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Determination of Chlorinated Hydrocarbons in Industrial and Municipal Wastewaters

IT Enviroscience, Inc., Knoxville, TN

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DETERMINATION OF CHLORINATED HYDROCARBONS IN INDUSTRIAL AND MUNICIPAL WASTEWATERS

By

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The objective of this report is to present the data and the research carried out to develop an analytical test procedure for the analysis of specific organic toxic substances in effluent wastewaters. The procedure is for the analysis of nine of the 114 priority or toxic pollutants identified by the EPA as Category 3 — Chlorinated Hydrocarbons.

The procedure consists of several steps, including extraction, concentration, clean up, and quantification by gas chromatography with electron-capture detection and flame-ionization.

The report describes the work done leading to selection of the procedures and includes data and information on a literature search, sample preservation procedures, elution of the compounds on various gas chromatographic columns, several solvent extraction efficiencies versus pH, stability of compounds in water-soluble solvents, sample extract clean up procedures, and application of the procedures on effluent wastewaters.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

Under authority of Sections 304(h) and 501(a) of the Federal Water Pollution Control Act of 1972 and the Clean Water Act of 1977, the Environmental Protection Agency is required to promulgate guidelines establishing test procedures for the analysis of pollutants. This report represents the state-of-the-art for the measurement of chlorinated hydrocarbons in industrial wastewaters.

Robert L. Booth, Director
Environmental Monitoring and Support
Laboratory - Cincinnati

ABSTRACT

The objective of this report is to present the data and the research carried out to develop an analytical test procedure for the analysis of specific organic toxic substances in effluent wastewaters. The procedure is for the analysis of nine of the 114 priority or toxic pollutants identified by the EPA as Category 3 -- Chlorinated Hydrocarbons.

The procedure consists of several steps, including extraction, concentration, clean up, and quantification by gas chromatography with electron-capture detection and flame-ionization.

The report describes the work done leading to selection of the procedures and includes data and information on a literature search, sample preservation procedures, elution of the compounds on varius gas chromatographic columns, several solvent extraction efficiencies versus pH, stability of compounds in water-soluble solvents, sample extract clean up procedures, and application of the procedures on effluent wastewaters.

The report was submitted in fulfillment of Contract No. 68-03-2625 by IT Enviroscience under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period November 1977 to March 1979, and work was completed as of March 1979.

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LIST OF ABBREVIATIONS

DMCS	Dimethylchlorosilane
ODCB	Orthodichlorobenzene
MDCB	Metadichlorobenzene
PDCB	Paradichlorobenzene
HCE	Hexachloroethane
HCBD	Hexachlorobutadiene
TCB	1,2,4-Trichlorobenzene
HCCPD	Hexachlorocyclopentadiene
2-CN	2-Chloronaphthalene
HCB	Hexachlorobenzene

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SECTION 1

INTRODUCTION

The Federal Water Pollution Control Act Amendments of 1972 (PL 92-500) and more recently the Amendments of 1977 (PL 95-217) require in Section 304(h) that the Administrator of the U.S. Environmental Protection Agency promulgate guidelines establishing test procedures for the analysis of the priority pollutants, which are separated into 12 categories. This report covers the research activity required in the method development for Category 3 -- Chlorinated Hydrocarbons.

The nine compounds in Category 3 -- Chlorinated Hydrocarbons are hexachloroethane, hexachlorobutadiene, hexachlorocyclopentadiene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, hexachlorobenzene, and 2-chloronaphthalene.

The study includes a literature search from 1960 through 1978, sample preservation studies, evaluation of solvents for liquid-liquid extraction, stability studies of the compounds in water-miscible solvents, and evaluation of sample and extract clean up procedures.

The gas chromatographic characteristics data of the category compounds are presented and include information on retention times with various gas chromatography columns at different temperatures, responses to both electron-capture and flame ionization detectors, linearity curves and chemical data for all compounds, and calculated and practical minimum detectable levels.

Based on the information gathered in the research program, methods were proposed for Category 3. These proposed methods were then used to develop data on overall compound recoveries in spiked distilled water and wastewater effluent samples.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The results of the experiments performed indicate that the samples are best preserved when the pH is adjusted to 2 and when they are dechlorinated with sodium thiosulfate, exposed to a minimum amount of light (UV), and stored and shipped at a temperature of 4°C. These procedures should be implemented as soon as possible after the samples have been collected. Even under these conditions, however, storage for seven days at low levels (<10 μg/L) led to losses ranging from 22 to 76%, whereas at the higher level (200 to 300 μg/L) losses were only from 2 to 18 percent.

Extraction of the samples with dichloromethane should be carried out at a pH of 2 to give the maximum extraction efficiency. Data on spiked distilled water show that the extraction efficiencies at the μg/L level or less are lower (10 to 20%) than at concentration levels one to two orders of magnitude higher.

The concentrated solvent-substituted extract is then analyzed on a 1.8 m by 2 mm I.D. glass column packed with mixed phases of 1.5% OV-1 and 1.5% OV-225 on 80/100 mesh Gas-Chrom Q at two isothermal conditions, 75°C and 165°C. All nine compounds are resolved by this column, and the minimum resolution of 0.7 occurs between the meta- and paradichlorobenzene isomers. This resolution between all the dichlorobenzenes and hexachloroethane, however, is quite variable with concentration; that is, high μg/L levels of hexachloroethane may make detection difficult at the μg/L level of para- and orthodichlorobenzene.

The original gas chromatographic packing was prepared by mixing equal volumes of 1.5% OV-1 on Gas-Chrom Q and 1.5% OV-225 on Gas-Chrom Q. Problems were encountered in preparing reproducible lots of the packing. It was subsequently discovered that a blended gas chromatographic column packing of 1.5% OV-1 and 2.25% OV-225 on Supelcoport gave identical results and performance to the orginal mixed phase packing yet was reproducible from lot to lot. Therefore, the blended packing has been recommended for the analyses of the chlorinated hydrocarbons.

The category compounds' responses were linear by GC/FID over the concentration ranges of 10 to 1000 mg/L injected and by GC/EC over the range of 1 to 10,000 μg/L injected.

Evaluation of the solvent stability in 2-propanol and 2-butanone indicates the latter solvent to be superior in promoting stability, since the

concentration of all the Category-3 compounds except hexachlorocyclopentadiene remained within an average of ±7% after a 90 day storage period at room temperature in the presence of light. Hexachlorocyclopentadiene proved to be highly unstable in both solvents, with significant decomposition occurring in as little as 10 days. In a separate study with hexachlorocyclopentadiene alone in the two solvents, the results were similar to those of the initial study. Shorter but similar studies with methanol and acetone as the solvent also showed decomposition. Stability of hexachlorocyclopentadiene in dichloromethane sealed in ampules and screw cap vials was tested for 45 days. Again, decomposition occurred between 10 to 30 days but was most severe in the sealed ampules.

The Florisil® column clean up procedure is rapid, keeps all category compounds in one eluant, and allows separation for more polar halogenated extracted components that may interfere with the analysis. The clean up allows elimination of many late eluting components that slow down analysis turnaround time.

Three treated industrial effluent samples and a municipal primary effluent sample were analyzed by the complete method. Two of the industrial effluents showed no Category-3 compounds. The municipal wastewater showed five of the compounds at less than 20 µg/L and the remaining industrial wastewater showed seven of the nine compounds at 0.4 to 120 µg/L. The method may be applicable to a wide variety of wastewater effluents, but confirmation by a secondary technique, previous sample knowledge, or gas chromatography/mass spectrometry will be required at times.

The accuracy of the method based on spiked solutions of distilled deionized water expressed as percent of recovery varied from 65% for hexachlorobenzene to 91% for 2-chloronapthalene at the low µg/L level. The method precision, based on spiking the worst sample evaluated, had a single operator coefficient of variation that ranged from 15% for p-dichlorobenzene to 52% for hexachlorobenzene.

RECOMMENDATIONS

In future studies a more effective research schedule for a method development project of this type should allow for the development of sample clean up techniques before extraction and preservation studies are begun. Such a schedule would allow application of the clean up procedure to the extraction and preservation studies, particularly the latter, whereas the formation of many additional compounds hampered both the quantification and precision of these studies.

Studies should be performed on the stability of hexachlorocyclopentadiene in water, since it lacks stability in the presence of UV light in several other polar solvents.

SECTION 3

RESULTS OF LITERATURE SEARCH

The literature review was made to determine the state of the art of analytical instrumentation and techniques utilized in the trace analysis of the nine chlorinated hydrocarbons that had been specified by the EPA. The resources of the University of Tennessee Science Library, the Oak Ridge National Laboratory Central Research Library, and IT Enviroscience's own facilities were used for this literature review.

The abstracts listed in Table 1 were searched from the years 1960 to 1979 for key words or subjects including methods of analysis for each of the two categories of compounds, sample collection and preservation methods, concentration techniques, clean up procedures, derivatization techniques and applications of chromatography.

TABLE 1. ABSTRACTS

Analytical Abstracts
Aquatic Sciences Abstracts*
Chemical Abstracts, 1960-1972
Chemical Abstracts Condensates, 1976-1977*
CASIA, 1972-1976*
NTIS*
Pollution Abstracts
Recon Files*

*Computer searches.

Several abstracts were manually searched, but five were searched by computer programs utilizing the key words or subjects mentioned in the last paragraph, along with the topic compound's registry numbers. CASIA is the computer program that searched Chemical Abstracts from 1972 to 1976. More recently, abstracted articles were found when the Chemical Abstracts Condensate program was run. The Recon File is a data bank of key articles that have been compiled by the Oak Ridge National Laboratory Central Research Library for its employees and is available publicly through the University of Tennessee Library.

Table 2 lists the periodicals most often cited by the abstracts. In addition to articles that appeared in these periodicals, numerous books, governmental publications, and minutes of symposia and meetings were cited.

TABLE 2. PERIODICAL LIST

Analyst
Analytical Chemical Acta
Analytical Biochemistry
Analytical Chemistry
Analytical Letters
Bulletin of Environmental Contamination and Toxicology
Environmental Pollution
Environmental Research
Environmental Science and Technology
International Journal of Air and Water Pollution
Journal of Agricultural and Food Chemistry
Journal of American Waterworks Association
Journal of the Association of Official Agricultural Chemists
Journal of the Association of Official Analytical Chemists
Journal of Chromatography
Journal of Chromatographic Science
Journal of Environmental Science and Health
Journal of Industrial Hygiene and Toxicology
Journal of Water Pollution Control Federation
TAPPI
Vom Wasser
Water, Air and Soil Pollution
Water and Sewage Works
Water Pollution Control
Water Research

Copies of the most pertinent articles were obtained and will be kept on file by IT Enviroscience throughout the lifetime of this project. A complete reference of pertinent publications is given in Section 6.

Table 3 is a summary of the results of the literature search for the analysis of chlorinated hydrocarbons. While the main interest was in finding articles dealing with any or all of the nine topic compounds, articles that dealt with compounds of a similar nature and whose analyses might have been applicable to any of the topic compounds were also cited. Therefore, while only 97 references were found that dealt directly with the analysis of one or more of the nine compounds, an additional 182 were found for similar chlorinated compounds.

TABLE 3. CITATIONS FOUND IN LITERATURE FOR CHLORINATED HYDROCARBONS

Total citations	182[a]	(97)[b]
Sampling and preservation	15[a]	(0)[b]
Preservation techniques	6	
Concentration by liquid-liquid extraction	51[a]	(25)[b]
- Extraction solvents	30	
Concentration by carbon/Tenax adsorption	16[a]	(5)[b]
Concentration by macroreticular resins	19[a]	(11)[b]
Clean up	25[a]	(7)[b]
Techniques	4	
Analysis by GC	88[a]	(72)[b]
GC substrates	64	
Head space analysis	9[a]	(6)[b]
Purge/sparge technique	11[a]	(3)[b]
Analysis by LC	6[a]	(1)[b]

[a]First number refers to the number of citations found for the general class of chlorinated compounds.

[b]The number in parenthesis refers to the number of citations in which at least one of the topic compounds appears.

Sampling was most often mentioned in government publications, although a few articles printed in public periodicals did address themselves to this item. Two examples are cited in references 57 and 271. Most articles did stress the importance of specially cleaned sampling bottles and avoidance of contamination during the analysis for chlorinated hydrocarbons.(79)

Four preservation techniques, other than refrigeration, were published, but the two most often reported were the additions of ascorbic acid or potassium ferrocyanide to the water samples.(152, 189) Both chemicals, which are reducing agents, are added to eliminate residual chlorine, which can react with organic material in the water to generate erroneously high levels of chlorinated hydrocarbons.

The most commonly reported method of concentrating the chlorinated hydrocarbons in water was liquid-liquid extraction, which may or may not be

followed by distillation or evaporation of the extracting solvent. Thirty solvents were reported, but the most commonly used ones were diethyl ether, petroleum ether, hexane, and benzene.(181, 185, 189) Alternate concentration techniques mentioned were carbon adsorption followed by solvent elution or recovery of the chlorinated hydrocarbons on macroreticular resins such as XAD-2 followed by solvent elution. (87, 153) The chlorinated hydrocarbons have also been concentrated by head-space sampling techniques, purge and trap (or VOA), or spray evaporation techniques.(18, 41, 57, 188)

Clean up procedures in which column chromatography with silica gel, Florisil, or alumina was used were reported.(15, 27, 274) Thin-layer chromatography has been mentioned as a clean up tool for some chlorinated hydrocarbons, but recoveries generally are low.(16, 143) As an alternative, back extraction or the extraction solvent sometimes was sufficient to clean the sample, although the technique was never claimed to be a clean up procedure.

Particular notice was taken during the literature survey for conditions of gas chromatographic analysis for trace quantities of chlorinated hydrocarbons in water. A large number of GC substrates, many obscure, were reported. Five did stand out due to their frequent use: DC-200; QF-1 with DC-200; SE-30; OV-225; and Bentone 34 with OV-101.(4, 17, 66, 106, 143) Both flame ionization and electron-capture detectors were reported in use, with the latter being more sensitive for higher chlorinated compounds.(4) The limits of detection, however, were dependent on concentration factors, as well as on the type of detector used.

Thin-layer chromatography and liquid chromatography were also used for the analyses of some of the chlorinated hydrocarbons.(115, 205, 215) Generally, the level of detection was the mg/L level for these analytical methods. With special techniques and detectors, the level of detection can be lowered, but the former are not usually available to all laboratories.

Little was found in the literature about the stability of the nine chlorinated hydrocarbons in organic solvents.(112) More was mentioned about their instability under UV light.

SECTION 4

CHLORINATED HYDROCARBONS

The EPA has designated 114 organic compounds in 12 categories as priority pollutants. The purpose of this study was to develop an unexotic test procedure to quantify in wastewater the effluents of the nine chlorinated hydrocarbons in Category 3: m-dichlorobenzene, p-dichlorobenzene, hexachloroethane, o-dichlorobenzene, hexachlorobutadiene, 1,2,4-trichlorobenzene, hexachlorocyclopentadiene, 2-chloronapthalene, and hexachlorobenzene.

The technical objectives of this project included the determination of a sample preservation scheme to minimize compound loss, the derivation of an efficient extraction technique for recovering and concentrating the compounds from water, the establishment of a reliable and linear gas chromatographic method applicable to all nine compounds, the determination of the stability of the compound when dissolved in water-miscible solvents, the development of a suitable sample clean up procedure, the application of the final analytical method with a clean up procedure to industrial wastewater samples, and the utilization of spiked aliquots of the wastewater samples taken through the complete method to gather accuracy and precision data. The resulting method in EPA format is found in Appendix A.

Experimental results indicated that samples were best preserved when buffered to a pH of 2, dechlorinated with sodium thiosulfate, exposed to a minimum amount of light (UV), and stored and shipped at a temperature of 4°C. These procedures should be performed or implemented as soon as possible after the sample is collected. Since acid-preserved samples cannot be shipped by air, the EPA has recommended that the sample be adjusted to a pH of 6 or 8 for shipping purposes. However, IT Enviroscience still recommends that the extraction step in the EPA approved method be performed at a pH of 2 with dichloromethane ($MeCl_2$). The recommendation was based on the premise that the best extraction efficiency data were gathered at this pH value.

Analysis of the concentrated, solvent-substituted extract was performed on a 1.8 m long by 2 mm I.D. glass column packed with 1.5% OV-1 and 1.5% OV-225 on 80/100 mesh Gas Chrom Q at two isothermal conditions, 75 and 160°C. All nine compounds' responses were quite linear, both by GC/FID at concentrations of 10 to 1000 mg/L and by GC/EC over the 1 to 10,000 µg/L range.

Evaluation of the stability of Category 3 -- Chlorinated Hydrocarbons in 2-propanol and 2-butanone indicated the latter solvent to be superior in

promoting stability. The concentrations of all the Category-3 compounds except hexachlorocyclopentadiene (HCCPD) remained within ±7% after a 90 day storage period at room temperature in the presence of light. Hexachlorocyclopentadiene proved to be highly unstable in both solvents, with significant decomposition occurring in as little as 10 days. A 45 day stability study of the chlorinated hydrocarbons in dichloromethane indicated a 67% decomposition rate in flame sealed ampules and a 33% decomposition in 20 mL scintillation vials. Therefore, standards containing HCCPD should be prepared fresh as needed and be refrigerated in the dark to maximize unstable standard life. The method further recommends that all Category-3 standards stored under normal lighting conditions be used within 60 days, as the concentration of o-dichlorobenzene begins to decrease rapidly after that.

MATERIALS AND METHODS OF PREPARATION

Chemicals

The o-dichlorobenzene, m-dichlorobenzene, 1,2,4-trichlorobenzene, and hexachloroethane were obtained from Eastman Kodak Company; the hexachlorocyclopentadiene, 2-chloronaphthalene, hexachlorobutadiene, and hexachlorobenzene from Tridom Chemicals; the p-dichlorobenzene from Aldrich; and the Aldrin from Alltech Associates. Hydrochloric acid, potassium chloride, potassium dibasic phosphate, sodium hydroxide, boric acid, sodium bicarbonate, sodium sulfate, Florisil (grade 923; 60-100 mesh), alumina, sulfuric acid, and sodium thiosulfate were ACS reagent grade and were obtained from Fisher Scientific. Burdick and Jackson HPLC distilled in glass grade hexane, dichloromethane, and petroleum ether were purchased from Bodman Chemical and used without redistillation. Gas chromatographic column packings were obtained from Supelco, Inc. Prepurified nitrogen and 95% argon/5% methane were obtained from the Linde division of Union Carbide.

Water Purification

It was of the utmost importance that the water in these experiments be of a very high purity, so a high quality purification system was used. Distilled ionized water was prepared by filtering tap water through a Carborundum Company tube filtration unit, followed by elution through a Barnstead D8904 organic removal column, a Barnstead D8901 high-capacity ion exchange column, and finally a Barnstead D8902 ultrapure ion exchange column. The effluent water was then distilled in a Corning megapure distillation unit, which was modified to prevent any surfaces other than Teflon® and glass from contacting the water. All the plumbing and storage containers throughout the system were made of Teflon or glass.

Gas Chromatography Column Preparation

Glass wool treated with dimethylchlorosilane (DMCS) was placed in the detector end of a coiled glass column, which was then attached by flexible tubing to a water aspiration vacuum source. The desired packing material was then added to the other end of the column while suction was applied. After the column was filled, a vibrator was used in conjunction with the

suction to provide a uniformly packed column. Additional packing material was added, as before, if the previous treatment had reduced the volume of the packing material. Another piece of glass wool was inserted in the injector end of the column, with quarter-inch Swagelok fittings with Supeltex M-1 ferrules added to the columns and attached to the injector of the gas chromatography (M-2 Vespel ferrules may "freeze" onto the chromatograph fittings leading to column breakage). The columns were conditioned at ambient temperature for 30 minutes followed by a 1°C/minute temperature program up to 210°C and held there overnight.

Apparatus

Kuderna-Danish evaporators were prepared by Lab Glass, Vineland, New Jersey. Glass chromatography columns were obtained from Supelco, Inc. The remaining glassware used in the study was ordered from Fisher Scientific and modified to meet experimental specifications. Gas chromatographic determinations were performed on an HP 5713A gas chromatograph equipped with a ^{63}Ni electron-capture detector and an HP 5720A gas chromatograph equipped with a flame ionization detector. Chromatograms were recorded on either an HP 3380A or an HP 3380S recording integrator.

EXPERIMENTAL

This section describes the significant accomplishments and problems associated with the analytical methodology for the nine Category-3 chlorinated hydrocarbons.

Gas Chromatography

A gas chromatography/electron capture method was developed to provide separation of the nine Category-3 chlorinated hydrocarbons. Table 4 lists the GC columns evaluated for the analysis of the Category-3 compounds, of which five were found to be unsuitable. The most frequent problem was the inability of the column to separate the three dichlorobenzene isomers, especially the meta- and para-isomers. Column No. 5, the bentone/OV-101 column, gave an excellent separation of the dichlorobenzenes, but at the column temperature limit would not elute hexachlorobenzene in a reasonable time period.

The column that provided the best separation was No. 6, 1.8 m long X 2.0 mm ID glass with 1.5% OV-1 and 1.5% OV-225 on 80/100 Gas Chrom Q. The separation at two packed isothermal conditions is displayed in Figs. 1 and 2. The analysis temperature, retention time, and minimum detection level (MDL), calculated in an aqueous 1-liter sample and theoretical with model conditions, for each compound are listed in Table 5. Table 6 lists the GC conditions for the analysis of the chlorinated hydrocarbon data in Table 5. The calculated MDL is defined as the component concentration whose output signal is 10 times the base line noise.

TABLE 4. GC COLUMNS EVALUATED FOR CATEGORY 3 BY EC

GC Column No.	Packing	Description
1	OV-210 + OV-1	1:1 blend of 3% OV-1 and 3% OV-210 on 80/100 mesh AW-DMCS Chrom G; 1.8 m X 2.0 mm ID glass
2	DC-200	5% on 80/100 Chrom W-HP; 1.2 mm X 2.0 mm ID glass
3	OV-1	10% on 80/100 Gas Chrom Q; 1.8 mm X 2.0 mm ID glass
4	OV-225	3% on 80/100 Gas Chrom Q; 1.8 m X 2.0 mm ID glass
5	Bentone 34 + OV-101	5% Bentone 34 and 10% OV-101 on 100/120 Supelcoport 3 m X 2.0 mm glass
6	OV-225 + OV-1	1.5% OV-225 and 1.5% OV-1 on 80/100 Gas Chrom Q; 1.8 m X 2.0 mm ID glass

TABLE 5. GC RETENTION TIMES, ANALYSIS TEMPERATURES AND DETECTION LIMITS FOR CATEGORY 3 BY EC

Compounds	Analysis Temperature (°C)	Retention Time (min.)	MDL (μg/L)[a]	Aqueous Concentration (μg/L)[b]	Practical MDL in H_2O (μg/L)[c]
MDCB	75	5.30	9.0	0.009	0.9
PDCB	75	5.80	18.4	0.018	1.8
HCE	75	6.50	0.4	0.0004	0.04
ODCB	75	7.20	12.2	0.012	1.2
HCBD	75	15.10	1.2	0.001	0.1
TCB	75	16.70	5.8	0.006	0.5
HCCPD	160	1.60	0.8	0.001	0.1
2-CN	160	2.20	15.0	0.015	1.5
HCB	160	11.30	0.6	0.001	0.1

[a]Calculated MDL in μg/L (1 μL injection of standard).

[b]Calculated based on sample concentration of 1 liter to 1 ml (1 μL injection).

[c]Practical MDL based on IT Enviroscience experience.

COLUMN: 1.5% OV-2.25% OV-225 on Supelcoport
TEMPERATURE: 75°
DETECTOR: Electron Capture

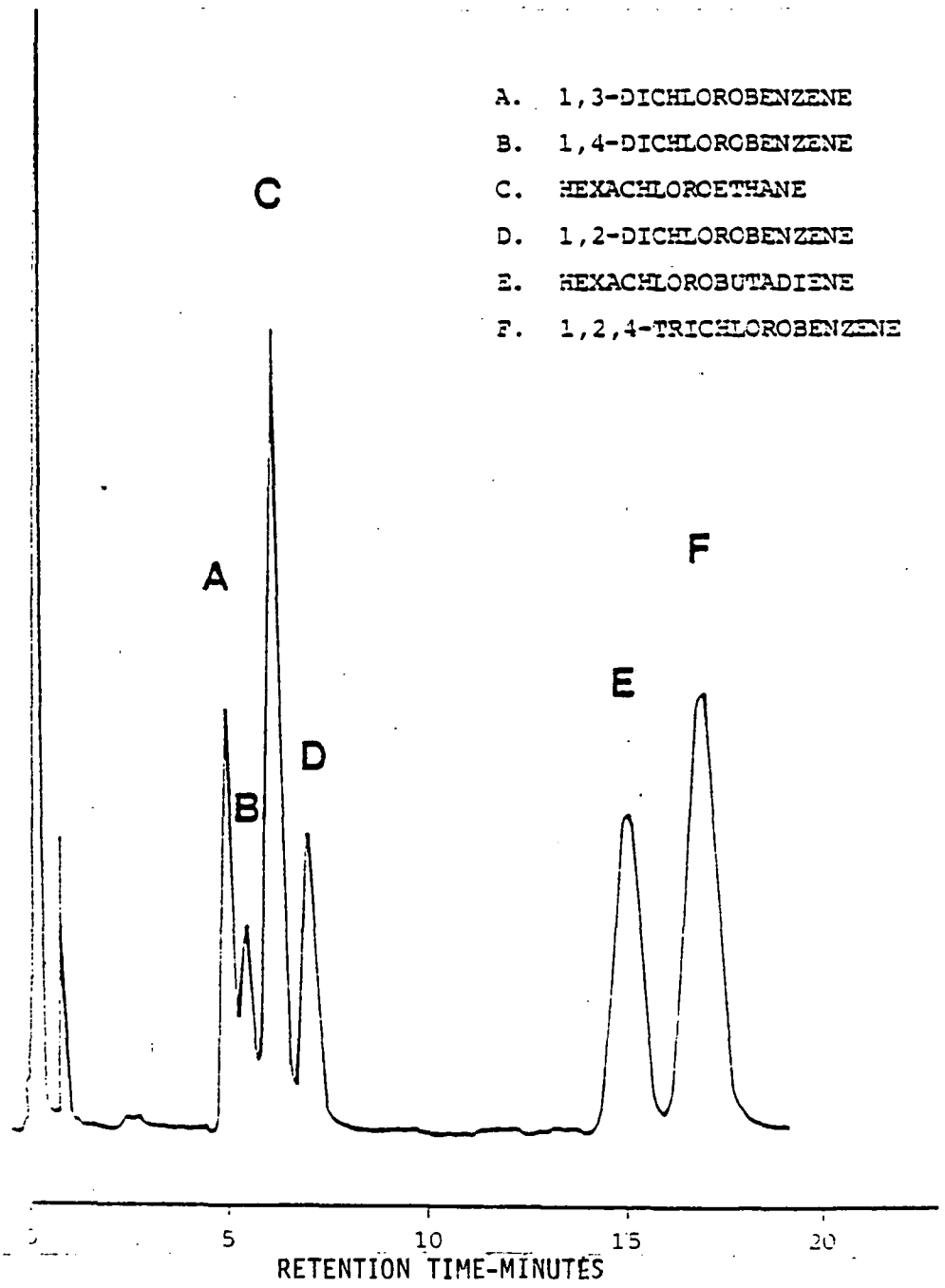

Figure 1. Gas Chromatogram of Chlorinated Hydrocarbons

COLUMN: 1.5% OV-1- 2.25% OV-225 on Supelcoport

TEMPERATURE: 165°C

DETECTOR: Electron Capture

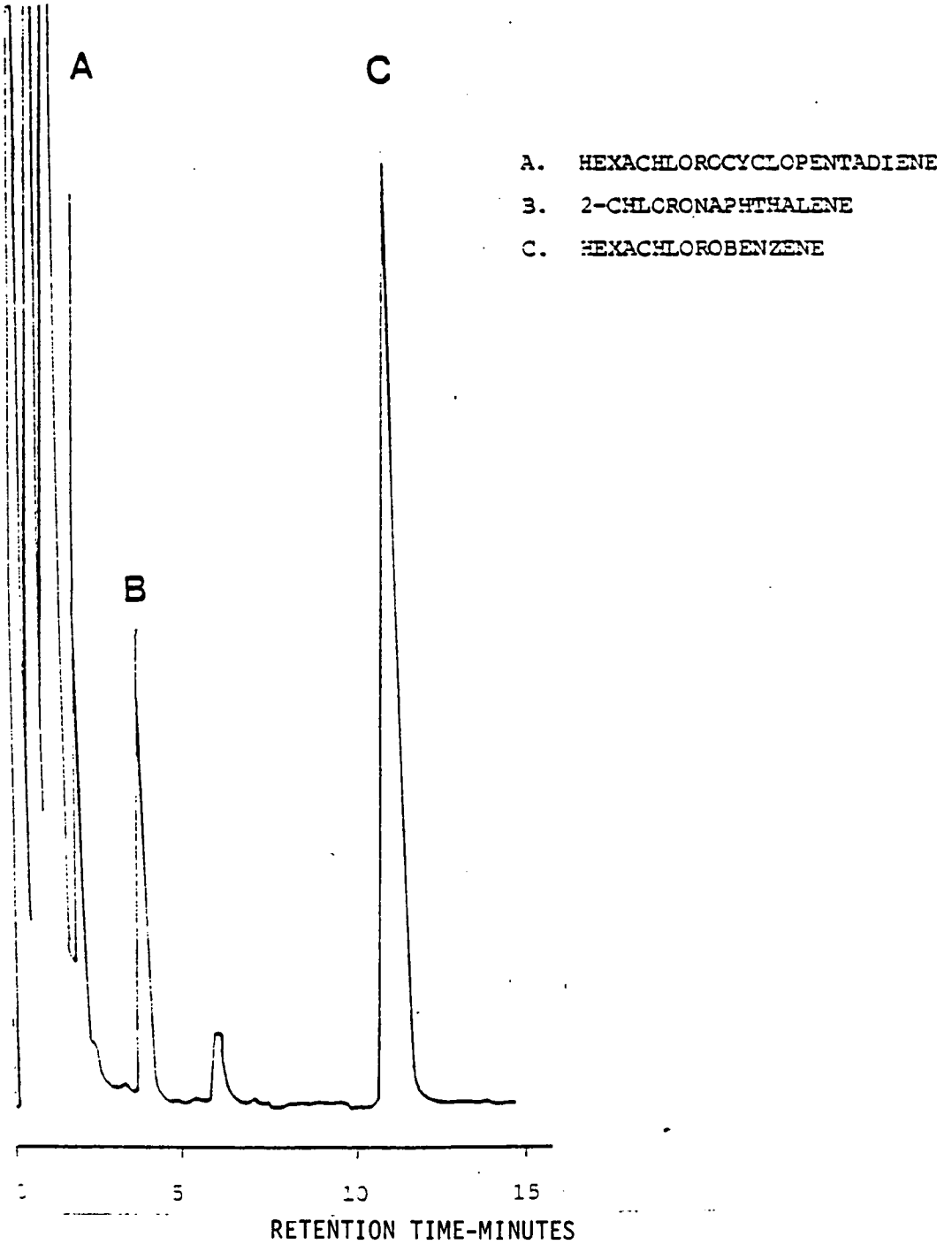

Figure 2. Gas Chromatogram of Chlorinated Hydrocarbons

TABLE 6. GC CONDITIONS FOR CATEGORY 3 BY EC

Electron Capture Detector Temperature, °C	300
Injector Temperature, °C	250
Oven Temperature, °C	75 and 160
Carrier Gas	5% Methane/95% Argon
Carrier Gas Flow Rate, cc/min	30

Duplicated parameters on a 3 m long column did not improve component separation, but merely increased the analysis time.

During the experiments, five OV-1/OV-225 columns were used, with no significant differences in the results observed between the columns. The one major problem encountered was the short one month column service life when the column was conditioned at temperatures in excess of 220°C.

Response and Linearity

The data on the response and linearity of the compounds at concentrations varying by three orders of magnitude for a flame ionization detector and four orders of magnitude for an electron-capture detector are presented in tabular form in Tables 7 and 8.

All Category-3 compounds were quite linear over the 10- to 1000-mg/L range by the FID detector with 2 µL injections. The EC detector was also evaluated for linearity by injection of 1 µL of a standard with the concentrations of the Category-3 compounds ranging from the approximate minimum detection level (MDL), 0.4 to 339 µg/L, to relatively high levels of 1 to 80 mg/L, depending on the compound. All the category compounds except hexachloroethane and hexachlorobutadiene were linear over the higher concentration, but the area response/unit concentration yields were lower than those at the lower concentrations. The other two compounds were linear, but the high concentration standards yielded a greater area response/unit concentration.

Resolution

The resolution of the peaks were calculated by the equation

$$R = 2d/(W_1 + W_2), \qquad (1)$$

where d = the distance between the two peaks' maxima and W = the width of the respective triangulated peaks' base-line. The resolution of the two most adjacent peaks, m-dichlorobenzene and p-dichlorobenzene, was 0.70. A value of 1.0 indicated that the peaks had been completely (98%) resolved.

Extraction Studies

The nine chlorinated hydrocarbons were extracted from water at a pH of 2, 7, and 10 with two different solvents. Before the extraction, the water

TABLE 7. RESPONSE AND LINEARITY FOR CATEGORY 3 BY FID

Compound	Concentration mg/l	Average Area Response mvsec	Compound	Concentration mg/l	Average Area Response mvsec
MDCB	13	10.5	TCB	15	28.7
	129	152		145	386
	1290	1687		1450	4043
PDCB	12	12.9	HCCPD*	49	48.4
	119	183		486	594
	1190	1855		4860	5779
HCE	9	13.4	2-CN*	14	32.1
	89	148		141	345
	890	1223		1410	3272
ODCB	13	19.2	HCB*	15	11.8
	131	252		149	118
	1310	2502		1490	1134
HCBD	17	15.4	ALDRIN*	28	31.6
	168	180		279	353
	1680	1826		2790	3521

Column - 1.8m long X 2mm ID glass packed with 1.5% OV-1/1.5% OV-225 on 80/100 mesh Gas chrom Q with nitrogen carrier gas at 30 mL/min flow rate. Column temperature is 75°C except where * indicates 160°C. Sample injection size is 2 μL.

TABLE 8. RESPONSE AND LINEARITY FOR CATEGORY 3 BY ECD

Compound	Concentration (μg/L)	Average Area (mm^2 X attn.)	Average Ht. (mm X Attn)	Compound	Concentration (μg/L)	Average Area (mm^2 X Attn)	Average Ht. (mm X Attn)
MDCB	6.2	37.2	13.8	TCB	5.2	128.2	17.8
	31	166.6	60.5		26	571.7	77.3
	310	1,468	534.4		260	6,263.2	798.4
	3,100	9,702.4	3,737.6		2,600	48,358.4	6,246.4
	30,090	76,595.2	31,232		26,10	433,664	54,579.2
PDCB	16.6	66.5	18	HCCPD*	1	36.5	40.5
	83	241.7	73.3		10	613.6	682.4
	830	2,016	672		100	7,648	8,499.2
	8,300	13,708.8	4.672		1,000	80,742.4	89,753.6
	83,200	104,550.4	39,424				
HCE	0.4	77.6	20.8	2-CN*	39	128.8	80.5
	2	214	70.3		390	994.4	686.4
	20	2,449.6	942.4		3,900	7,750.4	5,536
	200	37,222.4	14,310.4		39,000	57,907.2	1,369.6
	2,000	419,020.8	142,131.2				
ODCB	12.4	74.6	20.3	HCB*	1.5	231.2	82.5
	62	250.8	76		15	2,537.6	890.4
	620	2,584	728		150	30,240	10,080
	6,200	17,228.8	5,120		1,500	232,140.8	74,905.6
	62,400	148,377.6	44,339.2				
HCBD	0.6	58.8	10	ALDRIN*	3	1,070.3	139
	3	238.6	36.3		30	5,648.8	748
	30	2,903.2	492		300	42,214.4	6,208
	300	43,686.4	7,577.6		3,000	490,086.4	64,792
	3,300	469,708.8	71,168				

Column - 1.8m long X 2mm ID glass packed with 1.5% OV-1/1.5% OV-225 on 80/100 mesh gas chrom Q with 5% methane /95% argon carrier gas at 30mL/min flow rate. Column temperature is 75°C except where * indicated 160°C. Sample injection size is 1 μL.

was buffered by adding 50 mL concentrated buffer solution to 95 mL distilled deionized water in a 2 liter separatory funnel. The concentration buffer solutions used are listed in Table 9.

TABLE 9. SOLUTIONS NEEDED FOR PREPARATION OF pH BUFFERS 2, 7, and 10

pH	Solution[a]
2	74.6 g, KCl + 0.212 L, 1.0 N HCl
7	13.6 g, KH_2PO_4 + 0.059 L, 1.0 N NaOH
10	62.2 g, $NaHCO_3$ + 0.35 L, 1.0 N NaOH
10	62.0 g, H_3BO_3 + 0.88 L, 1 N NaOH

[a]Upon addition, dilute to 1 liter with distilled deionized water.

The pH-10 buffering scheme using 0.88 liter of 1 N NaOH and 62 grams of H_3BO_3 diluted to 1 liter with water proved to be unacceptable due to impurities and salt formation in the solvent concentrates. The water samples, after addition of appropriate buffer, were pre-extracted with 100 mL dichloromethane to minimize any remaining impurities in the water. Each pre-extracted, buffered water sample was injected with 50 μL of a standard containing approximately 2000 times the calculated MDL (see Table 10).

A total of 24 samples were spiked, 8 at each pH level. Of the eight samples at each pH, four were extracted with dichloromethane, and four were extracted with 15% dichloromethane—85% hexane by volume. Table 10 summarizes the extraction efficiencies and percent standard deviation of these results.

The pH-2 and pH-10 dichloromethane extractions yielded the best overall efficiencies, 76.6% and 71.3% respectively; however, the pH-2 extract contained fewer GC/EC responsive impurities; therefore pH 2 was selected as the extraction pH for this category of compounds.

The extraction data generated thus far were gathered from aqueous samples with individual component concentrations in the range of 0.2 to 3 μg/L. Additional data were gathered from another pH-2 dichloromethane extraction, utilizing aqueous component chlorinated hydrocarbon concentrations in the 2- to 300 μg/L range. Table 11 summarizes the extraction efficiencies at the two concentration levels. As seen in that table, the higher level extraction yielded an overall efficiency of 89.5%, a 12.9% increase over the lower level extraction. The standard deviations of the higher concentration extractions were smaller, indicating that a more reproducible extraction occurs at the higher levels.

TABLE 10. SUMMARY OF EXTRACTION EFFICIENCIES AND PERCENT STANDARD DEVIATION OF CATEGORY 3

pH	Solvent Type	Buffer[b]	MDCB	PDCB	HCE	ODCB	HCBD	TCB	HCCPD	2-CN	HCB
2	A	1	74.5[c]	95.7	82.7	119.3	76.4	82.4	36.5	70.2	72.0
			7.0[d]	9.8	8.3	24.0	7.3	7.3	18.8	13.7	18.5
2	B	1	77.3	85.4	81.9	89.1	80.0	85.7	44.2	76.6	69.0
			4.3	7.6	1.9	1.9	2.5	4.9	8.4	5.6	9.2
7	A	2	54.8	68.4	52.4	79.4	53.7	63.6	46.7	70.3	85.5
			5.4	17.4	10.2	31.3	11.0	8.6	10.3	4.3	8.3
7	B	2	52.6	62.1	53.0	69.2	48.0	55.7	45.7	69.7	75.9
			27.1	15.1	23.2	6.5	33.0	23.0	31.8	21.5	17.7
10	A	3	84.4	146.6[e]	80.2	273.8[e]	91.8	93.0	49.8	80.2	90.8
			7.0	2.1	13.7	2.1	10.2	8.6	21.3	9.8	16.4
10	B	4	68.8	88.3	75.6	95.8	67.7	72.6	81.0	60.0	85.7
			6.6	12.9	11.3	28.9	14.9	11.3	11.4	8.5	6.7
Spike Concentration (μg/L)			0.88	2.58	0.021	1.3	0.06	0.52	0.17	1.62	0.04

[a]Type A: 15% Dichloromethane/85% Hexane
Type B: Dichloromethane

[b]Buffer No. 1: HCl/KCl
Buffer No. 2: KH_2PO_4/NaOH
Buffer No. 3: H_3BO_3/NaOH
Buffer No. 4: $NaHCO_4$/NaOH

[c]Upper number is percent recovery.

[d]Lower Number is relative standard deviation.

[e]Interference: results invalid.

The extraction of the higher concentration aqueous sample yielded an average efficiency of 89.5%; there was relatively little interference as less sample concentration was required, and therefore a less sensitive GC attenuation setting could be used. The results also indicated the less volatile compounds could be recovered with greater efficiency then the more volatile ones. At this concentration level, the component extraction efficiency increased with decreasing compound volatility, as would normally be expected. Finally, the greatest improvement in efficiency was observed in the least volatile compounds, hexachlorocyclopentadiene, 2-chlorophthalene, and hexachlorobenzene.

TABLE 11. SUMMARY OF CATEGORY 3 EXTRACTION EFFICIENCIES AT TWO CONCENTRATIONS

Compound	Aq. Conc. (μg/L)	% Ext. Eff.	Aq. Conc. (μg/L)	% Ext. Eff.
MDCB	0.88	77.3	88	84.6
PDCB	2.58	85.4	258	86.7
HCE	0.021	81.9	2.1	87.1
ODCB	1.3	89.1	130	88.1
HCBD	0.06	80.0	6.0	99.9
TCB	0.52	85.7	52	91.3
HCCPD	0.17	44.2	17	90.2
2-CN	1.62	76.6	162	93.1
HCB	0.04	69.0	4	96.0

Preservation Studies

Twenty-four 1 liter samples were prepared by adding 50 ml of the appropriate buffer to 950 ml distilled, deionized water. The buffered water was pre-extracted with 100 ml of $MeCl_2$, the solvent decanted, and the water placed in clean 1 liter bottles. Half the samples were spiked with 2 ml of a solution containing 660 mg/L of Cl_2 in water to yield samples with 1.2 mg/L of Cl_2. All the samples were then spiked with 50 µL of a standard containing approximately 2000 times the minimum detection level of each of the nine chlorinated hydrocarbons. Half the samples were stored for seven days at 4°C, and half were stored for seven days at ambient temperature (23°C). All the samples were kept in the dark for the entire seven day period.

As shown in Table 12, very low recoveries were obtained under all conditions and many impurity peaks were seen on the chromatograms. The impurity peaks prevented quantification of almost all the pH-7 samples and all the pH-2 samples with 1.2 mg/L of Cl_2. The very low concentrations, 0.02 to 2.6 µg/L, made efficient recoveries improbable at best. Therefore, as in the extraction studies, pH-2 aqueous samples without Cl_2 were prepared at 100 times (2 µg/L to 260 µg/L) the level of the previous preservation samples. The percent loss due to preservation was calculated by subtracting the percent recovery obtained from the preservation sample from the extraction efficiency of the higher concentration extraction (Table 13).

As seen in Table 13, much better recoveries were obtained from the higher concentration study. At the higher concentration level, the percent loss due to preservation, for samples stored at ambient temperature, ranged from two to three times greater than when stored at 4°C. This information emphasizes the importance of refrigerating samples during shipment and storage.

An average 9.0% loss occurred in the samples stored at 4°C, which, although acceptable, demonstrates the importance of analyzing samples soon after they are taken. A longer term preservation study may be necessary in order to determine whether long storage periods result in additional loss of the chlorinated hydrocarbons.

The low level preservation study did determine that samples should be treated with 70 mg of sodium thiosulfate per liter of water to remove free Cl_2 from the samples as soon as they are taken, as the sample with free Cl_2 shows significantly larger and more numerous interference peaks when analyzed by GC/EC. Somewhat better recoveries were also obtained at pH 2 than at pH 10 from the low level samples, indicating that samples should be adjusted to pH 2 when they are taken.

Solvent Stability

Two standards with 2-propanol and 2-butanone as the solvents were prepared that contained approximately 2000 times the MDL of each of the nine chlorinated hydrocarbons. To each of the thirty 5 mL ampules was added 3 mL

TABLE 12. AVERAGE PERCENT LOSS DUE TO PRESERVATION

pH	Cl_2 Conc. (mg/L)	Temp. (°C)	Key*	MDCB	PDCB	HCE	ODCB	HCBD	TCB	HCCPD	2-CN	HCB
2	0	Amb.	A	77.3	85.4	81.9	89.1	80.0	85.7	44.2	76.6	69.0
			B	23.1	26.9	11.3	27.1	2.5	20.7	7.5	32.9	66.6
			C	54.2	58.5	70.6	62.1	77.5	65.0	36.7	43.7	2.4
2	0	4	A	77.3	85.4	81.9	89.1	80.0	85.7	44.2	76.6	69.0
			B	25.3	30.7	10.8	32.5	3.8	27.0	10.9	40.1	46.6
			C	52.0	54.7	71.1	56.6	76.2	58.7	33.3	36.5	22.4
7	1.2	Amb.	A	52.6	62.1	53.0	69.2	48.0	55.7	45.7	69.7	75.9
			B							22.7	51.1	34.3
			C							23.0	18.6	41.6
7	1.2	4	A	52.6	62.1	53.0	69.2	48.0	55.7	45.7	69.7	75.9
			B							7.4	50.6	34.1
			C							38.3	19.1	41.8
10	1.2	Amb.	A	68.8	88.3	75.6	95.8	67.7	72.6	81.0	60.0	85.7
			B	20.2	22.3	31.1	26.8	26.0	24.8	14.5	41.4	46.5
			C	48.6	66.0	44.5	69.0	41.7	47.8	66.5	18.6	39.2
10	1.2	4	A	68.8	88.3	75.6	95.8	67.7	72.6	81.0	60.0	85.7
			B	13.9	15.3	25.0	17.8	23.0	19.3	5.0	36.4	22.1
			C	54.9	73.0	50.6	78.0	44.7	53.3	76.0	23.6	63.6
10	0	Amb.	A	68.8	88.3	75.6	95.8	67.7	72.6	81.0	60.0	85.7
			B	15.4	16.3	26.4	20.2	24.6	16.1	9.5	21.8	38.6
			C	53.4	72.0	49.2	75.6	43.1	56.5	71.5	38.2	47.1
10	0	4	A	68.8	88.3	75.6	95.8	67.7	72.6	81.0	60.0	85.7
			B	11.0	10.3	21.8	17.3	15.7	7.3	2.7	10.4	16.7
			C	57.8	78.0	53.8	78.5	52.0	65.3	78.3	49.6	69.0
Spike Concentration (μg/L)				0.88	2.58	0.021	1.3	0.06	0.052	0.17	1.62	0.04

*A = Percent extraction efficiency
B = Recovery after seven days
C = Loss due to preservation

TABLE 13. AVERAGE PERCENT LOSS AT TWO CONCENTRATIONS DUE TO PRESERVATION AT pH-2 WITHOUT Cl_2

Rel. Conc. (μg/L)	Temp. (C)	Key*	MDCB	PDCB	HCE	ODCB	HCBD	TCB	HCCPD	2-CN	HCB
1	4	A	77.5	85.4	81.9	89.1	80.0	85.7	44.2	76.6	69.0
		B	25.3	30.7	10.8	32.5	3.8	27.0	10.9	40.1	46.6
		C	52.0	54.7	71.1	56.6	76.2	58.7	33.3	36.5	22.4
	Amb.	A	77.3	85.4	81.9	89.1	80.0	85.7	44.2	76.6	69.0
		B	23.1	26.9	11.3	32.5	2.5	20.7	7.5	32.9	66.6
		C	54.2	58.5	70.6	56.6	77.5	65.0	36.7	43.7	2.4
100	4	A	84.6	86.7	87.1	88.1	88.8	91.3	90.2	93.1	96.0
		B	78.6	81.7	69.7	84.6	71.3	87.5	72.0	90.8	88.4
		C	6.0	5.0	17.4	3.5	17.5	3.8	18.2	2.3	7.6
	Amb.	A	84.6	86.7	87.1	88.1	88.8	91.3	90.2	93.1	96.0
		B	69.5	73.2	54.9	76.1	46.5	77.3	53.0	84.4	67.1
		C	15.1	13.5	32.2	12.0	42.3	13.0	37.2	8.7	28.9

*Type A: Percent extraction efficiency
Type B: Recovery after seven days
Type C: Loss due to preservation

TABLE 14. AVERAGE PERCENT CHANGE OF CATEGORY 3 IN 2-PROPANOL

Compound	Day 0	Day 30	Day 60	Day 90
MDCB	+ 1.7	+ 4.5	-38.0*	- 2.7
PDCB	+ 1.0	+23.3*	- 1.4	- 1.1
HCE	0	+13.3	-31.0	-32.6
ODCB	0	+13.8	-17.8	+ 6.6
HCBD	+ 5.0	+ 8.5	-70.3*	-29.4
TCB	+ 3.9	+19.4	+15.1	+ 6.3
HCCPD	-14.8	-63.9	-72.6	-85.1
2-CN	+ 4.0	-15.5	+24.2	+7.2
HCB	- 0.8	+29.1	-46.5*	-12.6

*Variation in data possibly due to an error in standard preparation.

TABLE 15. AVERAGE PERCENT CHANGE OF CATEGORY 3 IN 2-BUTANONE

Compound	Day 0	Day 30	Day 60	Day 90
MDCB	- 3.5	- 4.0	+ 8.5	- 4.0
PDCB	- 3.3	+14.0	+ 2.4	- 5.0
HCE	-10.1	+10.1	+ 7.3	- 2.4
ODCB	- 8.9	+11.1	+ 2.8	-17.3
HCBD	- 7.6	+13.6	+ 1.7	- 6.8
TCB	- 4.0	+ 6.7	+ 3.4	- 4.9
HCCPD	- 0.3	-25.3	-30.3	-62.8
2-CN	+ 0.3	+16.4	+ 2.4	+ 4.3
HCB	- 0.8	+ 2.8	-54.6*	+ 4.5

*Variation in data possibly due to an error in standard preparation.

of the 2-propanol standard; 30 other ampules were similarly filled with the 2-butanone standard. The ampules were then cooled to 4°C to minimize the possibility of vapor ignition, flame sealed, placed in open test tube racks, and stored on a bench top under normal laboratory lighting conditions (fluorescence) for the duration of the study. Three ampules of each standard were opened immediately after they were flame sealed and were analyzed versus the standards used to fill the ampules. On subsequent 30 day intervals, up to 90 days, three ampules of each standard were opened and analyzed versus a freshly prepared standard in the same solvent. Tables 14 and 15 summarize the solvent stability of the Category-3 chlorinated hydrocarbons.

Table 14 demonstrates that 2-propanol is unsuitable as a solvent for the chlorinated hydrocarbons. The variability in the data cannot be due to experimental technique, particularly in view of the significantly lower level of variability found in the 2-butanone samples (Table 15). It is evident from a comparison of Tables 14 and 15 that 2-butanone is the superior solvent for preparing and storing chlorinated hydrocarbon standards. All component concentrations except two remained within ±7% of the original concentrations after 90 days.

Hexachlorocyclopentadiene (HCCPD) concentrations decreased so rapidly in both solvent systems that a separate stability study had to be made to define the cause of its high decomposition rate.

Table 16 illustrates that the decomposition of HCCPD occurred even in the absence of the other category compounds, indicating that the decomposition is not affected by them. Since the HCCPD priority-pollutant standard was prepared and shipped in dichloromethane, an additional stability study was performed that yielded a decomposition similar to that previously noted. In this study the HCCPD stock solution in dichloromethane was stored in ampules after being flame sealed and in 20 mL glass scintillation vials having Teflon lined caps. The later storage scheme was incorporated as a control related to HCCPD losses due to the flame sealing process. The results are given in Table 17.

TABLE 16. AVERAGE PERCENT CHANGE OF HEXACHLOROCYCLOPENTADIENE IN 2-PROPANOL AND 2-BUTANONE

Day	0	3	10	36
2-Propanol	+0.9	-9.8	-27.1	-63.4
2-Butanone	+1.2	-5.6	-18.0	-23.6

TABLE 17. AVERAGE PERCENT CHANGE OF HEXACHLOROCYCLOPENTADIENE IN DICHLOROMETHANE

Day	0	3	10	30	45
Flame Sealed Ampul	-2.48	-9.2	-9.04	-38.01	-66.87
Scintillation Vial	0.00	-2.2	-13.83	-10.66	-23.92

The other significant concentration change occurred with o-dichlorobenzene, which, although essentially unchanged at day 60, decreased by 17.3% by day 90. Subsequent analysis, versus a fresh standard, on day 150 yielded a change of -30.3% which confirmed a decrease in concentration over time.

The results of this study indicated that except for hexachlorocyclopentadiene a standard containing all the Category-3 compounds could be prepared in 2-butanone and stored in the presence of fluorescent light at room temperature for 60 days with a maximum change in any compound of less than nine percent. Refrigeration of the standards would undoubtedly increase their usable life. The change in hexachlorocyclopentadiene concentration discussed above indicates that standards containing this compound should be freshly prepared as needed.

Clean Up Studies

Initial clean up experiments involved the evaluation of both Florisil and aluminia as possible vehicles for sample extract clean up.

Florisil clean up experiments were accomplished using columns prepared by placing 12 grams of Florisil (activated at 130°C and corrected for lauric acid value) into a 300 mm long X 10 mm ID chromatographic column. After the Florisil was settled, with gentle tapping, approximately 1 gram of anhydrous granular sodium sulfate was added to the top. The column was then pre-eluted with 100 mL of petroleum ether after which a 10 mL aliquot of hexane, containing the compounds of interest at approximately 1000 times the calculated MDL (Table 5), was quantitatively transferred into the column. The column was then eluted using in order: 200 mL petroleum ether, 200 mL 6% ethyl ether in petroleum ether, 200 mL 15% ethyl ether in petroleum ether, 200 mL 50% ethyl ether in petroleum ether, and 200 mL of ethyl ether. Each of the eluates were collected and analyzed after being concentrated to 10 mL using Kuderna-Danish evaporators. The major portion of each of the compounds of interest were eluted in the single 200 mL petroleum ether eluate. Recovery data are given in Table 18.

TABLE 18. AVERAGE PERCENT RECOVERY OF CATEGORY 3 AFTER FLORISIL CLEAN UP

Compound	First Fraction (200 mL petroleum ether) Percent Recovery
MDCB	87
PDCB	89
HCE	85
ODCB	90
HCBD	89
TCB	94
HCCPD	100
2-CN	100
HCB	95

Aluminia clean up experiments were accomplished using columns prepared by placing 12 grams of alumina (activated at 400°C) into a 300 mm long X 10 mm ID chromatographic column. After the alumina was settled with gentle tapping, approximately 1 gram of anhydrous granular sodium sulfate was added to the top. The column was then pre-eluted with 150 mL of pesticide grade hexane after which a 10 mL aliquot of hexane, containing the compounds of interest at approximately 1000 times the calculated MDL (Table 5), was quantitatively transferred into the column. The column was then eluted using three successive 50 mL hexane eluates. The combined first two eluates' (100 mL) recovery data are given in Table 19.

TABLE 19. AVERAGE PERCENT RECOVERY OF CATEGORY 3 AFTER ALUMINA CLEAN UP

Compound	100 mL Hexane Fraction Percent Recovery
MDCB	101
PDCB	105
HCE	75
ODCB	88
HCBD	77
TCB	99
HCCPD	100
2-CN	92
HCB	93

The results of these experiments (Tables 18 and 19) indicated that the recovery of the Category-3 chlorinated hydrocarbons is quite similar using either Florisil or alumina columns.

Florisil was selected as the separation vehicle for the wastewater application because it is commonly used in most laboratories for the clean up of pesticides and because all the components are eluted in a single eluent of 200 mL of petroleum ether. Although not used in this study, alumina stands as an acceptable alternative to Florisil.

Wastewater Application

In this section the practical use of the described methodology is discussed as it relates to an environmental sample. Four Category-3 wastewater samples were analyzed by the methodology developed in this study. Upon the initial analysis of the first wastewater sample, the need for a clean up scheme was evident from the increased number of interferences indicated. The four wastewater samples were analyzed to evaluate the method. The background concentrations of the compounds of interest and the wastewater sample descriptions are listed in Table 20.

In subsequent analyses, the precision and accuracy of the method were developed based on a spiked distilled deionized water sample and a spiked wastewater sample (Plastic's Industry, 15-C1-05-44) determined to be "worst case" because it had the greatest number of interferences before clean up. Both of these samples were analyzed after being carried through the complete Florisil clean up scheme (Figs. 3 through 6). See analytical method, Appendix A.

Accuracy was based on percent recovery determined from the analysis of distilled deionized water and wastewater sample (Plastic's Industry, 15-C1-05-44) both of which were spiked with the compounds of interest. These two samples were analyzed using triplicate extractions of each and triplicate injections of each extract. Both mean recoveries and mean concentrations along with standard deviation were calculated using the critical-T analysis to discard outliers. The accuracy data and method precision determined from the analysis of the two samples are displayed in Tables 21 through 24.

In conclusion, when applied to wastewater samples, the method was demonstrated to be an acceptable reproducible and workable means by which quantitative data for industrial and municipal effluents can be gathered.

TABLE 20. RESULTS FROM ANALYSIS OF WASTEWATER APPLICATION SAMPLES[a]

Sample Number[b]	MDCB	PDCB	HCE	ODCB	HCBD	TCB	HCCPD	2-CN	HCB
A[c]	ND	ND	ND	ND	ND	ND	ND	ND	ND
B	26	120	d	76	1.9	1.0	0.99	ND	0.35
C	8	4	ND	13	ND	2.5	0.30	ND	ND
D	ND	ND	ND	ND	ND	ND	ND	ND	ND

[a]Concentration expressed in μg/L without correction for recovey data.

[b]A. "Effluent from a Plastics Industry Wastewater Treatment Plant," received from S. Bernotas, 8/24/78.

B. "Plastics Industry" (15-05-Cl-44; Final Effluent Grab), received from R. Libby, 9/05/78.

C. "Municipal Wastewater - Knoxville Third Creek Station."

D. "Final Effluent Grab - 12/12/78," received from Midwest Research Institute, Houston, TX, 12/14/78.

[c]analysis performed after Florisil clean up.

[d]not quantifiable (HCE peak not resolved from PDCB peak).

TABLE 21. METHOD ACCURACY EXPRESSED AS PERCENT RECOVERY BASED ON SPIKED, DISTILLED, DEIONIZED WATER

Sample	MDCB	PDCB	HCE	ODCB	HCBD	TCB	HCCPD	2-CN	HCB
1	82	72	75	76	72	96	60	90	63
2	77	72	75	83	73	89	60	94	65
3	63	70	75	81	61	78	57	89	67
$\bar{x}$	74	71	75	80	69	88	59	91	65
s	9.8	1.1	0.0	3.5	3.6	6.7	9.1	1.7	2.6
Spike concentration (μg/L)	0.90	2.6	0.04	1.3	0.06	0.52	0.12	1.6	0.21

$\bar{X}$ = Mean percent recovery
s = Standard deviation of percent mean recovery

COLUMN: 1.5% OV-1+ 1.5% OV-225 On Gas Chrom Q

TEMPERATURE: 75°C

DETECTOR: Electron Capture

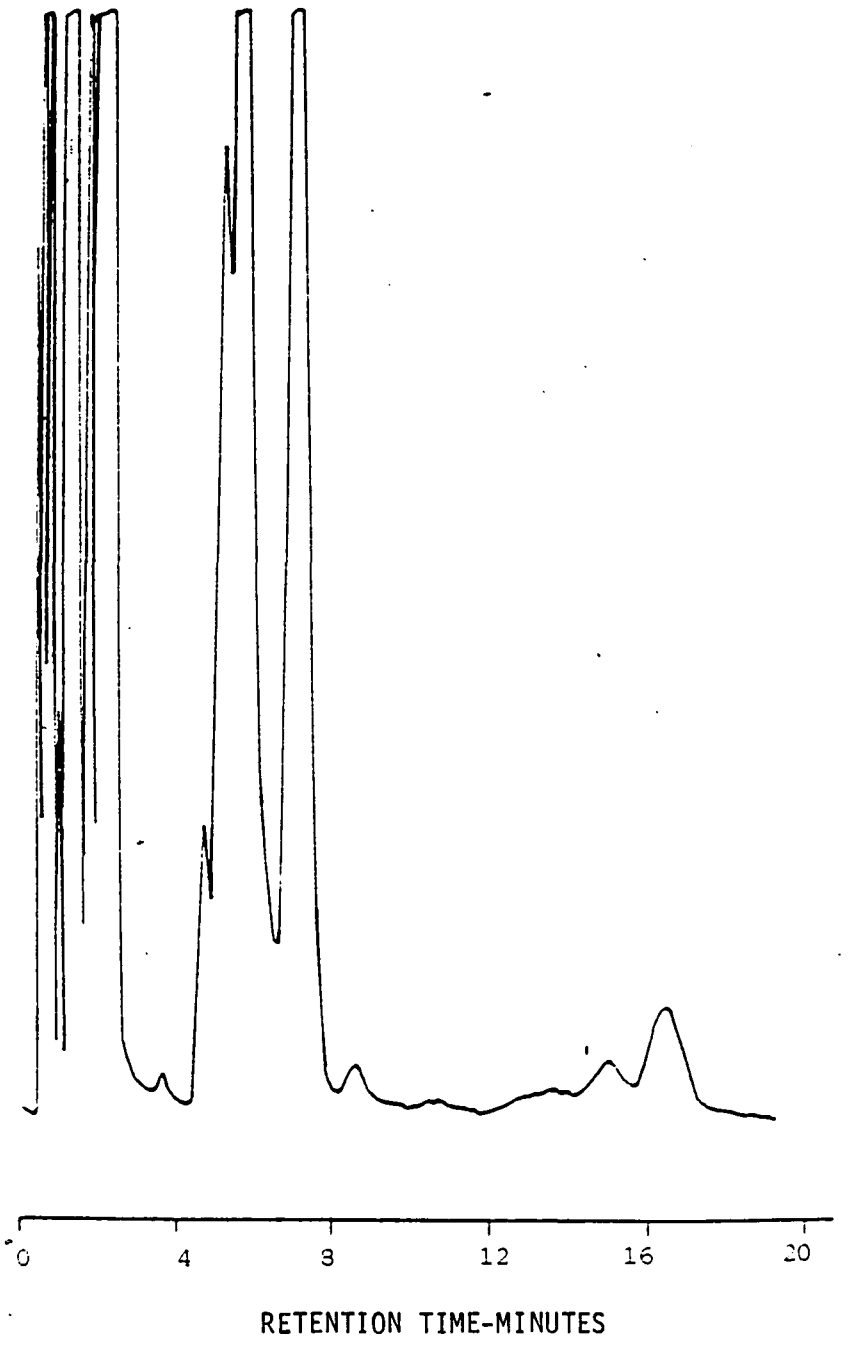

Figure 3. Gas Chromatogram of Wastewater (15-Cl-05-44) Extract After Clean Up

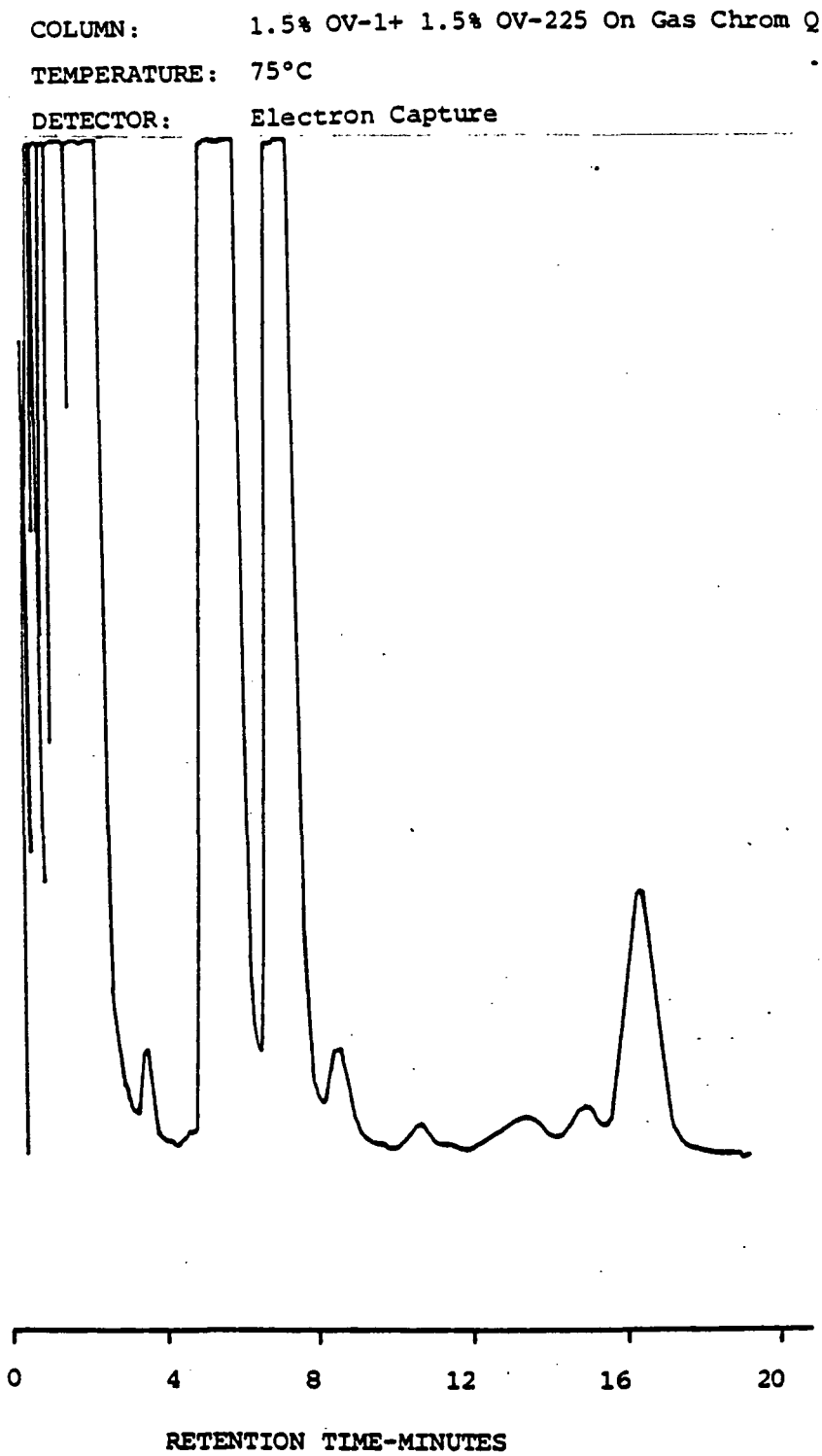

Figure 4. Gas Chromatogram of Spiked Wastewater (15-C1-05-44) Extract After Clean Up

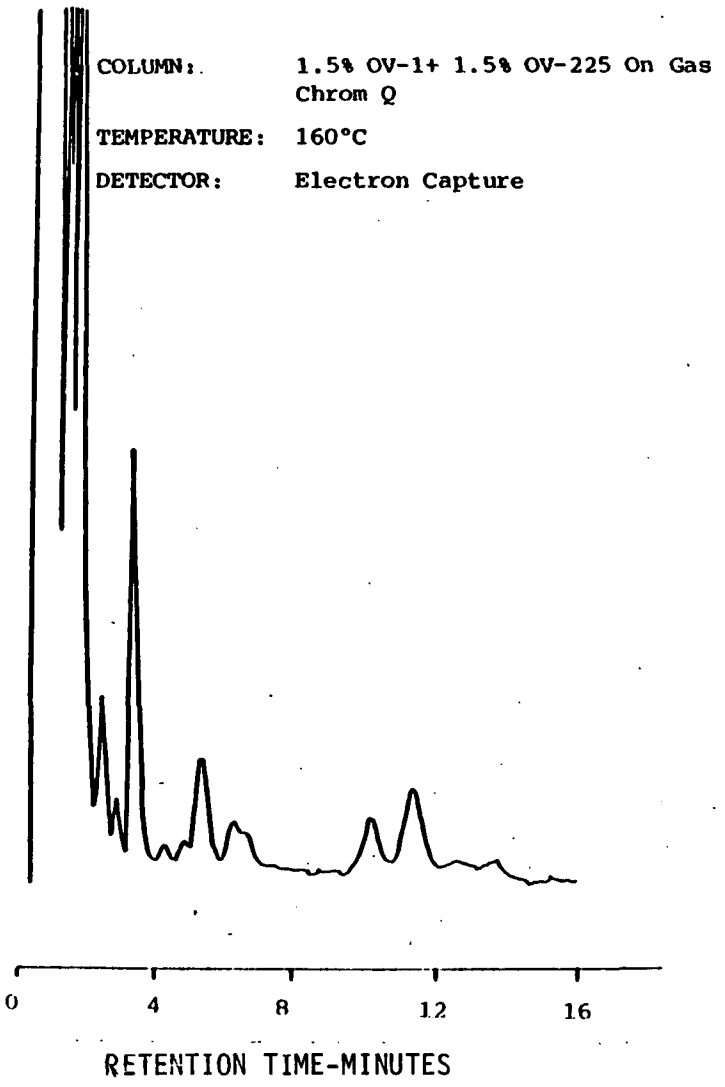

Figure 5. Gas Chromatogram of Wastewater (15-Cl-05-44) Extract After Clean Up

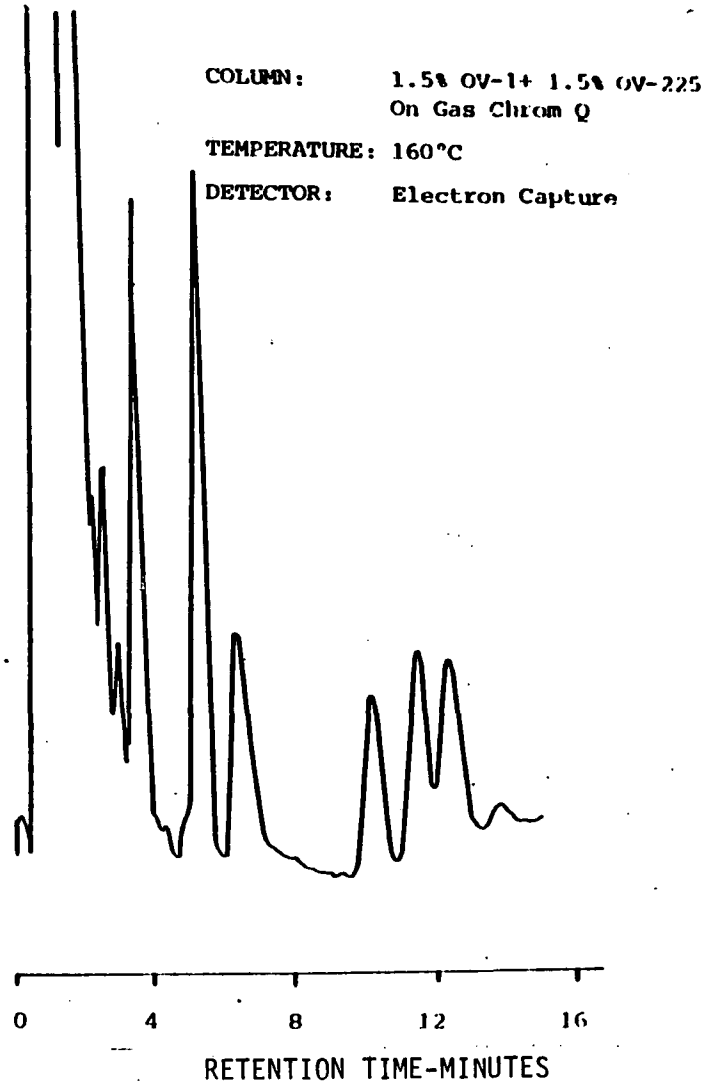

Figure 6. Gas Chromatogram of Spiked Wastewater (15-Cl-05-44) Extract After Clean Up

TABLE 22. METHOD PRECISION EXPRESSED AS CONCENTRATION (μg/L) BASED ON SPIKED, DISTILLED, DEIONIZED WATER

Sample	MDCB	PDCB	HCE	ODCB	HCBD	TCB	HCCPD	2-CN	HCB
1	0.74	1.87	0.030	0.99	0.043	0.50	0.12	1.44	0.13
2	0.69	1.87	0.034	1.09	0.044	0.50	0.12	1.50	0.13
3	0.57	1.82	0.033	1.06	0.037	0.41	0.11	1.42	0.13
x[a]	0.90	2.6	0.04	1.30	0.06	0.52	0.12	1.6	0.21
$\bar{x}$[b]	0.67	1.85	0.032	1.05	0.041	0.47	0.12	1.45	0.13
S[c]	0.09	0.03	0.002	0.05	0.004	0.05	0.006	0.04	0.0

[a]x = Concentration of spike added to the 1 liter sample.

[b]$\bar{x}$ = Mean concentration recovered.

[c]S = Standard deviation of the mean concentration.

Results based on triplicate injection of each sample.

TABLE 23. METHOD ACCURACY EXPRESSED AS PERCENT RECOVERY BASED ON A SPIKED, INDUSTRIAL, WASTEWATER SAMPLE PLASTIC'S INDUSTRY, 15-C1-05-44)

Sample	MDCB	PDCB	HCE	ODCB	HCBD	TCB	HCCPD	2-CN	HCB
1	75	79	a	76	50	66	111	62	73
2	103	105	a	104	135	96	84	45	53
3	107	110	a	114	91	93	169[b]	131[b]	158[b]
$\bar{x}$	95	98		98	92	85	97	53	63
S	17	17		20	43	17	19	12	14
True concentration (μg/L)	27	120		78	2.0	1.5	1.2	1.6	0.55

$\bar{x}$ = Mean percent recovery.
S = Standard deviation of percent recovery.

[a]Not quantifiable (HCE peak not resolved from PDCB peak).

[b]Rejected by critical T value test.

TABLE 24. METHOD PRECISION EXPRESSED AS CONCENTRATION (μg/L) BASED ON A SPIKED, WASTEWATER SAMPLE (PLASTIC'S INDUSTRY, 15-Cl-05-44)

Sample	MDCB	PDCB	HCE	ODCB	HCBD	TCB	HCCPD	2-CN	HCB
1	20.20	95.11	f	59.25	0.99	1.01	1.32	0.99	0.40
2	27.85	126.56	f	80.94	2.64	1.47	1.00	0.72	0.29
3	28.95	132.62	f	88.30	1.79	1.43	2.01	2.09	0.87
C_2[a]	26.11	117.89	f	76.22	1.90	1.01	0.99	ND	0.35
C_1[b]	0.90	2.60	0.04	1.30	0.06	0.52	0.20	1.60	0.20
C[c]	27.01	120.40	-	77.52	1.96	1.53	1.19	1.60	0.55
$\bar{x}$[d]	25.67	118.10	-	76.16	1.81	1.30	1.44	1.27	0.52
s[e]	4.8	20.1	-	15.1	0.83	0.25	0.52	0.73	0.31

[a] C_2 = Concentration of the unspiked sample in μg/L.

[b] C_1 = Concentration of the spike added to the sample in μg/L.

[c] C = Concentration of the spiked sample.

[d] $\bar{x}$ = Mean concentration of spiked sample recovered.

[e] s = Mean standard deviation.

[f] Not quantifiable. (HCE peak not resolved from PDCB peak).

Results based on triplicate injection of each sample.

SECTION 5

SUPPLEMENTAL SEVEN DAY PRESERVATION STUDY - CATEGORY 3

INTRODUCTION

In the development and application of this test procedure, IT Enviroscience carried out preservation studies under different conditions for the subject compounds in clean distilled water only. The purpose of this brief study was to carry out a seven day preservation study of the subject compounds spiked into a real world wastewater following the preservation techniques outlined in the resultant EPA Method 612 - Chlorinated Hydrocarbons (Appendix A).

EXPERIMENTAL

The wastewater selected for use in this study was a fresh sample of effluent wastewater from a Class B refinery producing gasoline, kerosene, jet fuel, heating oil, heavy fuels, and LPG. The wastewater treatment system consists of API oil/water separators, rapid sand filters, equalization tank, rotating biological contactors, and final clarifiers. Total flow from the plant is 3 to 4 MGD.

The pH of eight 1 liter samples was checked and found to be 6.5, which is within the 6 to 8 range that samples should be adjusted to for preservation, so no pH adjustment was necessary. Six of the eight sample bottles were each spiked with the subject compounds at concentrations ranging from 13 to 300 µg/L.

The bottles were mixed for 15 minutes, and three of the spiked sample bottles and one unspiked sample blank were analyzed following EPA Method 612. The remaining bottles were refrigerated for seven days at 4°C and then analyzed by the sample procedures. The results appear as Day 0 and Day 7 in Table 25.

DISCUSSION

The results presented in Table 25 represent the mean values from three spiked samples run on Day 0 and Day 7. The Day 0 recovery data are similar to spiked wastewater recovery data presented in Section 4 of this report with hexachloroethane and 1,2,4-trichlorobenzene having lower recoveries than previously. The Day 7 data show that the maximum loss after seven days was 52% for 1,2,4trichlorobenzene and the minimum loss was 9% for hexachlorobutadiene. Overall, these losses are less than the previous data indicated.

TABLE 25. SEVEN DAY PRESERVATION[a] STUDY OF CHLORINATED HYDROCARBONS IN WASTEWATER

Compound	Spike Level (μg/L)	Mean Concentration[b] (μg/L)		Mean % Recovery[b]	
		Day 0	Day 7	Day 0	Day 7
MDCB	204	92.0	57.8	45	28
PDCB	288	261	192	91	67
HCE	12.8	5.2	3.0	41	23
ODCB	298	227	167	76	56
HCBD	31.2	24.0	21.8	77	70
TCB	188	78.2	37.0	42	20
2-CN	268	241	163	90	61
HCB	14.9	10.2	6.2	69	42

[a]Preservation technique outlined in EPA Method 612.

[b]Results based on triplicate sample analysis.

SECTION 6

DEVELOPMENT OF METHOD DETECTION LIMITS

INTRODUCTION

A study was performed to determine method detection limits (MDL) for the chlorinated hydrocarbons. Previous practice was to determine the detection limits by either estimation or by calculation based on a specific concentration giving a signal equivalent to a specific signal/noise ratio. A detection limit determined by these previously employed techniques may not be achievable for the compounds of interest in either laboratory prepared water or matrices encountered in environmental samples.

The EPA developed a method to determine the MDL, defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is greater than zero. Three sample matrices were used in this study for the MDL determination. Based on the MDL, determined in this study, analytical curves were established for each of the eight chlorinated hydrocarbons in interference-free water.

EXPERIMENTAL

The MDL was determined for the chlorinated hydrocarbons in interference-free water and two industrial wastewaters. Seven separate replicate spiked samples were prepared for each of the three matrices. Spiking levels were based on experience and instrumental limitations.

All dosed samples were analyzed by the test method developed during the research program and described earlier in this report as well as in Appendix A.

Based on the MDL in intereference-free water, duplicate aliquots of interference-free water were spiked at 4, 7, 10, 100, and 1000 times the concentration level of the established MDL for each of the eight chlorinated hydrocarbons. The results were used to establish analytical curves.

RESULTS

Method Detection Limits -- Interference-Free Water

Table 26 lists data for the chlorinated hydrocarbons recovered from the seven separate replicate spiked aliquots of interference-free water. Included are the spike values, average recovered values, standard deviations, MDL values, and ratios of spike to MDL values for each chlorinated hydrocarbon.

TABLE 26. MDL OF CHLORINATED HYDROCARBONS IN INTERFERENCE-FREE WATER

Sample No.	MDCB	PDCB	HCE	ODCE	HCBD	TCB	2-CN	HCB
1	5.76	5.33	.024	6.75	.016	.177	3.23	.182
2	7.03	6.75	.032	7.56	.021	.180	3.74	.216
3	6.32	5.90	.035	7.20	.036	.184	3.23	.205
4	6.57	6.19	.027	7.50	.019	.157	3.68	.210
5	6.49	6.08	.047	7.32	.040	.204	4.00	.228
6	6.37	6.01	.050	7.25	.042	.206	3.77	.208
7	6.29	5.82	.036	7.17	.036	.173	3.36	.187
Method MDL Data								
Spiked Value (μg/L)	6.34	6.06	.043	6.26	.039	.198	3.88	.206
Average Recovered (μg/L) (n=7)	6.40	6.01	.027	7.20	.030	.183	3.57	.205
Standard Deviation	.378	.426	.0097	.364	.0112	.017	.300	.016
MDL = 3.143 X Standard Deviation	1.19	1.34	.03	1.14	.03	.05	.94	.05
Ratio = Spike/MDL	5	5	1	5	1	4	4	4

All concentrations are actual recovered values of μg/L based on water.

The Analytical Curve -- Interference-Free Water

Duplicates of five one-liter samples of deionized/distilled water were each spiked with specific concentrations of the eight chlorinated hydrocarbons. These specific concentrations represented 4, 7, 10, 100, and 1000 times the MDL. The concentrations are listed in Table 27.

TABLE 27. CONCENTRATION OF CHLORINATED HYDROCARBONS IN WATER

Compound	4 X MDL	7 X MDL	10 X MDL	100 X MDL	1000 X MDL
MDCB	4.78	8.36	11.9	119	1190
PDCB	5.35	9.37	13.4	134	1340
HCE	0.12	0.21	0.30	2.99	29.9
ODCB	0.59	8.04	11.5	115	1150
HCBD	0.14	0.24	0.34	3.41	34.1
TCB	0.22	0.39	0.56	5.60	56.0
2-CN	3.75	6.57	9.38	93.8	938
HCB	0.20	0.35	0.50	5.04	50.4

Concentration units - µg/L

Some of the sample extracts, representing samples that were prepared at 4, 7, 10, 100, and 1000 times the MDL, had to be diluted before analysis, because of the limited linear response range for electron capture detectors. For this reason, the analytical curve data can only be displayed as concentration spiked versus concentration recovered. The data are summarized in Tables 28-30.

Method Detection Limit - Industrial Wastewaters

The original spiking level in each of the two industrial wastewaters was determined from a combination of the results obtained for the MDL in interference-free water and the background analysis of the unspiked wastewaters. Tables 31 and 32 list the actual recovery values from the seven separate replicate spiked aliquots of industrial wastewater Codes COD-B and DCA-A along with spike values, average recovered values, the standard deviations, MDL values, and ratios of spike to MDL values.

DISCUSSION

The method detection limits determined for deionized/distilled water compare favorably with these labeled "Practical MDL" reported in Table 5.

Excluding the set of data points representing 1000 X MDL, the analytical curves for the chlorinated hydrocarbons in inteference-free water are linear. The recovery of all eight chlorinated hydrocarbons was lower at the concentration representing 1000 X the MDL. The reason for the low recovery at this concentration is unknown. The linearity of the electron capture

TABLE 28. ANALYTICAL CURVE DATA FOR 1,3-DICHLOROBENZENE, 1,4-DICHLOROBENZENE, AND HEXACHLOROETHANE IN INTERFERENCE-FREE WATER

1,3-Dichlorobenzene			1,4-Dichlorobenzene			Hexachloroethane		
Spike µg/L	Recovered µg/L	% Recovery	Spike µg/L	Recovered µg/L	% Recovery	Spike µg/L	Recovered µg/L	% Recovery
4.78	4.27	89	5.35	4.86	91	0.12	.09	75
4.78	4.42	92	5.35	4.96	93	0.12	.10	83
8.36	7.31	87	9.37	8.28	88	0.21	.18	87
8.36	7.12	85	9.37	8.26	88	0.21	.18	87
11.9	11.2	94	13.4	11.5	86	0.30	.29	97
11.9	12.2	102	13.4	14.2	106	0.30	.32	107
119	103	86	134	121	91	2.99	2.46	82
119	108	90	134	126	94	2.99	2.62	88
1190	946	79	1340	1120	84	29.9	19.8	66
1190	848	71	1340	1020	76	29.9	16.0	54

TABLE 29. ANALYTICAL CURVE DATA FOR 1,2-DICHLOROBENZENE, HEXACHLOROBUTADIENE, AND 1,2,4-TRICHLOROBENZENE IN INTERFERENCE-FREE WATER

1,2-Dichlorobenzene			Hexachlorobutadiene			1,2,4-Trichlorobenzene		
Spike µg/L	Recovered µg/L	% Recovery	Spike µg/L	Recovered µg/L	% Recovery	Spike µg/L	Recovered µg/L	% Recovery
4.59	4.38	95	0.14	.09	68	0.22	.22	97
4.59	4.54	99	0.14	.10	73	0.22	.24	107
8.04	7.31	97	0.24	.19	77	0.39	.36	92
8.04	7.69	103	0.24	.16	69	0.39	.41	106
11.5	14.6	127	0.34	.33	96	0.56	.55	98
11.5	14.5	126	0.34	.34	100	0.56	.62	111
115	112	97	3.41	2.57	75	5.60	5.22	93
115	119	103	3.41	2.83	83	5.60	5.77	103
1150	1010	88	34.1	17.0	50	56.0	43.4	77
1150	927	81	34.1	15.1	44	56.0	37.5	67

TABLE 30. ANALYTICAL CURVE DATA FOR 2-CHLORONAPHTHALENE AND HEXACHLOROBENZENE IN INTERFERENCE-FREE WATER

2-Chloronaphthalene			Hexachlorobenzene		
Spike µg/L	Recovered µg/L	% Recovery	Spike µg/L	Recovered µg/L	% Recovery
3.75	3.14	84	0.20	.17	83
3.75	3.84	102	0.20	.19	94
6.57	6.37	97	0.35	.35	98
6.57	6.55	100	0.35	.40	114
9.38	9.34	100	0.50	.49	97
9.38	11.3	121	0.50	.69	136
93.8	95.9	102	5.04	6.16	122
93.8	99.2	106	5.04	6.34	126
938	753	80	50.4	45.5	90
938	725	77	50.4	35.7	71

TABLE 31. MDL OF CHLORINATED HYDROCARBONS IN WASTEWATER CODE-COD-B

Sample No.	MDCB	PDCB	HCE	ODCD	HCBD	TCB	2-CN	HCB
1	7.26	8.24	.166	10.01	.050	.340	7.29	.314
2	11.85	14.11	.280	12.19	.208	.618	8.55	.505
3	11.13	12.81	.277	14.86	.247	.711	9.39	.602
4	11.03	12.52	.278	13.45	.221	.527	7.79	.488
5	10.71	12.14	.275	11.20	.169	.564	9.17	.488
6	11.73	13.37	.276	12.38	.145	.591	8.57	.527
7	12.26	13.84	.298	12.45	.172	.592	8.54	.532
Method MDL Data								
Spiked Value (μg/L)	11.94	13.38	.299	11.48	.341	.560	9.38	.504
Average Recovered (μg/L) (n=7)	10.85	12.43	.207	11.55	.174	.563	8.47	.494
Standard Deviation	1.67	1.98	.044	1.55	.064	.114	.732	.088
MDL = 3.143 X Standard Deviation	5.26	6.22	.138	4.86	.220	.357	2.30	.278
Ratio = Spike/MDL	2	2	2	2	2	2	4	2

All concentrations are actual recovered values of μg/L based on water.

TABLE 32. MDL OF CHLORINATED HYDROCARBONS IN WASTEWATER CODE-DCA-A

Sample No.	MDCB	PDCB	HCE	ODCB	HCBD	TCB	2-CN	HCB
1	10.98	11.92	.219	11.47	.208	.566	Interference	.367
2	10.75	9.69	.170	9.80	.157	.429		.374
3	9.53	10.79	.211	10.24	.211	.459		.305
4	9.58	10.81	.203	11.58	.132	.438		.464
5	8.92	10.04	.187	10.92	.187	.433		.386
6	8.76	9.92	.189	9.00	.171	.371		.341
7	8.62	9.80	.163	9.18	.136	.401		.266
Method MDL Data								
Spiked Value (μg/L)	11.94	13.38	.299	11.48	.341	.560	Interference	.504
Average Recovered (μg/L) (n=7)	9.59	10.42	.192	10.31	.172	.443		.358
Standard Deviation	.946	.799	.021	1.05	.032	.062		.063
MDL = 3.143 X Standard Deviation	2.97	2.51	.065	3.29	.100	.193		.198
Ratio = Spike/MDL	4	5	5	4	3	3		3

All concentrations are actual recovered values of μg/L based on water.

detector was not the cause, since the extract, representing the sample set prepared at 1000 X the MDL, was diluted to the same "as injected concentration" as the extract representing 100 X the MDL.

The method detection limits determined for industrial wastewater Code COD-B were approximately five times greater than those found for interference-free water. The MDLs in industrial wastewater Code DCA-A were approximately two times greater than in deionized/distilled water. The mean recoveries, for each of the chlorinated hydrocarbons, were higher in industrial wastewater Code COD-B than in wastewater Code DCA-A. Even though the spiking levels were the same in both industrial wastewaters, the average standard deviation was greater in wastewater Code COD-B than in wastewater Code DCA-A.

CONCLUSIONS AND RECOMMENDATIONS

The EPA method of determining the MDL appears to be satisfactory. However, the analyst should develop MDL, recovery, and precision data on the water type of concern.

The probability exists that in some cases MDLs lower than those determined in this study could be achieved. Some of the extraneous factors affecting the MDL determination are:

1. Lack of baseline separation - related to single versus multiple component solutions
2. "One of a kind" column
3. Peak broadening
4. Percent recovery
5. Analysis

Not all of the chlorinated hydrocarbons have baseline resolution from each other, therefore for compounds such as 1,3-DCB, 1,4-DCB, HCE, 1,2-DCB, HCBD, and 1,2,4-TCB a lower MDL might be achieved in a single component solution rather than in a mixture as used during this study. The degree of baseline spearation for these compounds in a mixture could vary from column to column.

Compounds such as HCBD, TCB, and HCB have less instrumental sensitivity due to peak broadening. If the analyst was only determining a single compound such as TCB, and interferences allowed a greater GC column temperature, a lower MDL probably could be achieved.

During this type of study an analyst could make an estimate for a MDL, based on a signal to noise ratio only, and determine a MDL (3.143 X S) that was derived from extracts representing a drastic reduction in the normal percent recovery for that specific compound. This concentration level could be below the method analytical curve break point without the analyst knowing it during the MDL determination. This type of phenomenon could occur due to a decrease in extraction efficiency, absorption, and other factors such as adsorption.

SECTION 7

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APPENDIX A

CHLORINATED HYDROCARBONS: ANALYTICAL METHOD 612

1. Scope and Application

1.1 This method covers the determination of certain chlorinated hydrocarbons. The following parameters may be determined by this method:

Parameter	STORET No.
Hexachlorocyclopentadiene	34386
Hexachlorobenzene	39700
Hexachlorobutadiene	34391
Hexachloroethane	34396
1,2-Dichlorobenzene	34536
1,2,4-Trichlorobenzene	34551
1,3-Dichlorobenzene	34566
1,4-Dichlorobenzene	34571
2-Chloronapthalene	34581

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent on the level of interferences rather than instrumental limitations. The limits of detection listed in Table A-1 represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. Summary of Method

2.1 A 1 liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried by passing through a sodium sulfate column and then

TABLE A-1. GAS CHROMATOGRAPHY OF CHLORINATED HYDROCARBONS

Compound	Retention Time (Minutes)	Detection † Limit (μg/L)
1,3-Dichlorobenzene	5.6	0.009
1,4-Dichlorobenzene	6.1	0.0018
Hexachloroethane	6.7	0.001
1,2-Dichlorobenzene	7.6	0.012
Hexachlorobutadiene	15.8	0.001
1,2,4-Trichlorobenzene	17.7	0.006
Hexachlorocyclopentadiene	2.0*	0.001
2-Chloronaphthalene	3.65*	0.015
Hexachlorobenzene	10.3*	0.001

Column conditions: Suplecoport 80/100 mesh coated with 1.5% OV-1/2.4% OV-225 packed in a 1.8 m long X 2 MM ID glass column with 5% methane/95% argon carrier gas at 30 mL/min flow rate. Column temperature is 75°C except where * indicates 165°C. Under these conditions R.T. of Aldrin is 27.4 minutes at 165°C.

†Detection limit is calculated from the minimum detectable GC response of the electron capture detector being equal to five times the GC background noise, assuming a 10 mL final volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

concentrated to a volume of 10 mL or less. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.

2.2 If interferences are encountered or expected, the method provides a selected general purpose clean up procedure to aid the analyst in eliminating them.

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending on the diversity of the industrial complex or municipality being sampled. While general clean up techniques are provided as part of this method, unique samples may require additional clean up approaches to achieve the sensitivities stated in Table A-1.

4. Apparatus and Materials

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle - Amber glass, 1 liter or 1 quart volume. French or Boston Round design is recommended. The container must be washed and rinsed with solvent before use to minimize interferences.

4.1.2 Bottle caps - Threaded to screw on sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive and foil is found to be interference free.

4.1.3 Compositing equipment - Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing or fittings may be used in the system.

4.2 Separatory funnel - 2000 mL, with Teflon stopcock.

4.3 Drying column - 20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask - 500 mL (Kontes K-47001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column - three ball macro (Kontes K-503000-0121 or equivalent).

4.4.4 Snyder column - two ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Boiling chips - solvent extracted, approximately 10/40 mesh.

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.6 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on column injection and all required accessories including electron capture detector, column supplies, recorder, gasses, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatography column - 300 mm long X 10 mm ID with coarse fritted disc at bottom and Teflon stopcock.

5. Reagents

5.1 Preservatives

5.1.1 Sodium hdroxide - (ACS) 10 N in distilled water.

5.1.2 Sulfuric acid - (ACS) Mix equal volumes of concentrated H_2SO_4 with distilled water.

5.2 Methylene chloride, hexane and petroleum ether (boiling range 30 to 60°C) - Pesticide quality or equivalent.

5.3 Sodium sulfate - (ACS) Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.4 Stock standards - Prepare stock standard solutions at a concentration of 1.00 µg/µL by dissolving 0.100 grams of assayed reference material in pesticide quality hexane or other appropriate solvent and diluting to volume in a 100 mL ground

glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just before preparing working standards from them.

5.5 Florisil - PR grade (60/100 mesh): purchase activated at 1250°F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch at 130°C in foil-covered glass containers.

6. Calibration

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table A-1 as 100µg/L in the final extract, for example, prepare standards at 10 µg/L, 50 µg/L, 100 µg/L, 500 µg/L, etc. so that injections of 1 to 5 µL of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table A-1. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 The clean up procedure in Section 10 utilizes Florisil chromatography. Florisil from different batches or sources may vary in absorption capacity. To standardize the amount of Florisil that is used, the use of lauric acid value (Mills, 1968) is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing this ratio by 110 and multiplying by 20 grams.

6.4 Before using any clean up procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7. Quality Control

7.1 Before processing any samples the analyst should demonstrate, through the analysis of a distilled water method blank, that all glassware and reagents are free of interference. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. Sample Collection, Preservation, and Handling

8.1 Grab samples must be collected in glass containers, leaving a minimum headspace. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, they should be adjusted to a pH range of 6.0 to 8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples should be extracted immediately and must be extracted within 7 days and completely analyzed within 30 days after collection.

9. Sample Extraction

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two liter separatory funnel. Check the pH of the sample with wide range paper and adjust to within the range of 5 to 9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 mL methylene chloride to the sample bottle, seal and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends on the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 250 mL Erhlenmeyer flask.

9.3 Add a second 60 ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erhlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containng 3 to 4 inches of anhydrous sodium sulfate, and collect it in a 500 ml Kuderna-Danish (K-D) flask equipped with a 10 mL concentrator tube. Rinse the Erhlenmeyer flask and column with 20 to 30 mL methylene chloride to complete the quantitative transfer.

9.5 Add 1 to 2 clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 to 2 mL, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Note -- The dichlorobenzenes have a sufficiently high volatility that significant losses may occur in concentration steps if care is not exercised. It is important to maintain a constant gentle evaporation rate and not to allow the liquid volume to fall below 1 to 2 mL before removing the K-D from the hot water bath.

9.6 Momentarily remove the Snyder column, add 50 ml hexane and a new boiling chip and replace the column. Raise the temperature of the water bath to 85 to 90°C. Concentrate the extract as in 9.5, except use hexane to prewet the column. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 102 mL of hexane. A 5 mL syringe is recommended for this operation. Stopper the concentrator tube and refrigerate if further processing will not be performed immediately.

9.7 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL.

9.8 Unless the sample is known to require clean up, proceed to analysis by gas chromatography.

10. Clean up and Separation

10.1 Florisil Column Clean up for Chrlorinated Hydrocarbons.

10.1.1 Adjust the sample extract to 10 mL.

10.1.2 Place a 12 gram charge of activated Florisil (see 6.3) in a 10 mm ID chromatography column. After settling the Florisil by tapping the column, add a 1 to 2 cm layer of anhydrous granular sodium sulfate to the top.

10.1.3 Pre-elute the column, after cooling, with 100 mL of petroleum ether. Discard the eluate and just before exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether washings. Discard the eluate. Just before exposure of the sodium sulfate layer to the air, begin eluting the column with 200 mL petroleum ether and collect the eluate in a 500 mL K-D flask equipped with a 10 mL concentrator tube. This fraction should contain all of the chlorinated hydrocarbons.

10.1.4 Concentrate the fraction by K-D as in 9.5 except prewet the column with hexane. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL hexane. Analyze by gas chromatography.

11. Gas Chromatography

11.1. Table A-1 summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sentitivities that should be achieved by this method. Examples of the separations achieved by this column are shown in Figs. A-1 and A-2. Calibrate the system daily with a minimum of three injections of calibration standards.

11.2 Inject 2 to 5 µL of the sample extract using the solvent-flush technique. Smaller (1.0 µL) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL, and the resulting peak size, in area units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further clean up is required.

12. Calculations

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/L = \frac{(A)\ (B)\ (V_t)}{(V_i)\ (V_s)}$$

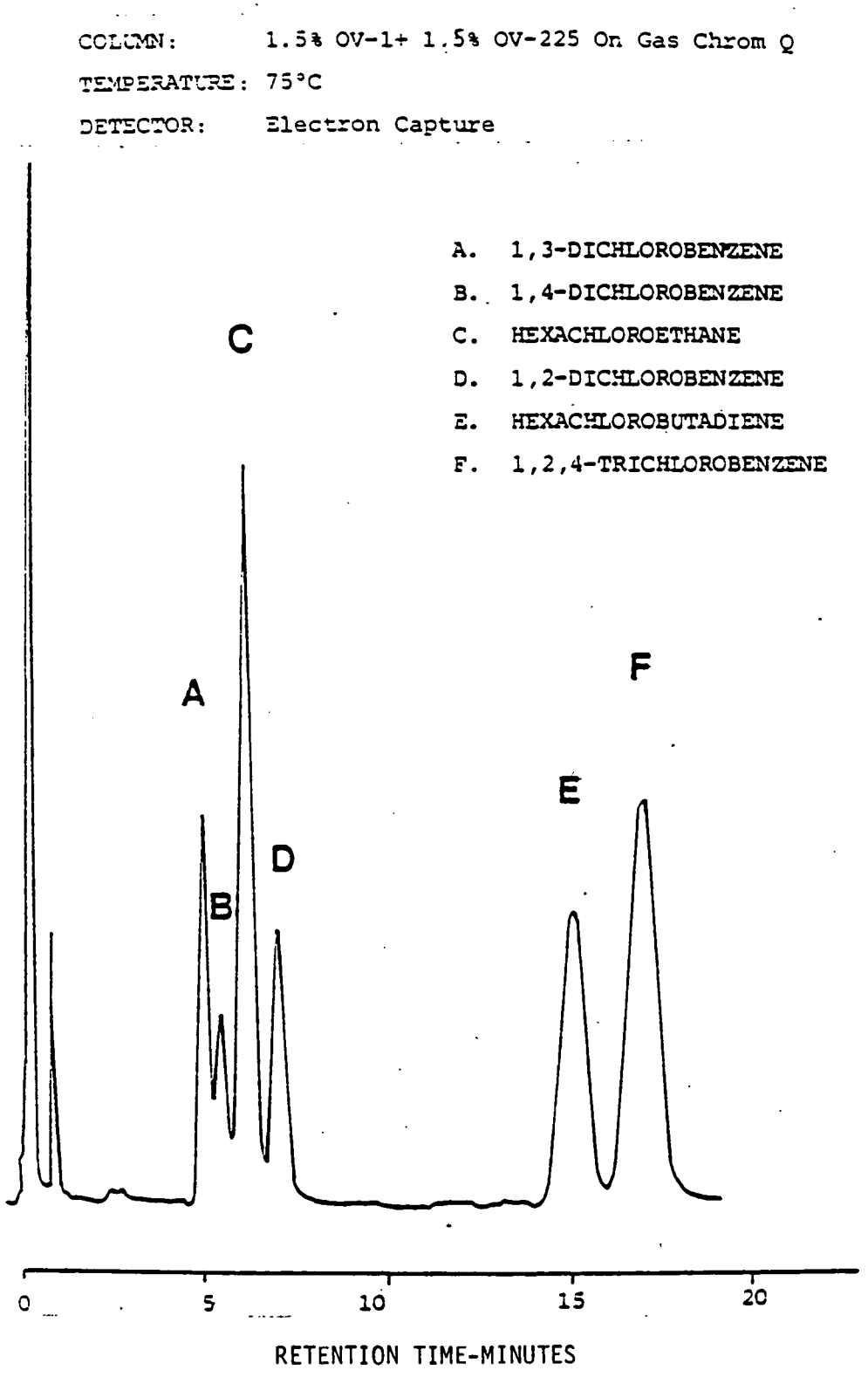

Figure A-1. Gas Chromatogram of Chlorinated Hydrocarbons

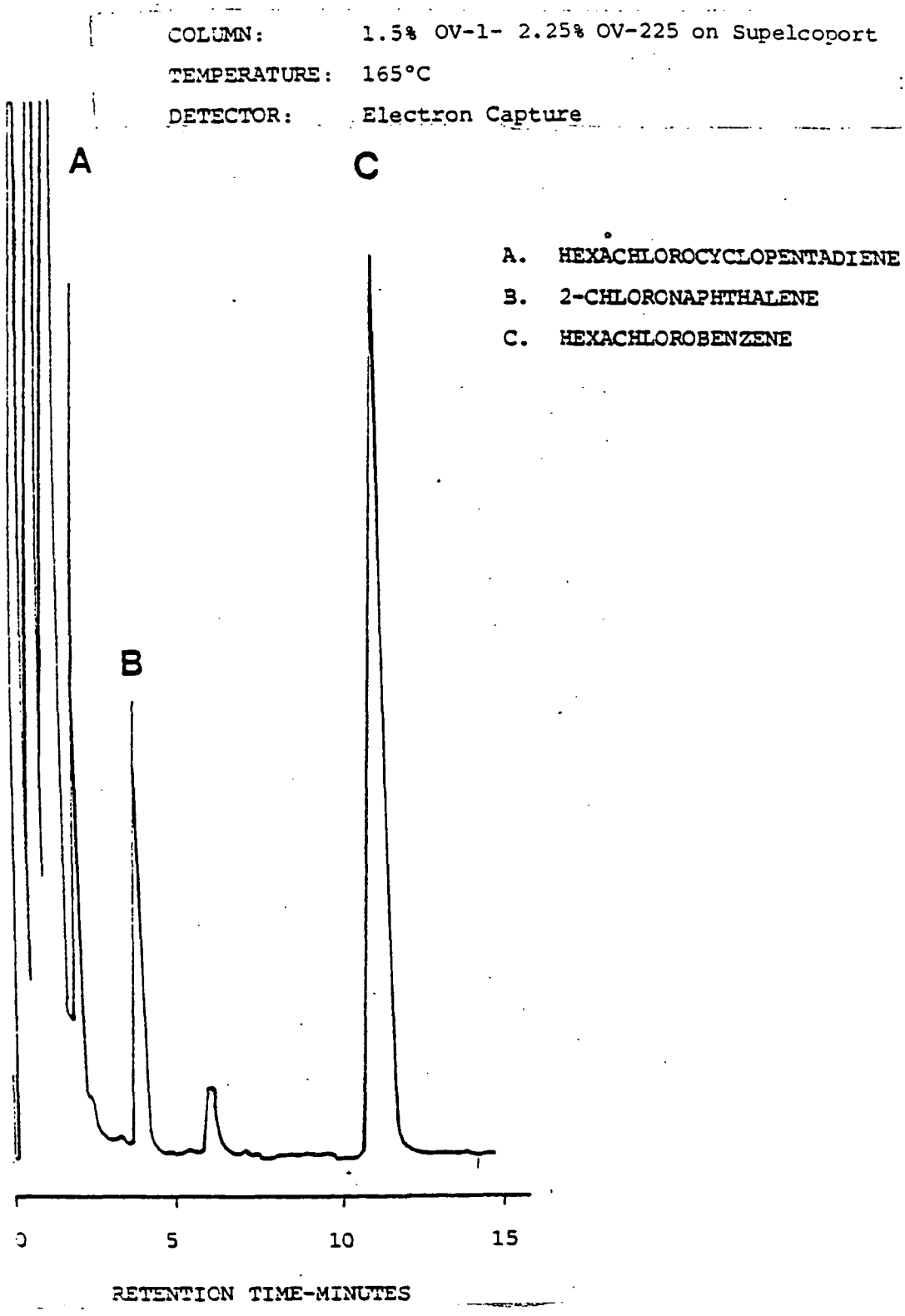

Figure A-2. Gas Chromatogram of Chlorinated Hydrocarbons

Where: A = Calibration factor for chromatographic system, in nanograms material per area unit

B = Peak size in injection of sample extract, in area units

V_i = Volume of extract injected (μ/L)

V_t = Volume of total extract (μL)

V_s = Volume of water extracted (ml)

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. Accuracy and Precision

The U.S. EPA Environmental Monitoring and Support Laboratory - Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of the test procedure.

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GLOSSARY OF TERMS

The terminology and statistical measurements used in this study report are defined as follows:

Accuracy as % Relative Error (Bias). The signed difference between mean value and the true value, expressed as a percent of the true value.

$$R.\ E.,\ \% = \frac{\bar{X} - X_{true}}{X_{true}} \times 100$$

F-tests A statistical test applied to the ratio of the squares of S and/or S_r data to estimate whether the water types used in the study were statistically different than the distilled water data.

The following formulae (4) were used:

$$F = \frac{(S\ \text{Distilled Water})^2}{(S\ \text{Any Other Water Type})^2}$$

$$F = \frac{(S_r\ \text{Distilled Water})^2}{(S_r\ \text{Any Other Water Type})^2}$$

To achieve a number greater than 1 the variances were reversed as needed. The resultant values were compared to a standard one-sided 99.5% critical value table (5) to determine deviation where:

f (degrees of freedom) = n -1

f' (degrees of freedom = n' -1

n = number of data points to calculate the S or S_r in the numerator;

n" = number of data points to calculate the S or S_r in the denominator.

If the calculated F exceeds the theoretical value found in the table, the data may be considered significantly different.

Mean Recovery. The arithmetic mean of reported values; the average.

$$\bar{X} = \frac{\Sigma X_i}{n}$$

Median. Middle value of all data ranked in ascending order. If there are two middle values, the mean of these values.

n. The number values (X_i) reported for a sample.

Outlier. A datum point determined by applying an Extreme Studentized Deviate T test at a selected probability level to be extreme in relationship to the other data and therefore rejected.

Range. The difference between the lowest and highest values reported for a sample.

Relative Deviation (Coefficient of Variation). The ratio of the standard deviation, S, of a set of numbers to their mean, $\bar{X}$, expressed as percent. It is an attempt to relate deviation (precision) of a set of data to the size of the numbers so that deviations at different mean values can be compared.

$$R.\ D. = 100\ \frac{S}{\bar{X}}$$

Single-Analyst Relative Deviation. The ratio of the single-analyst standard deviation, S_r, of a set of numbers to their mean, $\bar{X}$, expressed as percent. It is an attempt to relate deviation (precision) of a set of data for a single analyst to the size of numbers so that the deviations at different mean values and between analysts can be compared.

$$\text{Single-analyst R.D.} = 100\ \frac{S_r}{\bar{X}}$$

Standard Deviation (S). The most widely used measure to describe the dispersion of a set of data. For normally distributed data, $\bar{X} \pm S$ will include 68%, and $X \pm 2S$ will include about 95% of the data from a study.

$$S = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n - 1}}$$

Standard Deviation: Single Analyst (S_r). A measure of dispersion for data from a single analyst. Calculated here using an equation developed by Youden based on his nonreplicate study design.

$$S_r = \sqrt{\frac{\Sigma(D_i - \bar{D})^2}{2(n - 1)}}$$

Student's t-test. A statistical test performed to determine whether the mean recoveries, $\bar{X}$, for a particular water type when compared to distilled water data were significantly different. The calculated t values were compared to a standard two-tailed t distribution table (5); calculated values exceeding the table values were considered significantly different.

When S_r values were found to be similar the following t-test was used:

$$t = \frac{\bar{X} - \bar{Y}}{\sqrt{n_x S_x^2 + n_y S_y^2}} \qquad \sqrt{\frac{n_x n_y (m_x + m_y - 2)}{n_x + n_y}}$$

which will have student t's distribution with $n_x + n_y - 2$ degrees of freedom.

Where:

$\bar{X}$ = the larger of the mean recoveries (water type or distilled water);

$\bar{Y}$ = the smaller of the mean recoveries (water type or distilled water);

n_x and n_y = the corresponding number of data points for $\bar{X}$ and $\bar{Y}$;

S_x and S_y = the corresponding S_r, single-analyst standard deviations for $\bar{X}$ and $\bar{Y}$.

When S_r values and were found to be significantly different the following formulas were applied:

$$t = \frac{\bar{X} - \bar{Y}}{\sqrt{\frac{S_x^2}{n_x} + \frac{S_y^2}{n_y}}}$$

Where the degrees of freedom were:

$$= \frac{\left(\frac{S_x^2}{n_x} + \frac{S_y^2}{n_y}\right)^2}{\frac{\left(\frac{S_x^2}{n_x}\right)^2}{n_x + 1} + \frac{\left(\frac{S_y^2}{n_y}\right)^2}{n_y + 1}}$$

T test. The difference between a single observation (X_n) and the estimated population mean ($\bar{X}$) expressed as a ratio over the estimated population standard deviation (S). The value obtained is compared with values from a table for the critical T distribution (3). If the calculated T value exceeds the theoretical T value at a prescribed confidence level, the analyzed value is

probably not from the same population as the rest of the data and can be rejected.

$$T = \frac{X_n - \bar{X}}{S}$$

Youden Pair. A set of two samples having slightly dissimilar concentrations of the constituent of concern, based on Youden's nonreplicate analysis technique.