafik et al. procedure.

Evaluation of 1-Fluoro-2,4-dinitrobenzene for Derivatization of Carbamates--

Holden (10) reported a procedure for the GLC determination of several of the carbamates used in this study. Reaction of 1-fluoro-2,4-dinitrobenzene (FDNB) with carbamates yielded ether derivatives of the phenolic moieties liberated from the carbamates. These derivatives were well-separated and readily quantitated on a DC-200 GLC column. We conducted an experiment to determine if the Holden procedure could be applied to extracts from polyurethane foam, and if it offered any advantage over the PFPA derivatization.

A blank was prepared by Soxhlet-extracting a PUF plug with 280 ml 1:1 hexane-acetone for five cycles. The solution was evaporated and 5 ml 5% aqueous borax solution and 0.5 ml FDNB reagent (1.5 ml FDNB in 25 ml acetone) were added. The contents were agitated in an ultrasonic bath, heated at 70°C for one hour in a water bath, and then extracted with 5 ml hexane. The extract was analyzed by GLC on a 3% DC-200 column, resulting in the chromatogram reproduced in Figure 25. If a carbamate were present in the extract at the 1- μ g level, this chromatogram would represent an injection of 40 pg of the carbamate. This high background level was shown, by derivatization of the carbamates by the same procedure and addition to the blank, to be prohibitive for quantitation of the carbamates. Consequently, the method was abandoned.

Effect of Diaminotoluenes on Quantitation of N-Methylcarbamates

When PUF degrades, two of the products are 2,4- and 2,6-diaminotoluene (15). These compounds would be detected by an electron-capture detector if they were present in the final extracts of the Sherma-Shafik procedure and thus might interfere with GLC analysis of organochlorine or carbamate pesticides. In the case of the carbamates, any diaminotoluenes occurring in liquid-chromatography Fraction III would have to be derivatized by PFPA to interfere with pesticide quantitation. Each of the diaminotoluenes has four reactive amino protons. If all four possible substitutions were accomplished by PFPA, the diaminotoluenes would be detectable at very low concentrations by electron-capture detection. We conducted tests to determine the likelihood and possible extent of the interference.

For the following tests, 2,4- and 2,6-diaminotoluene were purchased from a commercial source (Aldrich Chemical Co.) and recrystallized three times from absolute ethanol to remove impurities. Individual 1000-ppm standard solutions of both compounds were prepared by weighing 50 mg of the recrystallized material into a 50-ml volumetric flask and adding acetone. These standards were serially diluted to the 1 μ g/ml level in hexane. One ml of each of the diluted standards was evaporated, with five drops of paraffin oil keeper solution, and derivatized with PFPA. GLC analysis of the derivatives on a 3% DC-200 column showed that the two peaks were slightly separated and that the

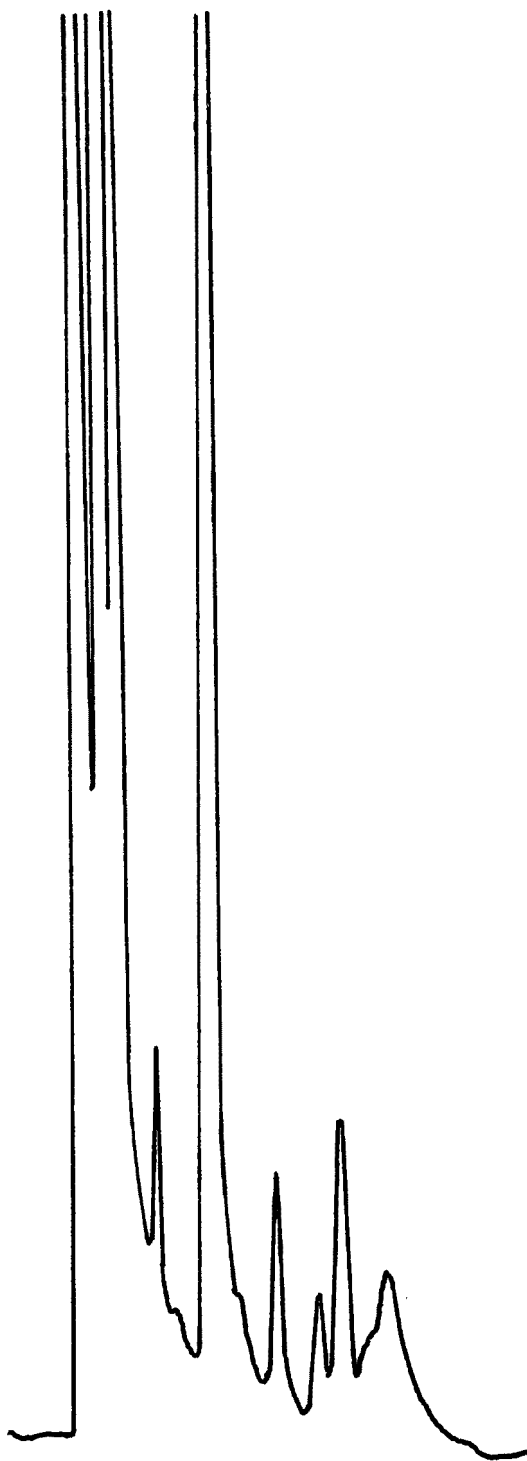


Figure 25. Electron-capture chromatogram of a PUF-plug blank extract derivatized with FDNB

retention times were very close to that of PFP-propoxur. To check this, a solution containing 1 μ g of propoxur was added to 1-ml aliquots of the 1-ppm diaminotoluene standards. These solutions were evaporated, derivatized and analyzed on a 3% DC-200 column. The chromatograms are presented in Figure 26. The propoxur peak was slightly removed from that of 2,6-diaminotoluene, but was not separated from the 2,4-diaminotoluene peak. Electron-capture response of the PFP-diaminotoluenes was very high. Each peak in Figure 26 represents an injection of 40 pg of material; the peak heights of the diaminotoluenes were almost four times that of propoxur. The diaminotoluenes have been reported to occur in concentrations as high as 400 ppm in PUF, and this test shows that they could interfere with quantitation of propoxur on 3% DC-200 if they are present in Fraction III.

A further test was conducted to determine if the PFP-diaminotoluenes would interfere with quantitation of carbamates on an SE-30 column. One ml of a standard solution containing 1 μ g of each of the pesticides that occur in Fraction III was added to 1 ml each of the 1-ppm diaminotoluene standards. This was evaporated with 5 drops of keeper solution, derivatized with PFPA, and quantitated by GLC on a 5% SE-30 column. The chromatogram is presented in Figure 27. The two PFP-diaminotoluenes appear as one peak that is adequately separated from PFP-propoxur.

After these tests, it remained to be determined whether the diaminotoluenes would appear in any of the three liquid-chromatography eluate fractions. One-ml aliquots of the 1-ppm diaminotoluene solutions, evaporated and resuspended in 0.5 ml hexane, were chromatographed on a silica-gel column as required by the Sherma-Shafik procedure. Each fraction was analyzed by ECGC, Fraction III being derivatized with PFPA before analysis. There were no unusual peaks in the chromatograms, so the diaminotoluenes apparently do not elute from the liquid-chromatography column.

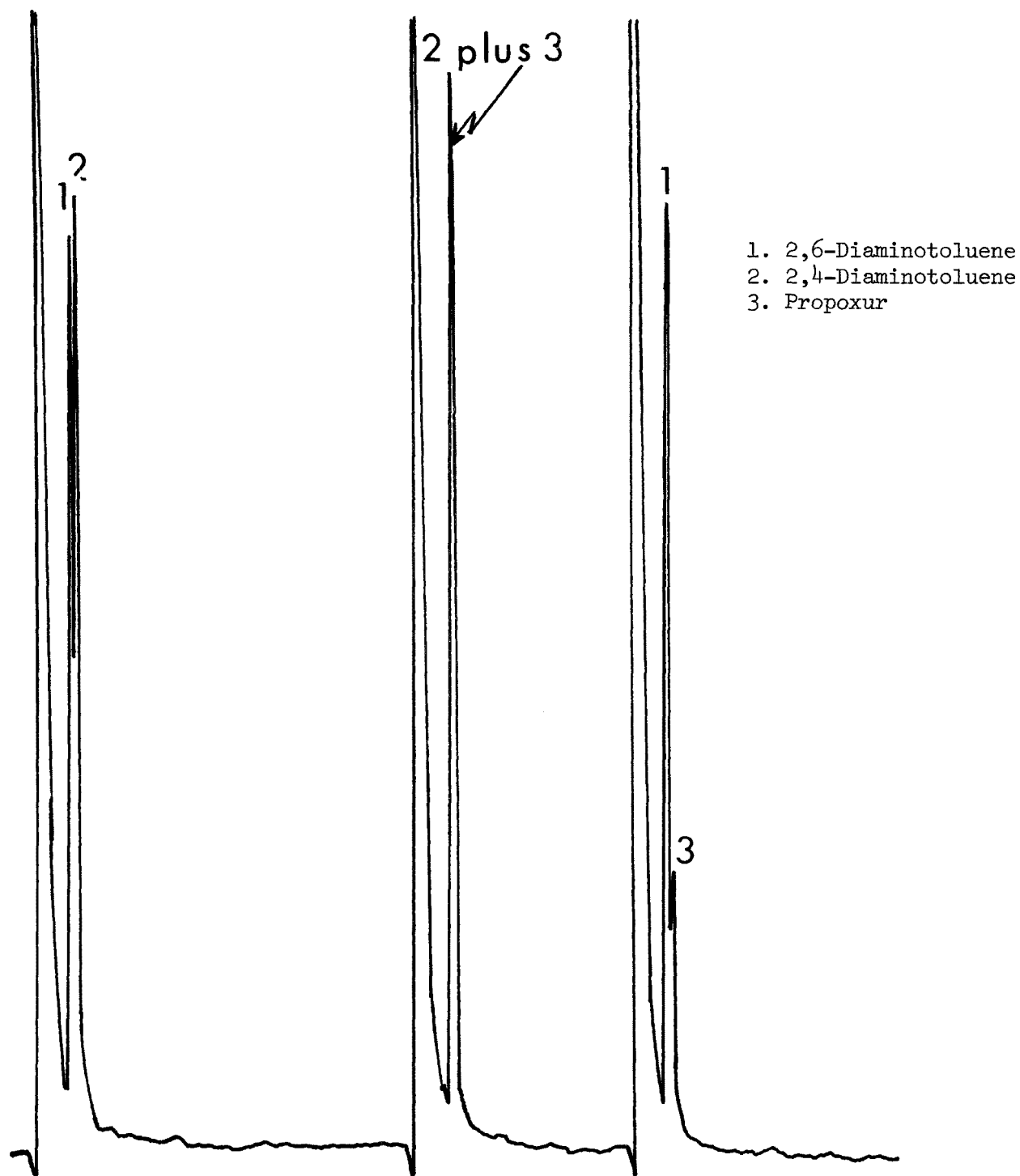


Figure 26. Electron-capture chromatograms of diaminotoluenes and propoxur, obtained on a 3% DC-200 column

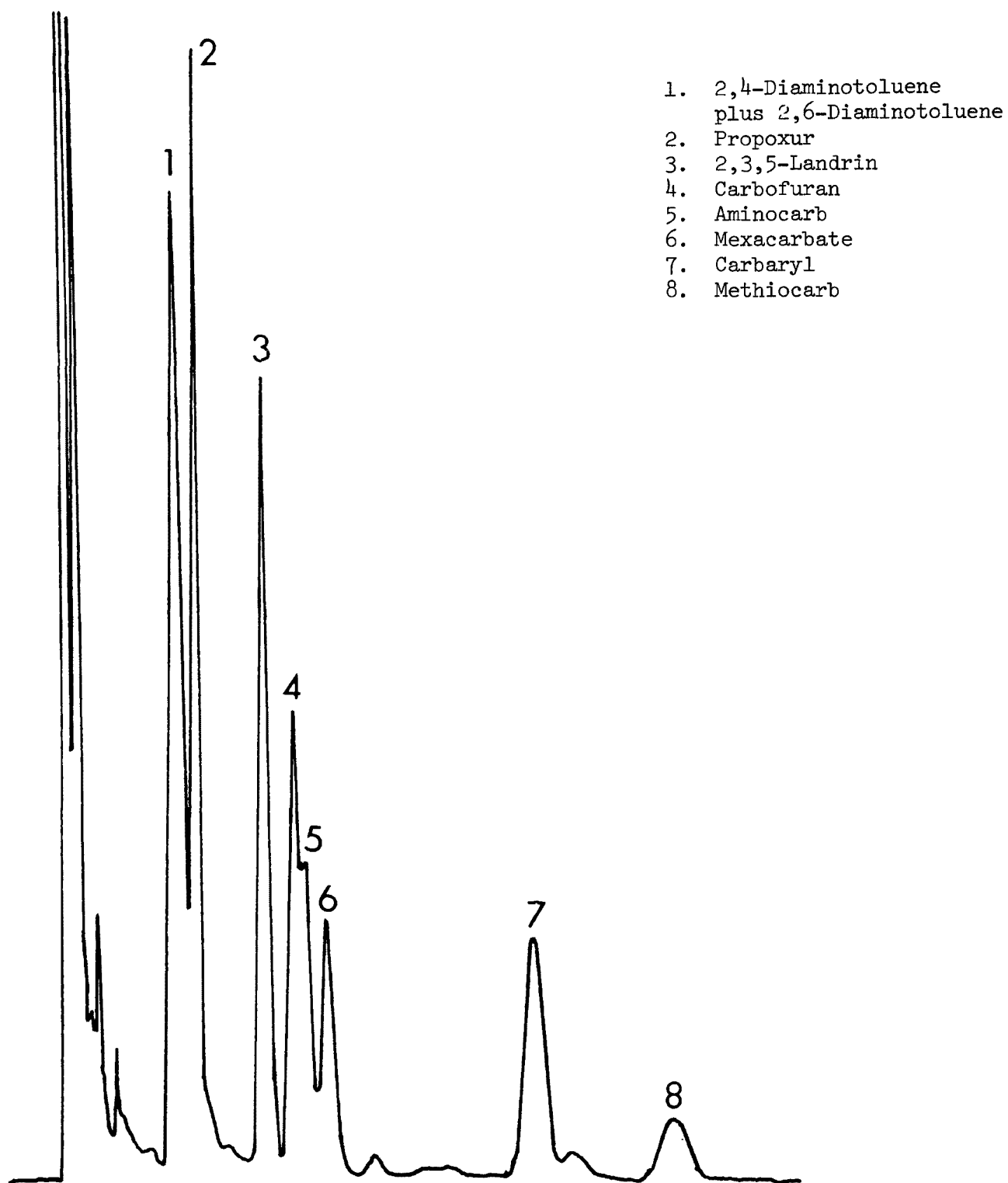


Figure 27. Electron-capture chromatogram of Fraction III pesticides plus diaminotoluenes, obtained on a 5% SE-30 column

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TECHNICAL REPORT DATA <i>(Please read instructions on the reverse before completing)</i>		
1. REPORT NO. EPA-600/4-80-008	2.	3. RECIPIENT'S ACCESSION NO.
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16. ABSTRACT <p>A method for determining levels of organochlorine, organophosphorus, and N-methyl carbamate insecticides in air was developed using 4.4 cm-diameter plugs of polyurethane foam as traps and a modified Sherma-Shafik multiresidue procedure for analysis of foam extracts. With this method, the minimum detectable air concentrations for vapors of 17 of the 18 organochlorine and organophosphorus pesticides tested was 0.1 nanogram per cubic meter or less. Six carbamate pesticides did not volatilize in sufficient amounts to allow analysis.</p> <p>The experimental program consisted of measurements of efficiency of foams for trapping vapors and aerosols, tests of foam compression during air sampling, evaluations of extraction solvents, evaluations of techniques for extracting pesticide residues from the foams, comparisons of the performance of the ester and ether forms of polyurethane foam, evaluations of the steps in the Sherma-Shafik analytical procedure, evaluations of GLC columns and instrumental parameters, and tests of derivatization procedures for electron-capture gas chromatography of the N-methylcarbamates.</p> <p>A 10-cm depth of foam was found to be an efficient trap for vaporized pesticides. Five-cycle Soxhlet extraction with 1:1 hexane-acetone was the best procedure for removal of pesticides from foam plugs.</p>		
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