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ISOLATION AND CONCENTRATION OF ORGANOPHOSPHORUS PESTICIDES FROM WATER USING A C₁₈ REVERSED PHASE

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SUMMARY

A simple, rapid and effective method for the extraction and enrichment of organophosphorus pesticides based on the use of Sep-Pak C₁₈ cartridges was studied as alternative method to those based on extraction with organic solvents. The influence of the elution solvent, pH, salinity and volume of water filtered was studied for ten organophosphorus pesticides. The pesticides were determined by gas chromatography with a BP-1 capillary column and a thermionic detector. Recoveries at the 100 and 200 ng/l spiking levels were greater than 85%, except for disulfoton.

INTRODUCTION

The occurrence of organophosphorus pesticides (OPs) in aquatic environments is mainly due to their increasing agricultural use. The analysis of water for organophosphorus pesticides by high-resolution gas chromatography with a thermionic detector is the most widely used procedure, and requires previous efficient extraction, concentration and clean-up procedures.

The use of partitioning, in which the OPs are extracted from one solvent into another^{1–3}, and liquid–solid chromatography using various adsorbents such as activated carbon⁴, silica gel⁵, synthetic polymers such as XAD-2^{6,7}, XAD-4^{8,9} and Tenax¹⁰ and commercially available cartridges packed with octadecylsilica by formation of ion-association complexes with tetraphenylarsonium cation¹¹ or by simple adsorption of the pesticides^{12,13} have been developed for the isolation and concentration of OPs in water.

In this work we examined the performance of Sep-Pak C₁₈ cartridges for the extraction and concentration of ten OPs from water. The effects of elution solvent, pH, salinity and volume of water filtered and a comparison with the Rodier² and the APHA methods³ are reported.

EXPERIMENTAL

Reagents

The OPs used were disulfoton, purity 97.1% (Bayer Hispania Comercial); ethion, purity 95% (Industrias Quimicas Argos); fonofos, purity 93.5% (Industrias Quimicas Serpiol); heptenophos, purity 93% (Industrias Quimicas Argos); malathion, purity 98% (Industrias Quimicas Serpiol); parathion-ethyl, purity 99.2% (Bayer Hispania Comercial); parathion-methyl, purity 80% (Bayer Hispania Comercial); phenthoate, purity 93% (Industrias Quimicas Serpiol); trithion, purity 90% (Industrias Quimicas Serpiol); and sumithion, purity 95% (Agrocros). Stock solutions of the OPs were prepared in ethyl acetate and diluted further with distilled water.

Sep-Pak C₁₈ cartridges were obtained from Waters Assoc.

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 gas chromatography (concentration 100:1). Buffer solutions of pH 2–9 were prepared¹⁴.

Apparatus

A Konik 2000-C gas chromatograph equipped with a splitless injector, an alkali flame ionization detector and a Spectra-Physics SP 4290 integrator was used. A 25 × 0.22 mm I.D. BP-1 0.25- μ m fused-silica capillary column provided by Scientific Glass Engineering with helium as the carrier gas was used to separate the pesticides. The injector and detector temperatures were 260 and 280°C, respectively. Splitless injection at 45°C was employed, followed by a 0.6-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 260°C at 5°C/min; the final temperature was maintained for 5 min.

Procedure

The cartridge was connected to a 1-l separating funnel with appropriate fittings. The cartridge was activated before use by passing 5 ml of methanol through it, followed by 10 ml of distilled water.

A volume of 1 l of water was spiked with a mixture containing 100–200 ng/l of each OP. This sample was eluted through the cartridge, by applying a vacuum by water aspiration, at a flow-rate of about 40–45 ml/min. The adsorbed residues were eluted with 5 ml of organic solvent. The organic layer was concentrated to 1 ml using a gentle stream of nitrogen. Samples of 2 μ l were injected into the gas chromatograph.

RESULTS AND DISCUSSION

Fig. 1 shows the chromatogram for the separation of the ten OPs after Sep-Pak extraction from water. This chromatogram, obtained using a nitrogen-phosphorus detector, did not contain extraneous peaks.

The recovery efficiency for evaluating the overall performance of the Sep-Pak C₁₈ cartridge was tested by analysing fortified distilled water samples. In order to establish the optimum conditions for the extraction of the pesticides, the elution solvent, pH, salinity and volume of water filtered were varied.

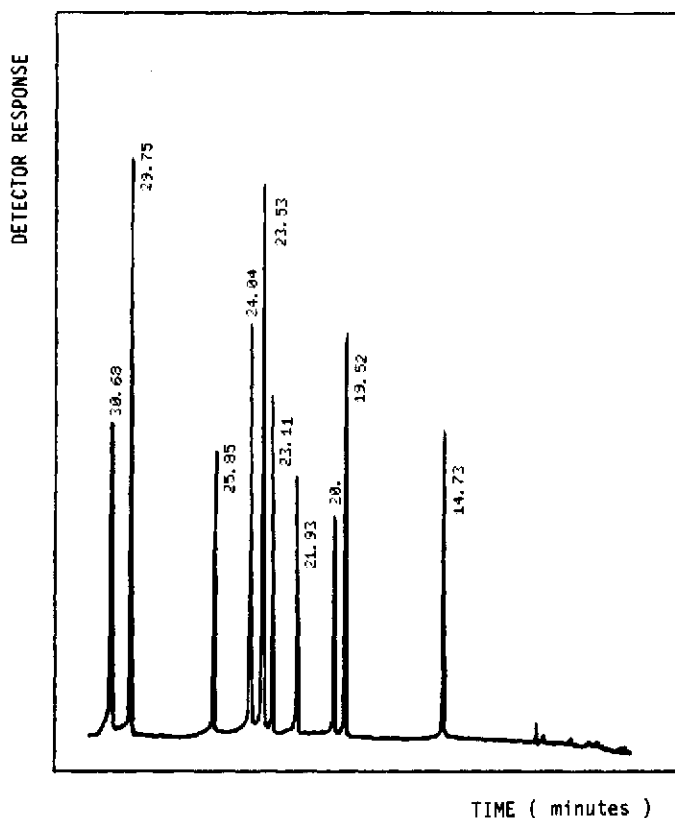


Fig. 1. Chromatogram for the separation of ten OPs. Volume injected, 2 μ l. Amount of OPs 200–400 pg. OPs and retention times (indicated at the peaks): heptenophos, 14.73 min; fonofos, 19.52 min; disulfoton, 20.0 min; parathion-methyl, 21.93 min; malathion, 23.11 min; sumithion, 23.53 min; parathion-ethyl, 24.04 min; phenthoate, 25.85 min; ethion, 29.75 min; trithion, 30.68 min.

The recoveries reported are means of five analyses. The pesticide concentrations in water was maintained constant through all the tests (0.2 μ g/l, except for disulfoton, ethion and fonofos, which were at 0.1 μ g/l). The coefficients of variation ranged between 5 and 10%.

Table I gives the recoveries obtained using 1 ml of ethyl acetate, *n*-hexane and light petroleum as eluents for the ten OPs at pH 7. A study of the effect of pH on the recovery of 1 ml of ethyl acetate it showed (Table II) that pH values between 4.8 and 8 give the best recoveries.

When the assay was carried out in presence of 35 g/l of sodium chloride at pH 7 and eluting with 1 ml of ethyl acetate, the followed recoveries were obtained: heptenofos 77%, fonofos 79%, disulphoton 68%, parathion-methyl 89%, malathion 99%, sumithion 93%, parathion-ethyl 85%, phenthoate 84%, ethion 73% and trithion 83%. Comparing these values with those in Tables I and II, a negligible effect of salinity, as in sea water, on the performance was observed.

For heptenofos, fonofos and ethion, the recovery was improved by increasing

TABLE I
PERFORMANCE OF Sep-Pak C₁₈ CARTRIDGES

Pesticide	Recovery (%)		
	Ethyl acetate	n-Hexane	Light petroleum
Heptenophos	75	36	29
Fonofos	83	71	89
Disulfoton	76	58	46
Parathion-methyl	96	81	79
Malathion	101	85	76
Sumithion	98	20	24
Parathion-ethyl	93	85	82
Phenthoate	83	69	65
Ethion	79	94	86
Trithion	89	90	80

TABLE II
EFFECT OF pH ON ADSORBENT PERFORMANCE

Pesticide	Recovery (%)						
	pH 2.0	pH 3.5	pH 4.8	pH 6.1	pH 7.0	pH 8.0	pH 9.0
Heptenophos	59	63	68	74	75	73	61
Fonofos	48	71	72	79	83	85	52
Disulfoton	43	60	69	72	76	81	37
Parathion-methyl	66	71	89	93	96	77	64
Malathion	69	72	88	98	101	98	60
Sumithion	67	78	91	95	98	89	57
Parathion-ethyl	57	80	87	89	93	85	65
Phenthoate	53	68	77	80	83	84	36
Ethion	42	63	70	76	79	79	45
Trithion	53	75	75	84	89	92	52

TABLE III
EFFECT OF VOLUME OF FILTERED WATER ON THE RECOVERY AND DETECTION LIMITS OBTAINED

Pesticide	Recovery (%)		Detection limit (pg)
	1 l	10 l	
Heptenophos	86	88	52
Fonofos	95	69	20
Disulfoton	74	89	15
Parathion-methyl	98	91	39
Malathion	99	97	78
Sumithion	98	93	15
Parathion-ethyl	94	92	52
Phenthoate	89	93	31
Ethion	95	89	18
Trithion	89	94	52

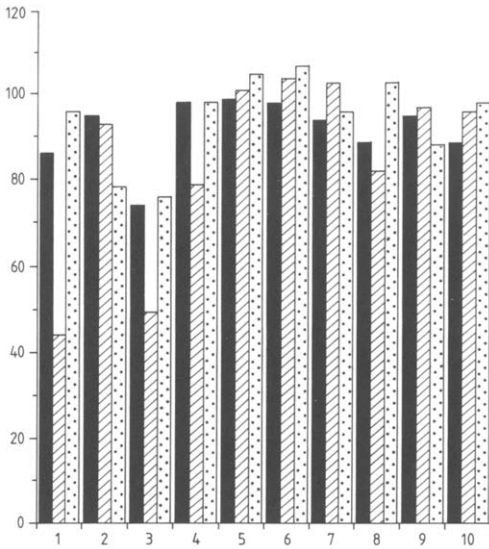


Fig. 2. Comparison of recoveries between the APHA³ (hatched) and Rodier² (shaded) methods and the present method (black). 1 = Heptenophos; 2 = fonofos; 3 = disulfoton; 4 = parathion-methyl; 5 = malathion; 6 = sumithion; 7 = parathion-ethyl; 8 = phenthoate; 9 = ethion; 10 = trithion.

TABLE IV

RECOVERY OF ORGANOPHOSPHORUS PESTICIDES ADDED TO 1 l OF DIFFERENT WATERS

Pesticide	Level of spike ($\mu\text{g/l}$)	Recovery (%)		
		Tap water	Lake water	Sea water
Heptenophos	1	87	83	88
	0.1	72	65	77
Fonofos	1	94	78	96
	0.1	85	63	81
Disulfoton	1	95	72	93
	0.1	76	56	79
Parathion-methyl	1	108	90	104
	0.1	91	87	89
Malathion	1	103	92	99
	0.1	98	85	96
Sumithion	1	99	95	102
	0.1	94	78	100
Parathion-ethyl	1	95	92	97
	0.1	91	81	89
Phenthoate	1	89	75	91
	0.1	80	69	80
Ethion	1	93	91	90
	0.1	79	68	85
Trithion	1	100	79	101
	0.1	90	60	88

the volume of ethyl acetate, the best recovery being observed with 5 ml of eluent (Table III). Greater volumes of ethyl acetate did not improve the results.

Similar recoveries were obtained with the same amount of pesticide but increasing the volume of filtered water from 1 to 10 l, except for fonofos and disulphoton, which gave lower and higher recoveries, respectively, as shown in Table III. Table III also gives the detection limits¹⁵ using a 10-l water sample. As a low volume of organic eluent is finally obtained (1 ml), a high preconcentration ratio is achieved (1:10 000), allowing a detection limit of lower than 0.4 ppt^a in all instances.

The recoveries reported here are in good agreement with those obtained using the methods reported by Rodier² and APHA³ (Fig. 2).

Table IV demonstrates the performance of the octadecyl-bonded porous silica when local environmental water samples were spiked with a mixture of the ten OPs. Fortified and non-fortified samples were run in parallel. Albufera lake waters were very muddy, requiring filtration through a 1- μ m glass filter prior to elution through the Sep-Pak C₁₈ cartridge, whereas the Mediterranean Sea and tap waters were eluted directly through the adsorbent.

This rapid and efficient method obviates the use of long sequential solvent extraction methods, thus substantiating the usefulness of Sep-Pak C₁₈ cartridges for determining OPs in water.

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^a The American trillion (10¹²) is meant.