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CONVERSION OF A CONVENTIONAL PACKED-COLUMN GAS CHROMATOGRAPH TO ACCOMMODATE MEGABORE COLUMNS

II. DETERMINATION OF ORGANOPHOSPHORUS PESTICIDES IN ENVIRONMENTAL WATER

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SUMMARY

Several methods involving solvent extraction or solid extraction (Amberlite XAD resins) were studied for the multi-residue recovery of fourteen organophosphorus compounds in water. It was found that extraction with ethyl acetate in a salted medium provided the most consistent data, both in terms of number of compounds recovered and percentage recovery. Amberlite XAD resins gave consistently high recoveries, and this was attributed to a matrix effect upon the particular nitrogen–phosphorus detector.

The evaluation was made using a megabore column installed in a conventional packed-column chromatograph, and the results show that such a system is amenable to the multi-residue analysis of organophosphorus pesticides at very low cost.

INTRODUCTION

Organophosphorus pesticides form a large class of compounds with various chemical structures. This presents a problem in terms of developing a multi-residue method for their analysis from environmental samples, since extraction and instrumental methods of analysis are not universal. Aqueous samples of organophosphorus pesticides may be extracted with an organic solvent, such as ethyl acetate, benzene, chloroform, dichloromethane or hexane. Suffet *et al.*[1] have determined that proper control of pH and ionic strength is necessary to obtain reproducible recoveries.

Solid phase extraction of aqueous samples has become very common in recent years. Amberlite XAD resin columns have been used for the recovery of fenitrothion and several breakdown products in water[2–4]. This technique has been extended to the recovery of organophosphorus pesticides from tap water by sampling large volumes[5]. Adsorption columns[6] and, more recently, reversed-phased adsorbants[7] have also been used.

The most popular approach to the analysis of organophosphorus pesticides is gas–liquid chromatography (GLC). Until recently mostly packed columns coupled to

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various detectors, such as the flame photometric[8], the thermionic[9], the electron capture[10] and the Hall[11], were used. However, the number of organophosphorous pesticides that may be analysed simultaneously with packed columns is limited by lack of resolution and lack of volatility.

Recently, dedicated capillary chromatographs[12–15] have been used with excellent results in terms of resolution, but limited capacity is a drawback. Megabore columns offer an alternative in the sense that they possess good resolution and capacity[16].

In the first part of this project[17] a packed-column gas chromatograph was converted into a megabore system and used for the analysis of fourteen organophosphorous compounds. In this part of the study the object was to evaluate several approaches to their multi-residue extraction in water using megabore column GLC.

EXPERIMENTAL

Materials and apparatus

These were as described in Part I[17]. The environmental water came from a lake used for drinking water.

Amberlite XAD resin column and extraction

The resin (500 g) in a 1-l beaker was cleaned with ethyl acetate by placing the container in an ultrasonic bath for 15 min. It was filtered, and cleaned again with ethyl acetate, then with methanol followed by purified water.

Columns were prepared as described earlier[2–4]. A 1-l water sample was processed by passage through an XAD resin column (gravity flow) and elution with two 100-ml volumes of ethyl acetate. The final volume was adjusted to 10.0 or 1.0 ml.

Solvent extraction of organophosphorus compounds from water

A 1-l water sample was fortified with the multi-residue standard at the appropriate concentration, and the sample was stirred for 10 min. The sample was then extracted with three 100-ml volumes of solvent (ethyl acetate, dichloromethane or hexane). The extract was dried with anhydrous sodium sulphate, evaporated to a small volume on a rotary evaporator, then adjusted to 10.0 ml. Duplicate extractions were done for each set of conditions. Whenever variation was observed a third or fourth sample was processed until agreement was obtained.

Purified water (pH 5.8) was used as control. A series of samples was also prepared by adjusting the pH to 3.0 using HCl (1.0 *M*). Another set of samples was prepared by adding 50 g of NaCl to purified water.

RESULTS AND DISCUSSION

In Part I[17] it was established that fourteen organophosphorus compounds could be separated on a SPB-5 megabore column and that the limit of quantitation using a multi-residue standard was 1.0 ng. At this level the coefficients of variation (C.V.) varied between 5 and 27%, with an average of 12%. Bearing this in mind, water samples were fortified at the 10 μg/l (ppb) level and extracted using Amberlite XAD-4, Amberlite XAD-7, ethyl acetate, dichloromethane or hexane. Extraction was also performed under different conditions of pH and salinity. Percentage recoveries were obtained by comparing peak heights with those of a multi-residue external standard of the same concentration.

The results for purified water are presented in Table I. Values for each pesticide are expected to vary according to the respective C.V.[17], which is a parameter indicative of the precision of the gas chromatographic analysis using standard solutions. For instance, the value for fenitrothion recovery with hexane should be 93% ± 7%, that for phosmet should be 118% ± 27%. Several data were outside the normal error range of the method: these are indicated in Table I. This indicates that some additional factor has an influence on the reproducibility. Accuracy, or how close to 100% the recovery values will be, is another matter. It depends on the effectiveness of the recovery step and many factors interfere along the way. At the limit of quantitation of a method the variation may be very high, and it becomes difficult to decide what is acceptable. Thus, in this study, for the purpose of comparison between methods, values within a range of 100% ± 25% will be considered acceptable.

The data for hexane in Table I show that nine pesticides are well recovered, four cannot be detected and one value is too low. This is reflected by the recovery ratios (9:4:1:0), which have been used in this study to compare the effectiveness of the various methods. The recovery ratio for dichloromethane shows that only three recoveries are acceptable (3:3:8:0). Good results were obtained with ethyl acetate with a ratio of 10:2:2:0. With Amberlite XAD-7 the ratio 10:2:1:1 indicates good performance, although the same pesticides are not involved. With Amberlite XAD-4 the

TABLE I

PERCENTAGE RECOVERY OF ORGANOPHOSPHORUS PESTICIDES (10 ppb) FROM PURIFIED WATER (pH 5.8)

ND = Not detected.

Pesticide	*Extractant*				
	Hexane	*Dichloromethane*	*Ethylacetate*	*XAD-7*	*XAD-4*
Methamidophos	ND	ND	ND	ND	16[a]
Acephate	ND	ND	ND	ND	9[a]
Trichlorfon	ND	ND	21[a]	63[a]	104
Phorate	99	70[a]	99	85	95
Dimethoate	ND	51[a]	66[a]	113[a]	161[a]
Fonofos	104	71[a]	110	89	92
Diazinon	93	69[a]	95	89	101
Disulfoton	98	67[a]	101	107	117[a]
Fenitrothion	93	71[a]	93	95	108[a]
Malathion	93	68[a]	102	88	103
Ethyl-parathion	92	68[a]	93	101	105
Tetrachlorvinphos	95	80[a]	91	106	126[a]
Fensulfothion	53[a]	94	90	112[a]	147[a]
Phosmet	118	105	86	213[a]	251[a]
Recovery ratios[b]	9:4:1:0	3:3:8:0	10:2:2:0	10:2:1:1	9:0:2:3

[a] Recovery is outside the C.V. range[17].

[b] Recovery ratio means acceptable recovery:not detected:low value:high value.

recoveries for methamidophos and acephate are out of range because of low results, and three values are excessively high. Overall the results with ethyl acetate and Amberlite XAD-7 are equivalent, although not similar for all pesticides. An explanation for the high values with XAD resins will be offered later.

Some extraction procedures are known to improve at lower pH, particularly when acidic compounds are present. Thus the pH was adjusted to 3.0. The results, presented in Table II, indicate that a decrease in pH has a favourable effect with dichloromethane but very little effect with the other solvents. With XAD resins more of the values are greater than 125%. Some high values are also observed with the organic solvents. Several attempts to increase recoveries were made at pH 7.5, 8.5 and 9.5, but without success.

Sometimes, particularly with slightly water-soluble solvents and to increase the partition coefficient of a solute in an organic solvent, the water sample is saturated with sodium chloride. The results, presented in Table III, show that salt addition favours recovery with organic solvents but with the resins more higher values are obtained.

The overall picture (compare recovery ratios) indicates that, among the three organic solvents, recoveries with ethyl acetate are better and more organophosphorus pesticides are recoverd. Recoveries with hexane are good, with the exception of four compounds. Recoveries with dichloromethane are positive but the values are low. In general, recoveries are better at a lower pH or in a salt-saturated medium. Recoveries with Amberlite XAD resins are sometimes high, particularly at low pH or in a salt medium. However, Amberlite XAD-4, in particular, recovers some part of all the

TABLE II

PERCENTAGE RECOVERY OF ORGANOPHOSPHORUS PESTICIDES (10 ppb) FROM PURIFIED WATER (pH 3.0)

ND = Not detected.

Pesticide	*Extractant*				
	Hexane	*Dichloromethane*	*Ethylacetate*	*XAD-7*	*XAD-4*
Methamidophos	ND	ND	ND	12[a]	ND
Acephate	ND	ND	ND	11[a]	ND
Trichlorfon	ND	ND	25[a]	71[a]	82
Phorate	112[a]	98	95	61[a]	98
Dimethoate	ND	101	80	156[a]	140[a]
Fonofos	122[a]	109	119[a]	89	97
Diazinon	105	95	93	92	100
Disulfoton	109	94	96	15[a]	134[a]
Fenitrothion	115[a]	106	104	127[a]	114[a]
Malathion	117[a]	103	108	97	103
Ethyl-parathion	112[a]	104	100	97	113[a]
Tetrachlorvinphos	118[a]	111	98	115[a]	128[a]
Fensulfothion	88	159[a]	102	143[a]	134[a]
Phosmet	192[a]	171[a]	121[a]	204[a]	236[a]
Recovery ratios	9:4:0:1	9:3:0:2	11:2:1:0	5:0:5:4	7:2:0:5

[a] Recovery is outside the C.V. range[17].

TABLE III

PERCENTAGE RECOVERY OF ORGANOPHOSPHORUS PESTICIDES (10 ppb) FROM PURIFIED WATER SATURATED WITH SODIUM CHLORIDE

ND = Not detected.

Pesticide	*Extractant*				
	Hexane	*Dichloromethane*	*Ethylacetate*	*XAD-7*	*XAD-4*
Methamidophos	ND	ND	ND	ND	10[a]
Acephate	ND	ND	ND	ND	11[a]
Trichlorfon	ND	ND	41[a]	93	112[a]
Phorate	104	79[a]	96	111[a]	92
Dimethoate	ND	66[a]	87	163[a]	175[a]
Fonofos	110	88	105	107	99
Diazinon	105	76[a]	99	108	110
Disulfoton	106	72[a]	96	130[a]	89
Fenitrothion	108	84	99	122[a]	119[a]
Malathion	105	79[a]	96	114[a]	110
Ethyl-parathion	105	81	95	114[a]	111
Tetrachlorvinphos	110	88	98	132[a]	127[a]
Fensulfothion	95	124[a]	102	143[a]	161[a]
Phosmet	133[a]	119[a]	87	215[a]	249[a]
Recovery ratios	9:4:0:1	9:3:4:0	11:2:1:0	7:2:0:5	8:0:2:4

[a] Recovery is outside the C.V. range[17]

organophosphorus pesticides tested. None of the above extraction methods successfully recovered methamidophos or acephate, although Amberlite XAD-4 showed some recovery, and trichlorfon could not be recovered successfully with organic solvents.

The major cause for the high results, which is more pronounced with Amberlite XAD-4, is attributable to a matrix effect. A standard solution of the pesticides was prepared in ethyl acetate that had been eluted through a resin column. The results compared to a regular standard in ethyl acetate are presented in Table IV. They show that the detector response increases tremendously in some cases (300% phosmet), indicating a definite matrix effect. The fault in this case lies mostly with the filament bead of the nitrogen–phophorus detector and not on the XAD resin. If it was not for the matrix effect, Amberlite XAD-4 columns would probably have given quantitative recoveries for twelve out of fourteen pesticides. Therefore Amberlite XAD resin columns should not be discounted as an extraction procedure for organophosphorus pesticides.

To reduce the matrix effect the data were recalculated using the internal standard approach. Usually an internal standard has a structure and chromatographic properties similar to those of the analytes, and the peak must be well resolved. Thus, using tetrachlorvinphos as internal standard gave the results in Table IV for purified water. The results are very similar to those obtained with the external standard (*cf.* Tables I–III) except for dichloromethane, where the values are now mostly in the acceptable range. The use of fenitrothion as internal standard was also tested and the same conclusion was obtained, *i.e.* the internal standard approach can correct for

TABLE IV

EFFECT OF CO-EXTRACTIVES FROM AMBERLITE XAD-4 RESIN ON DETECTOR RESPONSE

Pesticide	*Peak height (cm) of standard in purified methyl acetate*	*Peak height (cm) of standard in ethyl acetate extract*	*Increase (%)*
Methamidophos	13.0	21.5	65.4
Acephate	8.3	14.5	74.7
Trichlorfon	3.8	4.7	23.7
Phorate	21.8	24.5	12.4
Dimethoate	23.2	38.3	65.1
Fonofos	77.8	85.0	9.3
Diazinon	34.5	38.5	11.6
Disulfoton	50.5	58.0	14.9
Fenitrothion	43.3	59.3	37.0
Malathion	67.8	78.5	15.8
Ethyl-parathion	62.5	77.8	24.5
Tetrachlorvinphos	38.8	55.3	42.5
Fensulfothion	12.3	28.3	130
Phosmet	4.0	16.0	300

TABLE V

PERCENTAGE RECOVERY OF ORGANOPHOSPHORUS PESTICIDES (10 ppb) FROM DISTILLED WATER (pH 5.8) WITH TETRACHLORVINPHOS AS INTERNAL STANDARD

ND = Not detected.

Pesticide	*Extractant*				
	Hexane	*Dichloromethane*	*Ethylacetate*	*XAD-7*	*XAD-4*
Methamidophos	ND	ND	ND	ND	12[a]
Acephate	ND	ND	ND	ND	7[a]
Trichlorfon	ND	ND	23[a]	59[a]	82
Phorate	104	88	103	81	74[a]
Dimethoate	ND	64[a]	73[a]	108	128[a]
Fonofos	110	89	121[a]	85	74[a]
Diazinon	97	87	105	84	81
Disulfoton	104	85	112	102	94
Fenitrothion	98	89	102	90	86
Malathion	98	85	113	84	82
Ethyl-parathion	97	86	102	83	84
Tetrachlorvinphos	–	–	–	–	–
Fensulfothion	56[a]	119[a]	100	106	116[a]
Phosmet	124[a]	132[a]	95	200[a]	198[a]
Recovery ratios	8:4:1:0	8:3:1:1	9:2:2:0	9:2:1:1	7:0:4:2

[a] Recovery is outside the C.V. range[17].

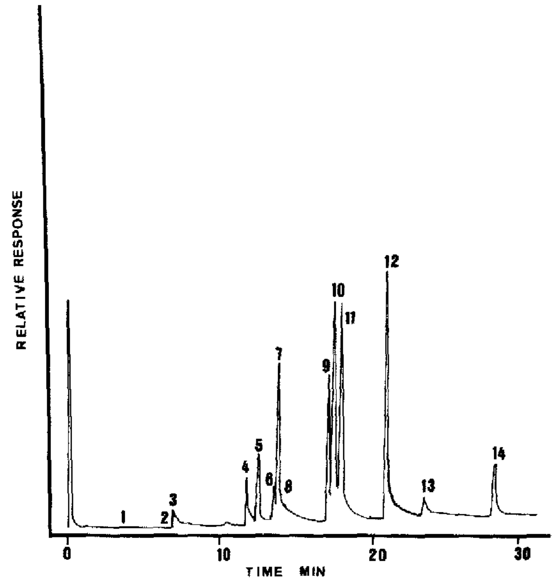

Fig. 1. Chromatogram of an extract of fourteen organophosphorus pesticides in environmental water at 1.0 μg/l. Extraction with ethyl acetate and sodium chloride. Peaks: 1 = methamidophos; 2 = acephate; 3 = trichlorfon; 4 = phorate; 5 = dimethoate; 6 = fonofos; 7 = diazinon; 8 = disulfoton; 9 = fenitrothion; 10 = malathion; 11 = ethyl-parathion; 12 = tetrachlorvinphos; 13 = fensulfothion; 14 = phosmet.

matrix effects in some cases but overall the picture is not much better than with an external standard. This was expected since the detector response to the matrix is not equivalent for each OP (see Table IV).

Determination of the limit of quantitation in environmental water

It has already been established that, at 10 ppb, eleven out of fourteen organophosphorus pesticides may be recovered successfully from water with ethyl acetate in a salt-saturated medium (methamidophos, acephate and trichlorfon are not well recovered). Under the same extraction conditions fonofos, disulfoton and fensulfothion cannot be quantitated at the 1.0 ppb level, as shown in Fig. 1. Only diazinon, fenitrothion, malathion and ethyl parathion may be determined quantitatively using the multi-residue approach.

CONCLUSION

This study confirms that a megabore column installed in a conventional gas chromatograph may be used for the separation and quantitation of organophosphorus compounds from a multi-residue sample of water. Evaluation of a liquid extraction procedure *versus* solid extraction showed that extraction with ethyl acetate in a salted medium gave the most reliable recoveries for eleven compounds out of fourteen. Extraction with Amberlite XAD-4 gave excellent recoveries with twelve out of fourteen compounds, but some of the values were consistantly high, a phenomenon attributed to a matrix effect towards the nitrogen–phosphorus (thermionic) detector.

Sasaki *et al.*[16] have studied the use of megabore columns in a dedicated capillary gas chromatograph for the multi-residue determination of organophosphorus compounds in various crops. They used megabore columns, 10–12 m × 0.53 mm I.D., containing CBP-10, CBP-1 or 5% phenyl methyl silicone. The last stationary phase compares favourably with SPB-5 used in this study. Their results showed a limit of detection five to ten times better than ours with comparable resolution (for those organophosphorus compounds in common) using a flame photometric detector. However, such a limit of detection could be attained with a modified megabore system using the nitrogen–phosphorus detector, provided the latter is performing as it should.

Thus it is fair so say that the megabore dedicated capillary system used by Sasaki *et al.* gave a slightly better performance than the modified conventional megabore system used in this study. However, we feel that the results obtained with the modified system are satisfactory in terms of performance, and the method proposed in this study (extraction with ethyl acetate in salted medium) is applicable to the multi-residue analysis of organophosphorus pesticides in environmental water, although the use of Amberlite XAD-4 should not be discounted. Conversion of a conventional chromatograph to megabore (and back to packed columns) is simple and involves little cost. It is felt that improvements in resolution and quantitation could be made with better conversion kits and a more reliable nitrogen–phosphorus detector.

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