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Determination of triazines and organophosphorus pesticides in water samples using solid-phase extraction

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ABSTRACT

Octadecyl (C_{18})-bonded porous silica was evaluated for the extraction of triazine and organophosphorus pesticides from natural water. The extraction results showed an effective performance when 1 l of water was passed through small glass columns containing 500 mg of 50–100-μm C_{18}bonded porous silica. The adsorbed compounds were removed with ethyl acetate, evaporated to 200 μl and determined by gas chromatography. The overall average recoveries were greater than 85% except for dimethoate and trichlorfon. Application of this procedure to the analysis of natural water samples gave results that agree well with those obtained by solvent extraction methods.

INTRODUCTION

In recent years, the need for increased agricultural productivity has led to pesticide residues in natural waters at greater than ppb levels. Organophosphorus pesticides and triazine herbicides are currently the major types used on a worldwide scale as most organochlorine pesticides have been withdrawn from use because of their toxicity, persistence and bioaccumulation in the environment. Hence there is a need for methods suitable for detecting large numbers of those water pollutants at concentrations less than EEC the limit of 0.1 ng/l.

Several methods have been developed. The traditional approach involving solvent partition [1,2] is time consuming and expensive because of the high cost of the solvents. To reduce the analysis time and costs in multi-residue determinations [3], liquid–solid extraction methods were first introduced in 1974 [4] and more recently improved upon [5–8]. Among the solid supports available for solid-phase extraction of organic components from aqueous solution, octadecyl-bonded porous silica has become the most popular [9–15]. Its availability in inexpensive cartridges from several suppliers has contributed to an increase in the application of solid-phase extraction methods. However, when gas chromatography (GC) with electron-capture detection is used, some extraneous peaks appear that interfere in the analysis [16], caused by the plastics used for the cartridges. The use of glass microcolumns has the great advantage of avoiding contamination of the sample with plasticizers [17]. We report

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here the application of this technique to the determination of several pesticides in field studies of both surface and ground waters.

EXPERIMENTAL

Reagents

The organophosphorus pesticides used were cumaphos, purity 98% (Chemical Services), diazinon, purity 98.5% (Inquinasa), dimethoate, purity 97% (Argos), formothion, purity 96% (Sandoz), phorate, purity 93.5% (Chemical Services), piridafenthion, purity 99% (Inagra), pyrazophos, purity 99.2% (Hoechst), quinalphos, purity 99.5% (Sandoz), tetrachlorvinphos, purity 98.3% (Shell), triazophos, purity 93% (Hoechst), and trichlorfon, purity 92% (Afrasa). Triazine herbicides (prometryne, propazine and simazine) were obtained from Polyscience with purities of 99%. Stock solutions of the pesticides were prepared in ethyl acetate and diluted as required with distilled water.

Preparative octadecylsilica (55–105 μm) was obtained from Waters–Millipore.

Dichloromethane, ethyl acetate, diethyl ether, *n*-hexane, methanol and light petroleum (b.p. 40–60°C) were glass distilled and free from interfering residues as tested by GC (concentration 100:1). Buffer solutions of pH 2–9 were prepared [18].

Apparatus

A Konik 2000-C gas chromatograph equipped with a splitless injector, alkali flame ionization detector and a Spectra-Physics SP 4290 integrator was used. Two fused-silica capillary columns, one 25 m × 0.22 mm I.D., BP-5 (0.25 μm), provided by Scientific Glass Engineering, and the other 30 m × 0.24 mm I.D., DB-17 (0.25 μm), provided by J & W Scientific, with helium as the carrier gas were used to separate the pesticides. The injector and detector temperatures were 280 and 300°C, respectively. Splitless injection at 50°C was employed, followed by a 0.8-min delay before heating the column to 140°C at 30°C/min. The column temperature was maintained at 140°C for 2 min followed by further heating to 280°C at 5°C/min, the final temperature being maintained for 5 min.

Procedure

Microcolumn preparation. A 0.5-g amount of actadecylsilica was inserted in a Vidrafoc glass column (100 mm × 9 mm I.D.) with a sintered-glass coarse frit (No. 3) and covered with a plug of 0.1 g of silanized glass-wool. The microcolumn was conditioned with 5 ml of methanol and 10 ml of distilled water.

Sample extraction. The microcolumn was connected to a separating funnel with glass joints. A volume of 1 l of water sample was passed though the microcolumn. Vacuum by water aspiration was applied in order to obtain a flow-rate of about 40–45 ml/min. The C_{18}-bonded porous silica was then dried by drawing room air through the cartridge using a vacuum. The adsorbed residues were eluted with 5 ml of ethyl acetate by water aspiration at a flow-rate of 2–3 ml/min. The organic layer was concentrated to 0.2 ml using a gentle stream of nitrogen. Samples of 2 μl were injected into the gas chromatograph.

RESULTS AND DISCUSSION

Fig. 1 shows the simultaneous determination of the fourteen pesticides after solid-phase extraction from water. The BP-5 capillary column provided excellent resolution at the picogram level with baseline separation of all the pesticides and with a run time of *ca.* 30 min.

To confirm the results obtained, an additional capillary column of different

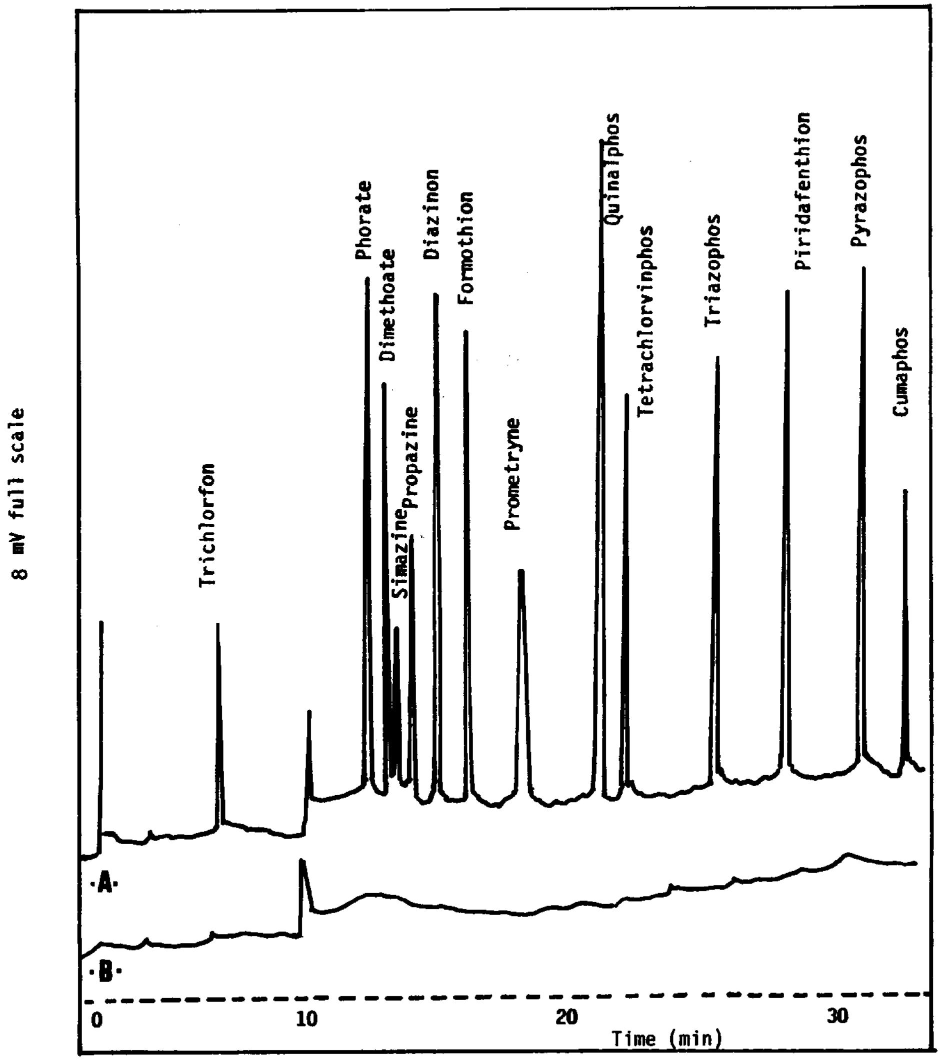

Fig. 1. (A) Gas chromatogram showing the separation of triazine herbicides and organophosphorus pesticides. Volume injected: 1 μl. Amounts injected (ng): trichlorfon 54, phorate 3, dimethoate 4, simazine 33, propazine 22, diazinon 1, formothion 3, prometryne 50, quinalphos 4, tetrachlorvinphos 4, triazophos 6, piridafenthion 2, pyrazophos 4 and cumaphos 7. For original concentrations, see Table I. (B) Chromatogram of a laboratory water blank.

polarity was employed for each real sample. The differences in elution order and retention times of the pesticides between the semipolar DB-17 and non-polar BP-5 columns aloowed the use of the two columns to confirm the identities of the pesticides.

In previous work [17], several pesticides were conveniently extracted and concentrated from water samples using a glass microcolumn containing 500 mg of C_{18}-bonded porous silica. Several additional herbicides and insecticides were included in the present study in order to examine further the effect of pH, salinity and eluent on the recovery efficiency.

The recoveries reported represent the means of five analyses. The pesticide concentrations in water were maintained constant throughout all the tests (see Table I).

The results given in Table I show the effect of the eluent on the recoveries of the fourteen pesticides at pH 7. Ethyl acetate was found to be the best eluting solvent.

Table II shows the effect of the pH of the spiked water samples on the performance of the octadecyl-bonded porous silica column. The results indicated that pH values between 6.0 and 8.0 give the best recoveries. The use of sea water had a negligible effect on the performance.

The effect of the volume of eluent (1–10 ml) was investigated. The maximum recovery was obtained with 4 ml for all the pesticides; 5 ml was adopted because it was found that the relative standard deviation was slightly lower.

Test were also performed to determine whether the sample volume affected the recovery of the pesticides. The recoveries for all compounds were satisfactory with 1 l

TABLE I

RECOVERIES OF PESTICIDES FROM SPIKED WATER USING DIFFERENT ELUENTS FOR SOLID-PHASE EXTRACTION

Pesticide	Amount added (μg/l)	Recovery (%)[a]		
		Ethyl acetate	*n*-Hexane	Light petroleum
Triazine herbicides				
Prometryne	10.00	94.8 ± 8.2	6.9 ± 18.1	6.8 ± 26.6
Propazine	5.00	79.6 ± 9.7	8.7 ± 28.6	5.5 ± 17.8
Simazine	7.00	75.6 ± 9.7	2.2 ± 17.4	0.4 ± 23.5
Organophosphorus pesticides				
Cumaphos	1.40	98.4 ± 8.1	36.4 ± 11.4	36.8 ± 10.8
Diazinon	0.20	84.9 ± 9.3	70.2 ± 8.0	78.7 ± 9.8
Dimethoate	10.00	16.2 ± 23.0	–	–
Formothion	0.80	65.1 ± 15.0	8.3 ± 29.6	11.1 ± 31.3
Phorate	1.00	59.4 ± 10.1	43.5 ± 10.1	52.0 ± 9.9
Piridafenthion	0.40	97.7 ± 7.9	–	–
Pyrazophos	0.80	93.5 ± 8.3	11.3 ± 33.6	11.9 ± 25.9
Quinalphos	0.80	89.8 ± 9.0	75.6 ± 8.9	78.7 ± 8.7
Triazophos	1.20	90.6 ± 8.7	5.5 ± 15.8	–
Tetrachlorvinphos	0.80	97.2 ± 7.4	4.1 ± 23.6	2.6 ± 26.9
Trichlorfon	180.00	6.9 ± 20.8	–	–

[a] Mean ± R.S.D. (%) ($n = 5$).

TABLE II

EFFECT OF pH ON ADSORBENT PERFORMANCE

Pesticides	Recovery (%)						
	pH 2.0	pH 3.5	pH 4.8	pH 6.1	pH 7.0	pH 8.0	pH 9.0
Triazine herbicides							
Prometryne	80.3	79.8	80.3	100.5	94.8	91.7	85.8
Propazine	10.4	45.1	66.6	90.2	79.6	71.1	72.0
Simazine	34.2	36.0	35.7	69.8	75.6	65.0	53.0
Organophosphorus pesticides							
Cumaphos	78.3	84.1	95.6	98.4	97.3	89.1	80.9
Diazinon	80.7	82.9	84.2	84.9	82.0	81.6	79.0
Dimethoate	8.1	8.8	10.8	8.9	16.2	8.3	–
Formothion	36.6	37.6	72.8	60.3	65.1	–	–
Phorate	–	–	8.7	17.7	59.4	69.3	74.4
Piridafenthion	22.7	47.7	69.9	99.9	89.8	78.7	75.1
Pyrazophos	36.0	50.1	66.6	92.5	93.5	32.0	4.0
Quinalphos	8.1	16.0	47.7	99.4	89.8	78.7	75.1
Triazophos	29.1	33.4	72.3	93.6	90.6	92.2	95.6
Tetrachlorvinphos	81.8	81.0	82.2	100.6	97.2	83.5	76.6
Trichlorfon	–	–	–	4.2	6.9	2.5	–

of sea, tap and lake water samples. When large amounts (10 l) of water samples containing the same amounts of pesticides were passed trichlorfon, phorate, prometryne, dimethoate, formothion, piridafenthion and pyrazophos were not recovered. Under the same conditions, the recoveries of quinalphos, triazophos and cumaphos decreased to 20, 65 and 16%, respectively. The recoveries of all the other pesticides studied showed no significant differences when 10-l samples were used.

Therefore, the optimum conditions for maximum recoveries of the pesticides were established as volume of water used for the extraction, 1 l; pH of the water, 7.0; and 5 ml of ethyl acetate as the extraction solvent.

As a low volume of organic eluent is finally obtained (200 μl), a high preconcentration ratio is achieved (1:5000), allowing a detection limit of lower than 0.1 μg/l, except for trichlorfon (see Table III), which shows a lower recovery and strong variations. The limit of detection was calculated by extrapolation from diluted samples that produced a chromatographic peak having a height equal to three times the standard deviation of the baseline noise [19].

A comparison of the recoveries obtained with C_{18} and with the solvent extraction procedures is shown in Fig. 2.

The application of the proposed method was tested on natural water samples, which were subjected to the trace-enrichment procedure described here. Albufera lake waters were very muddy, requiring filtration through a 1-μm glass filter prior to elution through the microcolumn, whereas the Mediterranean sea and tap waters were eluted directly through the adsorbent. The recoveries obtained for spiked waters demonstrate the applicability of the method (Table III).

The water samples analysed were collected in the Comunitat Valenciana during 1989–1990. Forty lake, irrigation and sea-water samples from different locations were

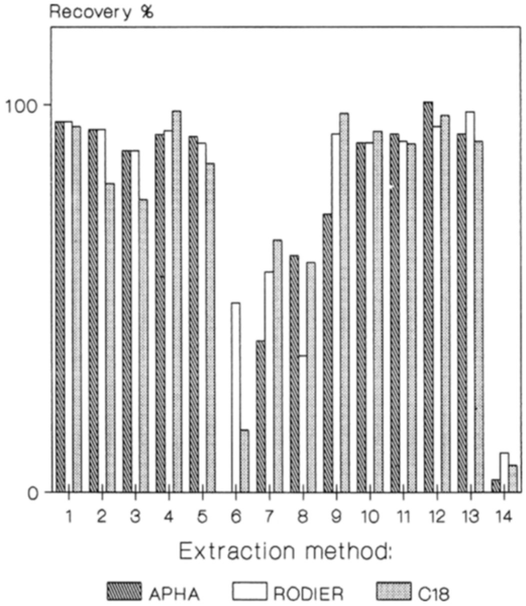

Fig. 2. Comparison of recoveries between the APHA [2] and Rodier [1] solvent extraction methods and the present (C_{18}) method. Pesticides: 1 = prometryne; 2 = propazine; 3 = simazine; 4 = cumaphos; 5 = diazinon; 6 = dimethoate; 7 = formothion; 8 = phorate; 9 = piridafenthion; 10 = pyrazophos; 11 = quinalphos; 12 = tetrachlorvinphos; 13 = triazophos; 14 = trichlorfon.

TABLE III

RECOVERY OF ORGANOPHOSPHORUS PESTICIDES AND TRIAZINE HERBICIDES ADDED TO 1 l OF DIFFERENT WATER SAMPLES AND DETECTION LIMITS OBTAINED

Pesticide	Detection limit (μg/l)	Recovery (%)		
		Tap water	Lake water	Sea water
Triazine herbicides				
Prometryne	0.052	99.6	97.3	96.4
Propazine	0.037	98.3	95.2	96.7
Simazine	0.092	71.0	71.4	59.9
Organophosphorus pesticides				
Cumaphos	0.045	82.4	98.4	90.0
Dimethoate	0.089	9.0	10.2	6.4
Diazinon	0.001	90.4	89.1	89.1
Formothion	0.016	61.0	64.2	60.9
Phorate	0.001	51.0	61.9	46.0
Piridafenthion	0.024	87.6	81.2	80.7
Pyrazophos	0.007	97.2	96.3	92.0
Quinalphos	0.002	81.3	90.0	89.0
Triazophos	0.048	87.0	86.9	84.0
Tetrachlorvinphos	0.010	88.7	84.7	86.2
Trichlorfon	0.729	5.5	5.7	6.3

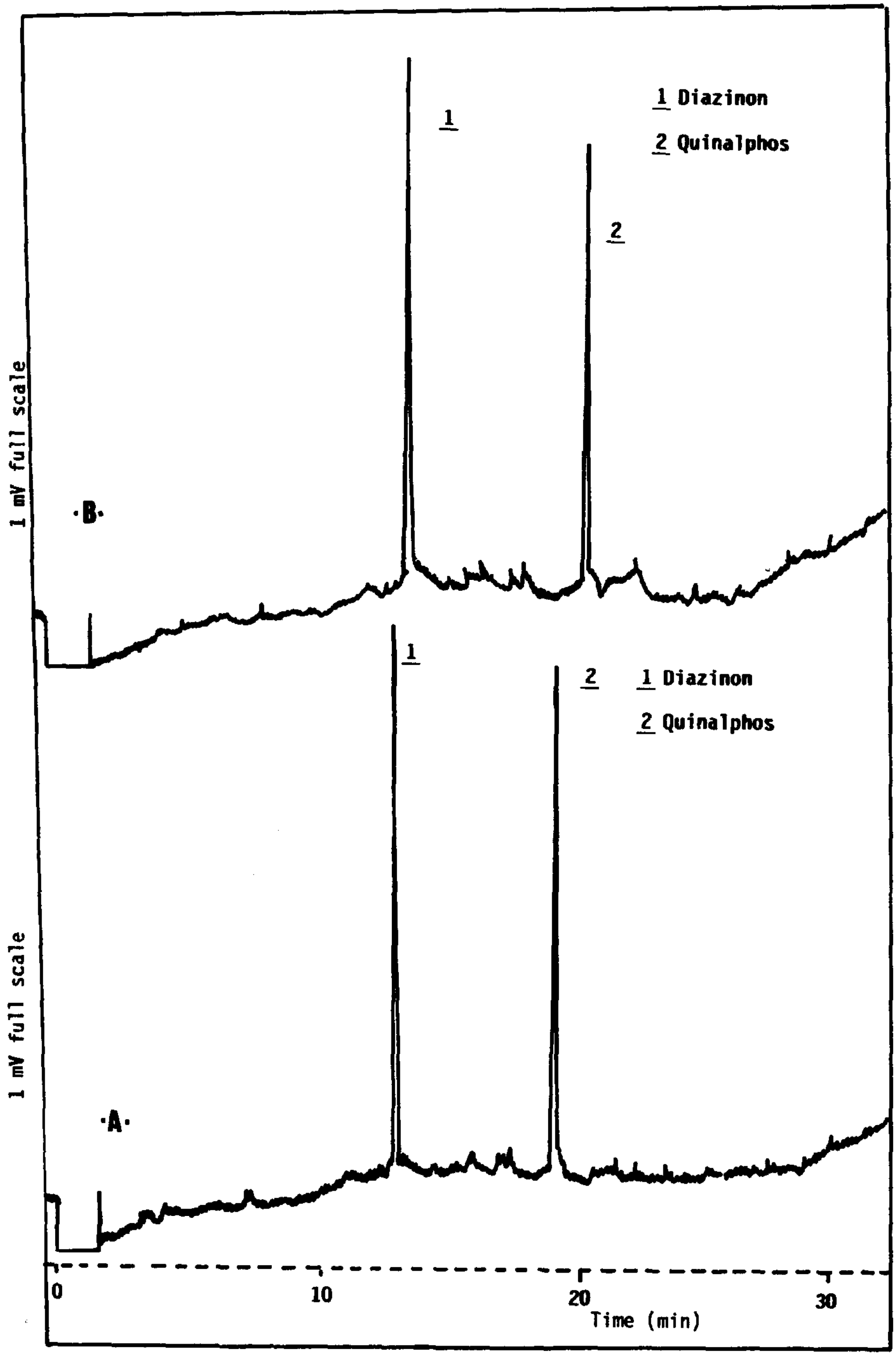

Fig. 3. Chromatograms for a 1-l irrigation channel water sample from Sueca, Valencia. (A) BP-5 column; (B) DB-17 column. Peaks: 1 = diazinon; 2 = quinalphos.

TABLE IV

LEVELS OF ORGANOPHOSPHORUS AND TRIAZINE COMPOUNDS IN NATURAL WATERS OF THE COMUNITAT VALENCIANA

Location	Compound	Level (μg/l)
Albufera lake	Diazinon	0.007
Irrigation channel, Marjal Pego	Cumaphos	0.152
Irrigation channel, Cullera	Simazine	0.308
Irrigation channel, Sueca	Diazinon	0.032
	Quinalphos	0.012
Irrigation channel, Sueca	Prometryne	0.176
	Tetrachlorvinphos	0.074
Irrigation channel, Perello	Prometryne	0.176
	Simazine	0.629
Irrigation channel, Mareny de les Barraquetes	Propazine	0.444
	Tetrachlorvinphos	0.036
Serpis river	Atrazine	0.734
	Triazophos	0.069
Irrigation channel, Sueca	Piridafenthion	0.053
Irrigation channel, Sueca	Piridafenthion	0.048
Irrigation channel, Mareny de Sant Llorens	Piridafenthion	0.039

analysed. Cumaphos, diazinon, piridafenthion, prometryne, propazine, quinalphos, simazine and tetrachlorvinphos were detected in 30% of the samples. The levels of pesticides found in the waters are given in Table IV.

Fig. 3 shows the chromatograms of irrigation channel water from Sueca. The pesticides found were diazinon and quinalphos.

In conclusion, the use of solid-phase extraction provides a rapid, efficient and reproducible method for the simultaneous determination of various pesticides in waters. The two-step extraction and concentration procedure minimizes residue losses and contamination problems. The simplicity of the analysis is complemented by good GC results.

The widespread occurrence of pesticide residues in the natural waters of the Comunitat Valenciana indicates pollution as a result of agricultural activity.

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