

Screening of Pesticides via Solid-Phase Extraction and Gas Chromatography

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Abstract

This work describes an analytical method for the screening of pesticide residues in water. The developed method identifies and quantitates a variety of pesticides in water samples such as organochlorine, organophosphate, chloronitrile, phthalimide, dicarboximide, and triazine. The analytical technique employed for the extraction and cleanup step involves solid-phase extraction with C-18 cartridges. The identification and determination of concentration is carried out with gas chromatography. Two columns of different polarity and two specific detectors are used. An electron capture detector is used for organochlorine, and a thermionic detector is used for organonitrogen and organophosphate. The good resolution achieved with the temperature program and the combination of columns is shown in the chromatograms obtained. The limits of detection, percent recovery, and their respective standard deviations are determined for each product. According to the results obtained, this method permits monitoring of the pesticides mentioned, many of which are moderately to highly toxic to aquatic organisms.

Introduction

The intensive agriculture implies the use of large quantities of pesticides, a great deal of which are transferred to natural courses of water. The study of the contamination of natural water requires multiresidue methods that permit the detection of minimum quantities and could be applied to products of distinct chemical classes.

Solid-phase extraction (SPE) is the base of the analytical technique used. The technique has been used extensively in surveys carried out by the scientists of renowned organizations like the U.S. Geological Survey, which demonstrate its feasibility (1,2).

The compounds chosen are among the pesticides that are used (or had been used, in the case of chloride pesticides) in the agricultural production of the province of Tucumán, Argentina.

They were chosen because of their high toxicity to aquatic organisms (3).

Experimental

Apparatus

An SPE Extraction Vacuum Manifold with accessories was purchased from Whatman (Clifton, NJ). SPE ENVI 18 cartridges (500 mg/6 mL) were purchased from Supelco (Bellefonte, PA). An HP 5890 gas chromatograph equipped with ⁶³Ni electron capture detector (ECD), thermionic detector (NPD), with split-splitless injector, and an injector adapted to capillary column (Hewlett-Packard, Palo Alto, CA) was used. J&W (Folsom, CA) DB210 (film thickness 30 m × 0.25 mm × 0.25 μm) and Hewlett-Packard HP 17 (10-m × 0.53-mm × 2.0-μm film thickness) columns were used.

Chromatographic Conditions

ECD parameters were at a temperature of 300°C and a make-up flow of 20 mL/min of N₂. NPD parameters had a temperature of 300°C and a gas supply of H₂ (4 mL/min) and air (100 mL/min).

The flow rate (N₂) for the DB210 column was split 1/50. The HP17 column's flow rate was 1.4 mL/min. The oven temperature program was 160°C (2 min) to 240°C (20 min), at a rate of 5°C/min.

Reagents

Pesticides

HCB; lindane; 2,4-dichlorodiphenyltrichloroethane (DDT); 4,4-DDT; chlorpyrifos; and procimidone (99% purity) were purchased from Riedel de Haën (Seelze, Germany). Aldrin, dieldrin, parathion methyl, and dicophol (98% purity) were purchased from Riedel de Haën. Chlorothalonyl (99% purity) was purchased from Chem Service (West Chester, PA). Captan (97% purity) was purchased from ULTRA Scientific (North Kingstown, RI). Iprodione (98% purity) was purchased from Chem Service.

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Solvents

Acetone, methanol, ethyl ether, and hexane were all nano-grade and purchased from Sintorgan (Buenos Aires, Argentina). Stock solutions of each pesticide were prepared in acetone at 100 µg/mL. They were stored at 4°C and diluted further with hexane, as required.

Calibration mixture

Each solution was diluted to 1:10 (v/v) with hexane. One volume of each diluted solution was mixed with one volume of all the other diluted solutions, and the mixture was completed to 10 volume with hexane. Two calibration mixtures were prepared. Solution A (1 µg/mL) contained HCB; lindane; aldrin; dieldrin; 2,4'DDT; 4,4'DDT; methyl parathion; captan; and

dicophol. Solution B (1 µg/mL) contained lindane, atrazine, methyl parthion, chlorpyriphos, chlorothalonyl, iprodione, and procimidone.

Analytical procedure

Extraction and cleanup

The SPE columns were conditioned by passing 2- to 6-mL portions of a solution of ethyl etherhexane (1:1, v/v) and then 6 mL of methanol.

Water spiked with the pesticides (500 mL) was passed through the SPE columns under vacuum at a flow rate of 10 mL/min. Throughout the procedure, care was taken to avoid the columns from drying out. The packing was then dried by passing N₂ through the columns under vacuum for 10 min.

Table I. Some Characteristics of the Selected Pesticides

Pesticide	Effects on aquatic organisms	Chemical class	Uses
Hexachlorobenzene HCB (5)	Slightly toxic for fish and aquatic invertebrates. Significant potential for bioaccumulation.	Organochlorine	Fungicide
Aldrin/Dieldrin (6)	Highly toxic for aquatic crustaceans. Daphnids are less sensitive to dieldrin than aldrin, mollusks are significantly more resistant. Both aldrin and dieldrin were highly toxic in acute tests on fish.	Organochlorine	
Lindane (5)	Highly to very highly toxic to fish and aquatic invertebrates.	Organochlorine	Insecticide
Chlorothalonyl (5)	Highly toxic to fish and aquatic invertebrates.	Chloronitrile	Fungicide
Chlorpyriphos (5)	Very highly toxic to freshwater fish and aquatic invertebrates.	Organophosphate	Insecticide
DDT (5)	Very highly toxic to many aquatic invertebrate species.	Organochlorine	Insecticide
Dicophol (5)	Highly toxic to fish, aquatic invertebrates, and algae.	Organochlorine	Insecticide
Atrazine (5)	Slightly toxic to fish and other aquatic life.	Triazine	Herbicide
Captan (5)	Very highly toxic to fish. Moderately toxic to aquatic invertebrates.	Phthalimide	Fungicide
Methyl parathion (5)	Moderately toxic to fish. Very highly toxic to aquatic invertebrates such as daphnia.	Organophosphate	Insecticide
Iprodione/Procimidone (5)	Moderately toxic to aquatic invertebrates.	Dicarboximide	Fungicide

Table II. RRT of Lindane in Each Column and Detector Used

Pesticide	RRT Lindane column DB210	RRT lindane column HP17	NPD	ECD
HCB	0.69	0.77		X
Lindane	1.00	1.00		X
Aldrin	1.11	1.26	X	
Dieldrin	1.73	1.86		X
Parathion	1.86	1.40	X	X
4,4'DDT	1.98	2.29		X
2,4'DDT	1.84	2.12		X
Chlorpyriphos	1.41	1.47	X	X
Atrazine	1.04	1.04	X	X
Chlorothalonyl	1.72	1.32	X	X
Iprodione	2.94	2.31	X	X
Dicophol	1.56	1.54		X
Captan	2.04	1.91		X
Procimidone	2.27	1.75	X	X

Table III. LOD, Average Percentage Recuperation, and SD for Each Pesticide

Pesticide	LOD	Recovery % (n = 3)	SD (%)
HCB	25	80	12
Lindane	25	95	9
Aldrin	25	70	9
2,4'DDT	25	80	11
Parathion	25	90	7
4,4'DDT	25	70	12
Dieldrin	25	85	10
Chlorpyriphos	25	90	7
Atrazine	70	70	14
Chlorothalonyl	50	90	5
Iprodione	70	60	10
Dicophol	50	75	7
Captan	50	60	12
Procimidone	50	70	5

The adsorbed pesticides were eluted three times with 1.5 mL of a solution of ethyl ether–hexane (1:1, v/v) and then concentrated to 1 mL using a gentle nitrogen stream. The injected volume was 5 μ L.

Procedure

The two columns and only the ECD were used for the calibration of solution A. For the calibration of solution B, the two columns and both the ECD and NPD were used.

The pesticides were identified by comparing the retention times (t_R) obtained from the chromatograms of the samples with those obtained from the chromatograms of the calibration solutions analyzed under identical conditions.

Quantitative determinations were performed by comparing

the areas of the peaks obtained from the chromatograms of the samples with those obtained from the chromatograms of the standards under identical conditions.

The recovery assays were carried out by preparing three samples containing 100 ng/L of each pesticide. The areas of the peaks were compared with the pertaining pesticide and calculated utilizing the external method of addition standard.

The limit of detection (LOD) for each pesticide was determined using the procedure recommended by the Environmental Protection Agency, revision 1.11 (6).

Results and Discussion

Some of the properties of the pesticides selected are mentioned in Table I. Table II shows the relative retention times

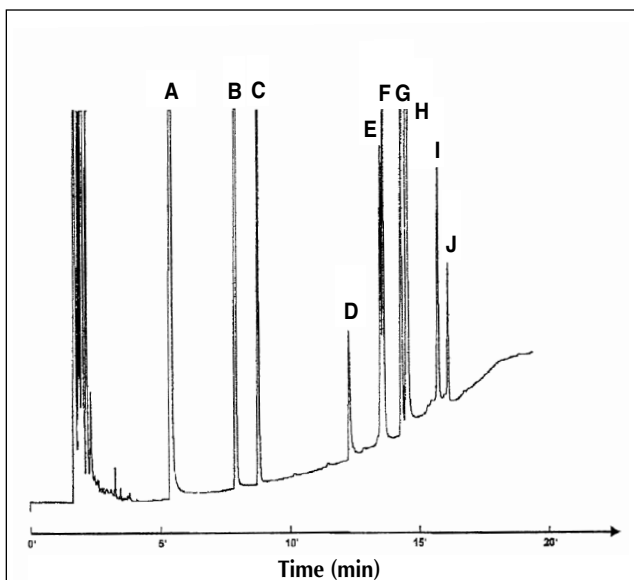


Figure 1. Solution A using a DB210 column and ECD. The peaks represent HCB (A); lindane (B); aldrin (C); dicophol (D); chlorothalonyl (E); dieldrin (F); 2,4'DDT (G); methyl-parathion (H); 4,4'DDT (I); and captan (J).

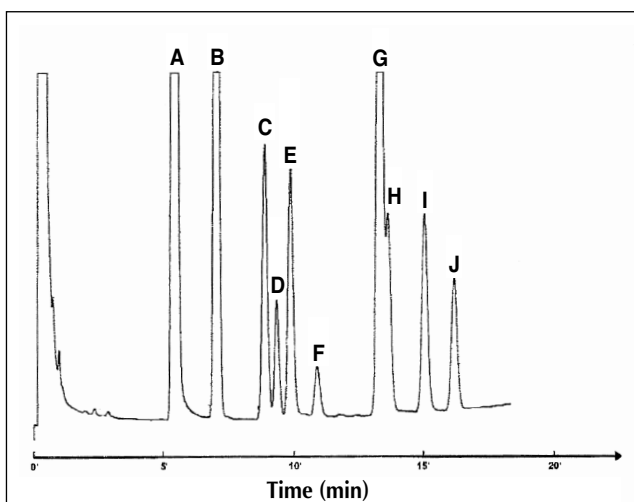


Figure 2. Solution A using an HP 17 column and ECD. The peaks represent HCB (A); lindane (B); aldrin (C); chlorothalonyl (D); methyl-parathion (E); dicophol (F); dieldrin (G); captan (H); 2,4'DDT (I); and 4,4'DDT (J).

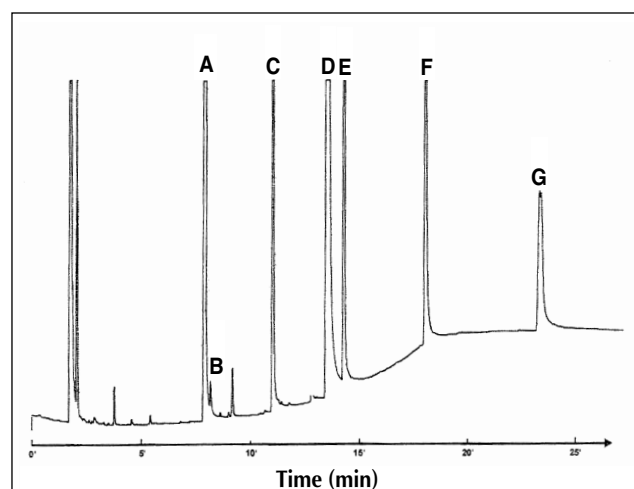


Figure 3. Solution B using a DB210 column and ECD. The peaks represent lindane (A); atrazine (B); chlorpyrifos (C); chlorothalonyl (D); methyl-parathion (E); procimidone (F); and iprodione (G).

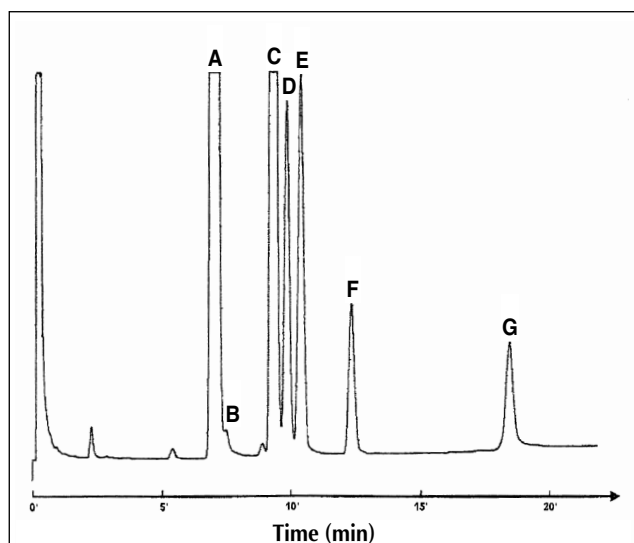
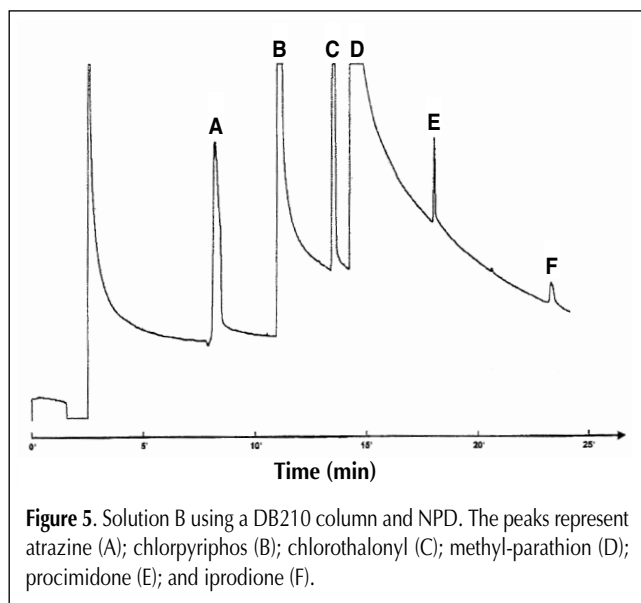


Figure 4. Solution B using an HP 17 column and ECD. The peaks represent lindane (A); atrazine (B); chlorothalonyl (C); methyl-parathion (D); chlorpyrifos (E); procimidone (F); and iprodione (G).



(RRT) of different pesticides in relation to lindane (4). In all cases, the references window was $\pm 1\%$. Table III presents the LOD of each pesticide and its respective recovery values. The standard deviation (SD) of the recovery is also presented.

The LODs are very acceptable taking into account the values of Lethal Concentration 50 (LC50), which is the concentration of the compounds that causes the death of 50% of organisms during incubation with toxicants for 24 h (3,4).

Figures 1–5 show representative chromatograms. It can be observed that the resolution of the pesticides presented coelutions, which made it difficult to identify some compounds. This inconvenience can be avoided by using two standard solutions (instead of only one) and the combination of columns and detectors mentioned above.

Examples of efficient separations in one condition and coelutions in another can be observed. For example, captan and dieldrin have a very good resolution in the DB 210 column (Figure 1), but coelute in the HP 17 column (Figure 2). Similar behavior can be observed with chlorothalonyl and dieldrin, which have very similar t_R in the DB210 column (Figure 1), but are clearly defined in the HP 17 column (Figure 2).

The behavior of lindane and atrazine is interesting. They do not have good resolution in the DB210 column (Figure 3) and

they coelute in the HP17 column (Figure 4), but when the NPD is used only the atrazine is detected (Figure 5).

The proposed method has the advantage of using SPE columns, which compared with the traditional liquid–liquid partition use less solvent, require less time, and result in higher recovery. These conditions are very important for safety and cost in this kind of analysis.

The proposed method was used in a survey of pesticide contamination of fresh waters (in preparation) with good results.

Acknowledgments

We would like to thank Liliana Di Marco and Ricardo Ferrari for their help in the pesticide selection and Roberto Ferrari (Agilent, Buenos Aires, Argentina) for the technical assistance.

This work was done with financial assistance from the Consejo de Investigaciones de la Universidad Nacional de Tucumán (CIUNT) (Tucumán, Argentina).

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Manuscript accepted December 23, 2002.