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Note

The use of Amberlite XAD-2 resin for the quantitative recovery of fenitrothion from water—a preservation technique

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Amberlite marcoreticular resins are hard, insoluble beads of porous polymer, ranging in physical properties from being essentially non-polar to very polar. They have been studied in terms of their usefulness for the recovery of various organic contaminants from environmental water.

For instance, Burham *et al.*[1] have used Amberlite XAD-2 for the quantitative recovery in the ppb range of methyl isobutylketone, ethyl butyrate, benzene, naphthalene, benzoic acid, 2,4-dimethylphenol, *p*-nitrophenol, 2-methylphenol, aniline and *o*-cresol. They have been used for the extraction and recovery of chlorinated insecticides and polychlorinated biphenyls from water[2,3]. This has led to the development of a multi-residue technique for the extraction of organochlorine pesticides and polychlorinated biphenyl from natural waters[4]. They have also been used to determine pesticides such as Atrazine, DDE and Dieldrin from various Iowa waters[5].

Recently Amberlite XAD-4 has been applied to the analysis of phosphorous-containing hydrolytic products of organophosphorous insecticides in water[6]. This has shown the potential of using Amberlite resins for the recovery of organophosphorous pesticides.

This study demonstrates the use of Amberlite XAD-2 resin for the recovery of fenitrothion, an organophosphorous insecticide, from aqueous environmental samples. More interesting is the fact that the insecticide is stable on the column for extended time periods making the procedure suitable as a preservation technique.

EXPERIMENTAL

Analytical grade fluorescamine was purchased from Fisher Scientific (Montréal, Canada) and a 0.025% (w/v) solution was prepared in acetone. A solution of stannous chloride was prepared by dissolving 0.5 g in 5 ml of concentrated hydrochloric acid and diluting to 120 ml with a solution of 50 ml of water plus 65 ml of acetone. This solution was always freshly prepared. Fenitrothion (Folithion) was obtained from Chemagro (Kansas City, Mo., U.S.A.). A stock solution was prepared 1 $\mu g/\mu l$ in ethanol and dilutions were made in *n*-hexane.

Layers (250 μm thick) of silica gel H (20 × 20 cm) were prepared using a

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mixture of 30 g of silica gel H (Brinkmann, Rexdale, Canada) and 80 ml of 0.1 *M* KH_2PO_4. The plates were left to dry in air and were not activated before use.

Amberlite XAD-2 resin was supplied by BDH (Toronto, Canada). Prior to use it was washed successively with 50 ml of ether, 25 ml of methanol and 1 l of distilled water. The glass column was 50 cm × 2.2 cm I.D. and had a PTFE stopcock.

Apparatus

A Turner Fluorometer Model III (G. K. Turner Assoc., Palo Alto, Calif., U.S.A.) equipped with a Camag thin-layer chromatography (TLC) scanner was used for all quantitative fluorometric measurements. Excitation filter no. 7-60 (360 nm) and secondary filter No. 2-A (> 415 nm) both available from Corning (New York, N.Y., U.S.A.) were utilized.

A Perkin-Elmer 3920 gas–liquid chromatograph (Montréal, Canada) equipped with a flame photometric detector (FPD) was also used. The column contained 3% OV-101 on Chromosorb W. The temperature was 190°.

Methods

Preparation of the column. A glass-wool plug is first inserted in the column which is then filled with distilled water. The stopcock is opened while the resin (in a water slurry) is added until the desired length is obtained. Another glass-wool plug is put on top of the column.

Flow-rate. The flow-rate is easily measured by observing the time it takes for a water sample to pass through a 10-cm length of column. A vacuum may be used to accelerate the flow.

Recovery of fenitrothion and/or degradation products from water. A 1000-ml water sample containing 50 ppb of fenitrothion is allowed to percolate down the column. The level of water in the column may be kept above that of the resin but the water may also be removed or the column allowed to drain *e.g.*, for field purposes, as a preservation technique.

The column is then eluted with an appropriate organic solvent *e.g.*, ethyl ether or ethyl acetate. The eluting solvent is then either evaporated to a smaller volume or diluted to a known volume for analysis.

Analysis. For TLC and *in situ* fluorometric analysis the eluted sample is concentrated to 1 ml or less and a 10-μl aliquot is spotted on a TLC plate. The latter is developed in hexane–acetone (4:1) along with appropriate standards.

The nitro group is reduced as follows: the plate is sprayed to saturation with stannous chloride, allowed to stand 5 min and dried in a stream of cold air. The excess acid is neutralized by spraying lightly with aqueous (2 *M*) sodium carbonate. Fluorescence is obtained by spraying with fluorescamine.

For gas chromatographic (GC) analysis the eluted sample is concentrated to 50 ml in a volumetric flask (*i.e.*, for a concentration of at least 50 ppb) and a 5-μl aliquot is injected in the chromatograph. For samples less concentrated than 50 ppb, the solvent can be evaporated as desired.

RESULTS AND DISCUSSION

The conventional technique of recovering fenitrothion from natural waters is

TABLE I

RECOVERY OF FENITROTHION FROM DISTILLED WATER USING XAD-2

Method, TLC and *in situ* fluorometry; eluting solvent, diethyl ether (3 × 30 ml); column length, 12 cm.

Experiment No.	*Flow-rate (ml/min)*	*Recovery (%)*
1	147	99
2	142	82
3	152	88
4	142	97
5	147	96
6	144	104
Average	146	94
Standard deviation		7.9

by solvent extraction using chloroform, as an example. Since fenitrothion is very unstable in water approx. 25 ml of chloroform are added to the bottle at the sampling site and the sample is rushed to the laboratory for quick analysis. Analyses are usually carried out by GC using an FPD[7] or by *in situ* fluorometry after TLC[8]. Both analytical procedures are used in this study for comparison.

In a first experiment the recovery of fenitrothion from water at the 50-ppb level using an XAD-2 column instead of solvent extraction, has been studied (Table I). The average percent recovery is good considering the inherent error with the *in situ* fluorometric technique of analysis. The flow-rate is given in ml/min, and is obtained by adjusting the flow such that it takes 14–16 sec for the water to cross a 10-cm length of the column. Since $V = \pi r^2 l$, where the length l is equal to 10 cm and the column radius r 1.1 cm, the volume V is 38 ml.

The flow-rate, adjusted to 1 min, is shown in Table I. A small vacuum is necessary to attain this flow-rate and it takes approx. 7 min to pass a 1-l sample of water through an XAD-2 column.

The *in situ* fluorometric results for fenitrothion are confirmed by GC (Table II) even though a different solvent is used for elution; ethyl acetate is preferred to diethyl ether as a solvent for GC. In this experiment the volume of eluting solvent as well as the column length are optimized. Three portions of 30 ml of ethyl acetate seem

TABLE II

RECOVERY OF FENITROTHION FROM NATURAL WATER USING XAD-2

Method, GC with FPD; percent recoveries are the averages of three separate analytical determinations.

Volume of eluting solvent (ethyl acetate)	*Column length (cm)*	*Recovery (%)*
3 × 30	12	95
3 × 30	12	91
3 × 30	12	90
3 × 30	10	92
3 × 30	8	93
3 × 30	6	66
3 × 20	10	56
2 × 45	10	77

TABLE III

PRESERVATION OF FENITROTHION ON A 12-cm XAD-2 COLUMN

I, TLC and *in situ* fluorometry; solvent, diethyl ether; recoveries are averages of 3 TLC developments. II, GC with FPD; solvent, ethyl acetate; recoveries are averages of 3 injections.

I		*II*	
Time (h)	*Recovery (%)*	*Time (h)*	*Recovery (%)*
0	92	0	95
24	106	—	—
48	108	48	97
72	94	504	92
96	96	840	92
192	105		
240	98		

most appropriate and at a concentration of 50 ppb a 10-cm column can be used for 1 l of water. Recovery starts to decrease when the XAD-2 resin length is less than 10 cm.

Experiments have been carried out to determine whether fenitrothion is stable in the column or not. Some results by *in situ* fluorometry are given in Table III, and they show that after 10 days degradation is not important. These results are confirmed by GC whereas no degradation is visible over a 5-week period.

CONCLUSIONS

The use of Amberlite XAD-2 resin to recover fenitrothion from environmental water is a worthwhile venture. The procedure is adequate for fenitrothion but remains to be adapted to its degradation products. The most important aspect, however, is that the compound is stable in the column and as such the method becomes a preservation technique. In practice the water sample containing fenitrothion can be processed in the field and the column can be eluted and its content analysed some time afterwards. During all this time fenitrothion remains unchanged in the column and its concentration is representative of the time the water was sampled. This is a great improvement over the current technique of adding chloroform to the sample bottle after collection to preserve the sample only for a few days.

Another advantage is that the columns can be regenerated and re-used many times. Some columns have been used 20 times to recover fenitrothion from water without showing any signs of deterioration.

Several conditions, however, should be optimized. These are: the size of the glass column and consequently the volume of resin in the column; the volume of water that can be processed and the volume and type of solvent to use; the type of resin. Work is currently in progress to optimize these conditions for fenitrothion and its degradation products in water.

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