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# Solid Phase Extraction of Pesticides with Determination by Gas Chromatography

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## Abstract

A simple, rapid, and effective method for the extraction of fifteen organochlorine and organophosphorus pesticides based on the use of solid phase Bond Elut C-18 cartridges was studied as an alternative method to those based on extraction with organic solvents. Solid phase extraction is an attractive chromatographic sample preparation technology that reduces analysis time, costs, labor, and solvent consumption relative to traditional liquid/liquid extraction methods. The sample recoveries with the use of solid phase extractions were excellent for most pesticides. Analyte concentration by a factor as great as 1000-fold was achieved readily. The adsorbed pesticides were eluted from the solid phase by an organic solvent. The influence of the elution solvent was studied. The best recoveries were obtained using methanol. The detection of the pesticides was made using OV-17 megabore capillary gas chromatography (GC) with electron capture detection. Pesticide extraction efficiencies using C-18 cartridges ranged from 64-100%, with the exception of mirex which was 56% at 0.2 µg/L spiking levels. Recovery precision studies demonstrate that relative standard deviations range from 1 to 9%. The compounds were identified by comparing the retention time with that of a standard under the same GC conditions, and quantitation was accomplished by comparing the peak areas.

## Introduction

The pesticides have conferred tremendous benefits on mankind both by controlling the arthropod vectors of serious human disease and by greatly increasing yields of many crops. There have been many reports of residues of persistent pesticides in air, rainwater, dust, rivers, the sea, and in the bodies of aquatic and terrestrial invertebrates (Edwards, 1973; Lincer, 1973; Duke, 1977). Those pesticides that are very persistent present a potential hazard to our environment. A large volume of work has been done on monitoring pesticides in the environment (Johnson and Ball, 1992). Pesticides will continue to be used in the production of food and fiber. Drastic reductions of pesticide usage would increase production costs and lower the quality of agricultural products.

Sample preparation strategies, while often excluded from method objectives, may be of equal or greater importance than other factors in improving the productivity of analytical methods. Sample preparation in modern instrumental analysis is often required for two reasons: clean up and concentration. The sample matrix frequently interferes with measurement. In many instances, the analyte concentration falls below the sensitivity range of the analytical method chosen. A faster, simpler, convenient, and efficient sample preparation method is a very important factor in improving the productivity of analytical methods. Solid phase extraction may be used in a variety of

disciplines to provide faster and more efficient sample preparation. In addition to its broad capabilities, solid phase extraction has the advantages of being faster, safer, and more economical than many traditional sample preparation techniques. Reduced sample handling and transfer and the elimination of emulsions contribute to more reproducible results. Solid phase extraction is an emerging chromatographic sample preparation technology that reduces organic solvent consumption relative to traditional alternatives. It was reported that the recoveries with the use of solid phase extraction were excellent for most of the pesticides (Bolygo and Atreya, 1991; Molto et al., 1990; Marvin et al., 1990; Brooks et al., 1990; Manes et al., 1990; Weigel et al., 2001; Sasano et al., 2000; Vandecasteele et al., 2000).

The purpose of this study is to develop simple, rapid, reliable, inexpensive procedures for the extraction and determination of different types of pesticides in water. Traditionally, liquid/liquid extraction has been used for the extraction of pesticides. This is very time consuming and involves costly high purity halogenated solvents. Also, halogenated solvents used in the procedure need to be disposed of in an environmentally acceptable manner. These extraction and concentration procedures make pesticides determination a time consuming and laborious analytical process with a large consumption of organic solvents. Any methods that can result in shorter analytical procedures and less use of organic solvents would be less

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expensive and more environmentally desirable. A simple, rapid, and effective method for the extraction of organochlorine pesticides based on the use of Bond Elut C-18 cartridges was studied as an alternative method to those based on extraction with organic solvents. The recoveries with use of cartridges were excellent for most pesticides. Analyte concentration by a factor as great as 1000-fold was achieved readily. The adsorbed pesticides were eluted from the solid phase by an organic solvent. The best recoveries were obtained using methanol. The detection of the pesticides was made using OV-17 megabore capillary gas chromatography with electron capture detection. Isolation of the pesticides peaks from each other on the gas chromatograms was very satisfactory with the use of the OV-17 column. The compounds were identified by comparing the retention time with those of standards under the same GC conditions, and quantitation was accomplished by comparing the peak areas.

### Materials and Methods

**Reagents.**--The following pesticide reference standards were obtained from Alltech Associates, Inc., Deerfield, IL: aldrin, dieldrin, endrin, HCB, heptachlor, heptachlor epoxide, and methoxychlor. Analytical standards of the pesticides endosulfan-1, endosulfan sulfate and mirex were obtained from Supelco, Inc., Bellefonte, PA. Metolachlor and trifluralin were obtained from AccuStandard, New Haven, CT 06511. Methyl parathion and metribuzin were obtained from Ultra Scientific, North Kingstown, RI 02852. All of the analytical standards were greater than 96% pure and EPA approved. Pesticide grade hexane, acetonitrile, methylene chloride, methanol, and ethyl acetate were obtained from Fisher Scientific, Fair Lawn, NJ. Redistilled industrial grade acetone and deionized water were used to clean all glassware and equipment.

**Equipment.**--The extraction of pesticides from the water samples was carried out using Bond Elut C-18 microcolumns [6 mL volume tubes containing 500 mg of C-18 octadecyl sorbent (Varian, Walnut Creek, CA)]. The samples were eluted under vacuum. A Hewlett-Packard 5880A Gas Chromatograph equipped with an electron capture detector was used to analyze the samples. The analytical column used was an OV-17 fused silica megabore (0.53 mm i.d.) column. The samples were injected using a 10- $\mu$ L Hamilton syringe. The data were collected and processed using a Hewlett-Packard 5880A series GC terminal.

**Stock Solutions.**--Standard solutions of 20  $\mu$ g/L were prepared for each of the 11 different organochlorine pesticides. These solutions were prepared in iso-octane and methanol. Further serial dilutions from the original solutions were made using methanol. The working standards were 0.2

$\mu$ g/L for 11 organochlorine pesticides. Organophosphorus pesticide standards were prepared at 250 ppm in methanol. Further serial dilutions from the original solutions were made using methanol. The working standards were 250  $\mu$ g/L with the exception of metolachlor which was 2.5 mg/L. One liter samples of distilled water were spiked with 1 mL of each of the standards to determine recoveries.

**Extraction.**--The extractions were carried out using a VAC-ELUT solid phase extraction system. Bond Elut C-18 columns (6 mL volume tubes containing 500 mg of C-18 octadecyl sorbent) were inserted into luer fittings, and the unused spaces were capped with plugs. A vacuum was applied and the sample eluents were collected in 10 mL volumetric flasks that were held under the columns in a stainless steel removable rack. All 15 standards were spiked into 1 L deionized water, each in duplicate, and then extracted through the C-18 cartridge to determine recoveries. One set of water samples was extracted directly while internal standards were added to a second set to monitor extraction efficiency. To determine the proper elution solvent, each of five duplicate spiked solutions was extracted with one of five different solvents. The C-18 cartridge was conditioned with methanol (10 mL) followed by 10 mL of deionized water. The column was not allowed to dry before the sample was added to the column. The water sample, 1 L, was slowly passed through the column using the vacuum. At no time from activation until the end of the retention were the columns allowed to go dry. After the sample had passed through, the vacuum was left on for 3 min to dry the column. The adsorbed pesticides were then eluted under vacuum with methanol (10 mL) into a volumetric flask. The extracted samples were stored in a freezer in small sample vials until GC analysis.

**Water Sample Collection.**--Thirty water samples were collected from different locations of Ouachita Parish from January to August. Water samples were taken from the top ten inches near the surface and placed in acetone rinsed wide-mouth quart jars fitted with aluminum foil under the lids. All samples were collected in duplicate. The sample were analysed for 11 organochlorine pesticides and 4 additional pesticides. The samples were extracted immediately after collection and stored in a freezer until analyzed.

**GC Analysis.**--Samples of 3  $\mu$ L were injected in the splitless mode at 225°C. The instrument used for analysis was a Hewlett-Packard 5880A Gas Chromatograph equipped with a Ni-63 electron capture detector. The column used was an OV-17 megabore column. Operating parameters were as follows:

Carrier gas = Nitrogen  
Oven Temperature = 180°C  
Injector Temperature = 225°C  
Detector Temperature = 320°C

The concentrations of the pesticides in the samples were determined by comparing their peak area with those of pesticide standards of known concentration. Corrections were made for percent recovery, which varied from sample to sample. The pesticides in the samples were identified by retention time.

### Results and Discussion

Water samples were spiked at the 0.2  $\mu\text{g/L}$  level with 11

organochlorine pesticides and at the 0.25 mg/L level with additional pesticides. Metolachlor was spiked at 2.5 mg/L level. Figures 1 and 2 show the chromatograms of the analysis of the pesticides after extraction from 1 L of water using SPE columns. The chromatograms were obtained using electron capture detection and contained no interfering peaks. Table 1 gives the average recoveries from six analyses of duplicate samples using SPE columns containing 500 mg of  $\text{C}_{18}$  sorbent with 10 mL of acetonitrile, methylene chloride, ethyl acetate, n-hexane, or methanol as

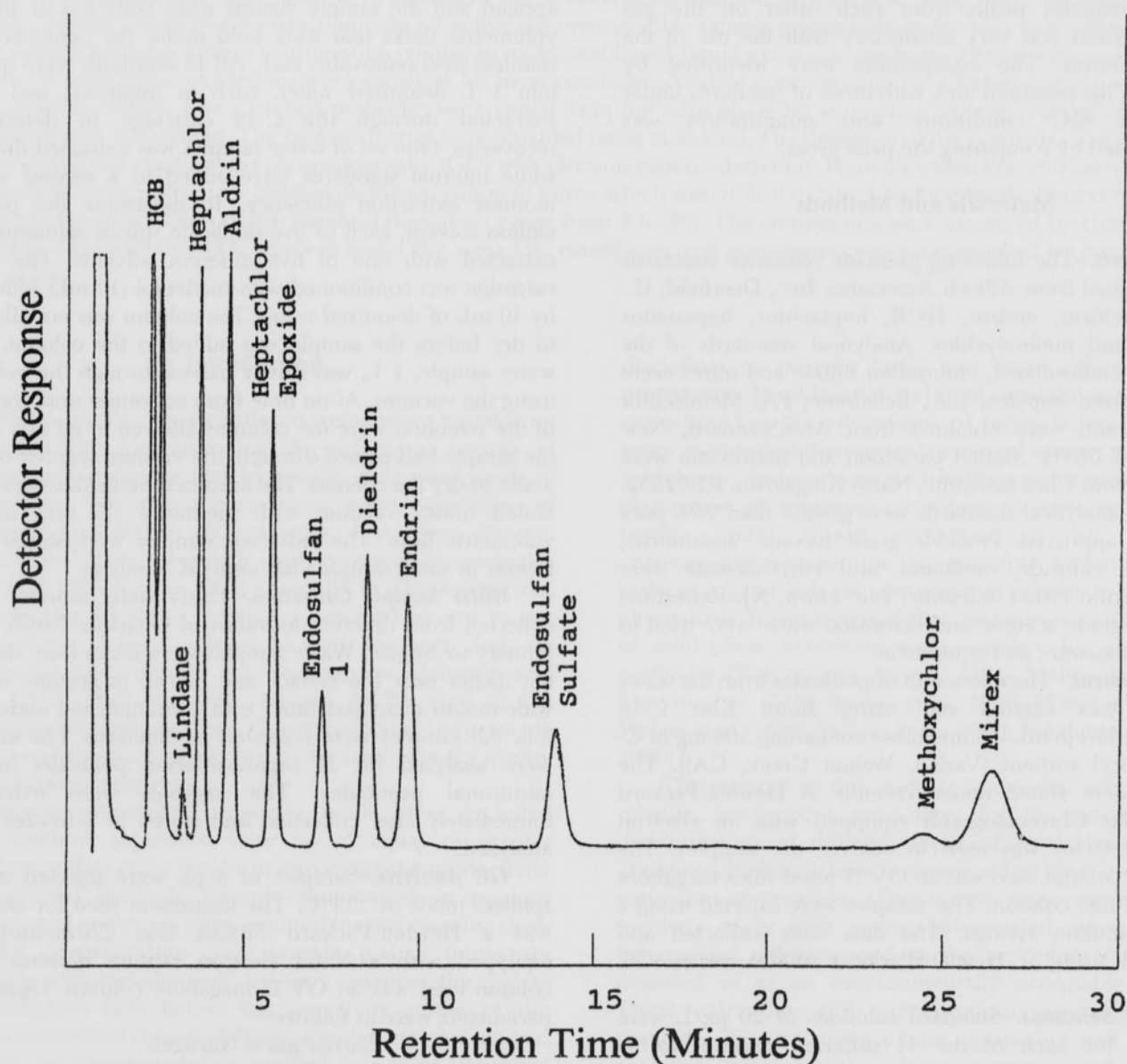


Fig. 1. Chromatogram of 11 Chlorinated Pesticides. Column: OV-17 Megabore Column; Column Temperature: 180°C; Electron Capture Detector; 3  $\mu\text{L}$  Sample. See text for experimental details.

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eluent for pesticides from water spiked at the 0.2 µg/L level. The variation in recovery efficiency, as well as the low recovery of mirex, can be attributed to the diversity, in terms of polarity and volatility, of the compounds studied. The highest recoveries were obtained using methanol. Other solvents may have greater eluting power in reversed-

phase chromatography but many are not water miscible. Acetonitrile & tetrahydrofuran are 100% miscible with water, are more non polar than MeOH and have higher vapor pressure so they evaporate easily. Ethyl acetate may be a good solvent (due to high polarity) for the desorption of relatively polar compounds from the octadecylsilica,

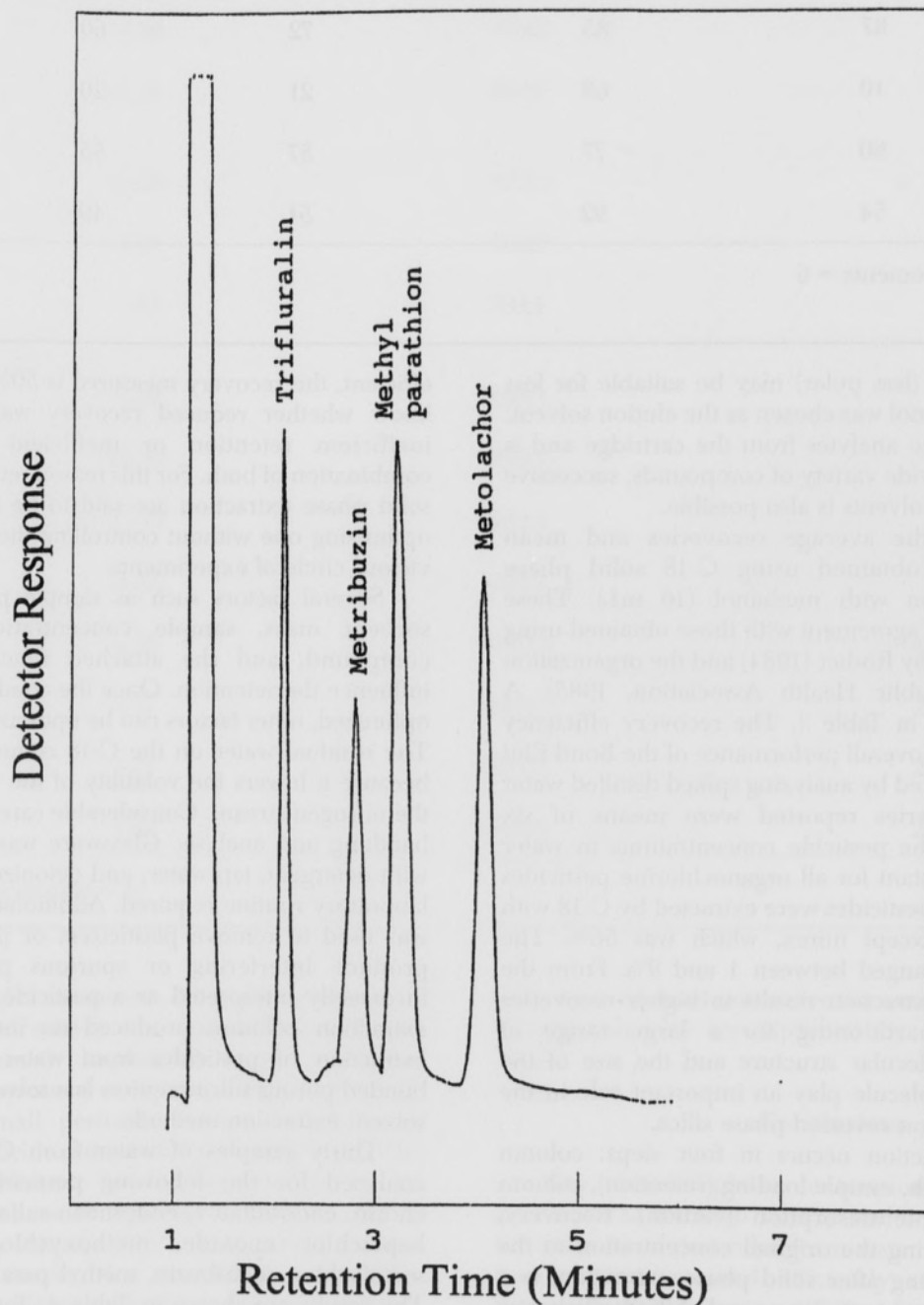


Fig. 2. Chromatogram of 4 Additional Pesticides. Column: OV-17 Megabore Column; Column Temperature: 180 °C; Electron Capture Detector; 3 µL Sample. See text for experimental details.

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Table 1. Recovery (%) of Pesticides from Water (Spiked at 0.2 µg/L) Using C-18 Bonded Silica and Different Eluents.

Pesticide	Acetonitrile	Methylene Chloride	Ethyl Acetate	n-Hexane	Methanol
Methoxychlor	71	86	87	67	89
Endosulfan sulfate	87	85	72	60	87
Mirex	40	68	21	20	56
Endrin	60	77	57	55	73
Endosulfan-1	54	92	51	49	92

n = number of measurements = 6

while light petroleum (less polar) may be suitable for less polar materials. Methanol was chosen as the elution solvent, as it eluted most of the analytes from the cartridge and is water miscible. For a wide variety of compounds, successive elution with different solvents is also possible.

Table 2 shows the average recoveries and mean standard deviations obtained using C-18 solid phase extraction and elution with methanol (10 mL). These recoveries are in good agreement with those obtained using the methods reported by Rodier (1984) and the organization APHA (American Public Health Association, 1985). A comparison is shown in Table 3. The recovery efficiency used in evaluating the overall performance of the Bond Elut C-18 cartridge was tested by analyzing spiked distilled water samples. The recoveries reported were means of six duplicate analyses. The pesticide concentrations in water were maintained constant for all organochlorine pesticides (0.2 µg/L). All of the pesticides were extracted by C-18 with 64-100% recovery, except mirex, which was 56%. The standard deviations ranged between 1 and 9%. From the results, solid phase extraction results in higher recoveries than liquid-liquid partitioning for a large range of compounds. The molecular structure and the size of the apolar part of the molecule play an important role in the retention mechanism on reversed phase silica.

Solid-phase extraction occurs in four steps: column preparation or prewash, sample loading (retention), column post-wash, and sample desorption (elution). Recovery, calculated by comparing the original concentration to the concentration remaining after solid phase extraction, is a function of both retention efficiency and elution efficiency: recovery = retention efficiency x elution efficiency. For example, if retention is 50% efficient but elution is 100%

efficient, the recovery measured is 50%. It is impossible to know whether reduced recovery was produced due to inefficient retention or inefficient elution or by a combination of both. For this reason retention and elution in solid phase extraction are said to be interdependent, and optimizing one without controlling the other can lead to a vicious circle of experiments.

Several factors such as sample pH, sample volume, sorbent mass, sample concentration, nature of the compound, and the attached functional groups may influence the retention. Once the conditions for elution are optimized, other factors can be optimized by trial and error. The residual water on the C-18 column is a disadvantage because it lowers the volatility of the eluted solvent under the nitrogen stream. Considerable care was taken in sample handling and analysis. Glassware was thoroughly cleaned with detergent, tap water, and deionized water as the usual laboratory routine required. Additionally, a methanol rinse was used to remove plasticizers or phthalates that might produce interfering or spurious peaks that may be incorrectly interpreted as a pesticide. The polypropylene extraction columns produced no interfering peaks. The extraction of pesticides from water with the octadecyl bonded porous silica requires less solvent than conventional solvent extraction methods.

Thirty samples of water from Ouachita Parish were analyzed for the following pesticides: aldrin, dieldrin, endrin, endosulfan 1, endosulfan sulfate, HCB, heptachlor, heptachlor epoxide, methoxychlor, mirex, lindane, metolachlor, metribuzin, methyl parathion, and trifluralin. The results are shown in Table 4. Twelve samples did not contain any detectable amount of pesticides. Eighteen of the samples contained detectable amounts of one or more

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Table 2. Selected Pesticides, Their Retention Times (RT), Average Recoveries, and Sample Concentration.

Compound	RT (min)	Recovery (%)	Conc. ( $\mu\text{g/L}$ )
Aldrin	4.26	79 $\pm$ 5	0.2
Dieldrin	8.61	91 $\pm$ 6	0.2
Endrin	9.40	73 $\pm$ 2	0.2
Endosulfan-1	6.74	91 $\pm$ 9	0.2
Endosulfan sulfate	13.76	87 $\pm$ 3	0.2
HCB	2.16	73 $\pm$ 2	0.2
Heptachlor	3.83	73 $\pm$ 1	0.2
Heptachlor epoxide	5.38	89 $\pm$ 3	0.2
Methoxychlor	24.12	89 $\pm$ 3	0.2
Mirex	25.77	56 $\pm$ 3	0.2
Lindane	2.23	76 $\pm$ 2	0.2
Metolachlor	4.38	100 $\pm$ 3	2500.0
Metribuzin	3.17	64 $\pm$ 3	250.0
Methyl parathion	3.21	95 $\pm$ 3	250.0
Trifluralin	1.64	94 $\pm$ 6	250.0

n = number of measurements = 6

pesticides. Two samples contained detectable amounts of aldrin, one contained endrin, ten contained endosulfan sulfate, five contained heptachlor, two contained methoxychlor, six contained mirex, and eight contained metolachlor. The small pesticide residue levels found suggest that these pesticide residues are present at levels that are far below the tolerance level recommended by the United States Department of Agriculture (USDA) (U. S. Government Printing Office, 1990). These levels are not surprising in light of the fact that most of these pesticides have either been banned or their use has been restricted. The extensive use of metolachlor may explain its presence in relatively large amounts in eight samples. The compounds were identified by comparing the retention time

with those of standards under the same GC conditions, and quantitation was accomplished by comparing the peak areas.

### Conclusions

The bonded-phase extraction columns are an alternative to the acid/base/neutral liquid-liquid extractions for isolation of pesticides from water for GC analysis. The bonded-phase method efficiently recovers a variety of organic pesticides having different functional groups in one step. In addition to involving less labor, time, glassware, and solvent, the method minimizes sample exposure of the technician to possibly hazardous samples. This aspect is

Table 3. Comparison Between the Reported Pesticide Recoveries from Water Using APHA, Rodier Methods, and This Study Using C-18 Bonded Porous Silica for Solid Phase Extraction.

Pesticide	APHA	% Reported Recovery Rodier	This study (using C-18)
Aldrin	75 ± 6	70 ± 11	79 ± 5
Dieldrin	90 ± 8	97 ± 7	91 ± 6
Endrin	106 ± 8	107 ± 9	73 ± 2
Endosulfan-1	92 ± 8	96 ± 6	91 ± 9
Endosulfan sulfate	94 ± 9	105 ± 6	87 ± 3
HCB	73 ± 11	86 ± 9	73 ± 2
Heptachlor	83 ± 10	73 ± 9	73 ± 1
Heptachlor epoxide	103 ± 8	90 ± 7	89 ± 3
Methoxychlor	90 ± 8	97 ± 10	89 ± 3
Mirex	90 ± 8	91 ± 8	56 ± 3
Lindane	108 ± 12	81 ± 10	76 ± 2
Metolachlor	---	---	100 ± 6
Metribuzin	---	---	64 ± 3
Methyl parathion	---	---	95 ± 3
Trifluralin	75 ± 8	76 ± 11	94 ± 6

n = number of measurements = 6

important in view of the increasing demand for analysis of hazardous-waste-related samples. Using this method in the field would avoid the shipment, and possible breakage in transit, of potentially hazardous water samples. New sample preparation methods such as these complement the advanced analytical instrumentation already available today. The use of solid-phase extraction provides a rapid, efficient, and reproducible method for the simultaneous determination of pesticides in ground water and obviates

the use of long sequential solvent extraction methods. The one step extraction and concentration procedure minimizes residue losses and the possible addition of contaminants. The simplicity of the analysis is complemented by good gas chromatographic results and a preconcentrated extract. The extract can then be analyzed immediately by mass spectrometry without the need for further removal of solvent.



Table 4. Residue Concentration of Analysed Pesticides in Water of Ouachita Parish

Sample No.	Residue in ppb														
	Aldrin	Dieldrin	Endrin	Endosulfan 1	Endosulfan sulfate	HCB	Heptachlor	Heptachlor epoxide	Methoxychlor	Mirex	Lindane	Metolachlor	Metribuzin	Methyl parathion	Trifluralin
1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2	nd	nd	nd	nd	0.6	nd	nd	nd	nd	1.2	nd	1600	nd	nd	nd
3	nd	nd	nd	nd	0.5	nd	nd	nd	nd	0.8	nd	3200	nd	nd	nd
4	nd	nd	nd	nd	0.3	nd	nd	nd	nd	0.6	nd	2400	nd	nd	nd
5	nd	nd	nd	nd	0.1	nd	nd	nd	nd	0.3	nd	2400	nd	nd	nd
6	nd	nd	nd	nd	0.1	nd	nd	nd	nd	nd	nd	2400	nd	nd	nd
7	nd	nd	nd	nd	0.1	nd	nd	nd	nd	nd	nd	2400	nd	nd	nd
8	nd	nd	nd	nd	0.1	nd	nd	nd	nd	nd	nd	2400	nd	nd	nd
9	nd	nd	nd	nd	0.1	nd	nd	nd	nd	nd	nd	2400	nd	nd	nd
10	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
11	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
12	nd	nd	nd	nd	nd	nd	0.1	nd	nd	nd	nd	nd	nd	nd	nd
13	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
14	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
15	nd	nd	nd	nd	nd	nd	0.1	nd	nd	nd	nd	nd	nd	nd	nd
16	nd	nd	nd	nd	nd	nd	0.1	nd	nd	nd	nd	nd	nd	nd	nd
17	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
18	nd	nd	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
19	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
20	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
21	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
22	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
23	nd	nd	nd	nd	nd	nd	nd	nd	1.0	nd	nd	nd	nd	nd	nd
24	0.2	nd	nd	nd	0.6	nd	nd	nd	0.8	1.0	nd	nd	nd	nd	nd
25	nd	nd	nd	nd	0.5	nd	nd	nd	nd	1.0	nd	nd	nd	nd	nd
26	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
27	nd	nd	nd	nd	nd	nd	0.1	nd	nd	nd	nd	nd	nd	nd	nd
28	nd	nd	nd	nd	nd	nd	0.1	nd	nd	nd	nd	nd	nd	nd	nd
29	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
30	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd - non detected

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