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A COMPARATIVE STUDY OF THE USE OF XAD-2 RESIN AND THE CONVENTIONAL SERIAL SOLVENT EXTRACTION PROCEDURE FOR THE ANALYSIS OF FENITROTHION AND SOME DERIVATIVES IN WATER-PRESERVATION TECHNIQUES

V. N. MALLET
Département de Chimie, Université de Moncton, Moncton, N.B. (Canada)
G. L. BRUN and R. N. MacDONALD
Environmental Management Service, Environment Canada, P.O. Box 861, Moncton, N.B. (Canada)
and
K. BERKANE
Département de Chimie, Université de Moncton, Moncton, N.B. (Canada)
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SUMMARY

An analytical technique using the macroreticular resin XAD-2 for recovering fenitrothion, fenitrooxon and aminofenitrothion in water is described. The procedure was evaluated directly in the field immediately after an aerial application of the formulated insecticide. Results compare well with those obtained by a modified serial solvent extraction method.

It was also found that water samples containing fenitrothion and the two derivatives could be processed on XAD-2 columns and that the chemicals would be stabilized for at least 6 days. The parent compound and its two degradation products were monitored in samples of natural river water but only the parent compound was detected.

INTRODUCTION

Analytical methods[1,2] to determine fenitrothion in water using gas–liquid chromatography (GLC) with a flame photometric detector (FPD) have been reported. The serial solvent extraction procedure is adequate for the parent compound but there is a lack of information on the efficacy of recovery of some possible degradation products, such as fenitrooxon and aminofenitrothion.

An *in situ* fluorometric method[3] to detect simultaneously fenitrothion, fenitrooxon, aminofenitrothion and nitrocresol on a thin-layer chromatogram has been developed and has been used in our laboratory to analyse for these compounds in a variety of substrates. On the other hand, fenitrothion, fenitrooxon and amino-

fenitrothion have been analysed simultaneously by GLC using an SE-30 + QF-1 column and an FPD in the phosphorus mode[4].

The use of Amberlite XAD-2 resin for the quantitative recovery of fenitrothion from water has been described in a preceding paper[5]. Good recoveries were obtained and it was discovered that the pesticide remained stable in the column for a prolonged period. It was also established that a column can be regenerated and re-used many times. Amberlite XAD-4 has been used recently to analyse other organophosphorus insecticides[6].

In this study it was intended both to investigate the ability of the XAD-2 resin to recover not only fenitrothion but also fenitrooxon and aminofenitrothion from water and also to determine the relative stability of these compounds in the column. The study incorporates the use of XAD-2 columns for the "on-site" extraction of stream water after the aerial application of fenitrothion to forests. The results are correlated with those obtained from samples to which an organic solvent was added in the field as a preservative, consequently taking into account field testing conditions not encountered in the laboratory.

EXPERIMENTAL

A more detailed description of fluorometric methods and apparatus is given in the preceding paper[3].

Materials

Fenitrothion (folithion) and fenitrooxon (folithion oxygen analogue) were obtained as analytical standards from Chemagro (Kansas City, Mo., U.S.A.). Aminofenitrothion was prepared according to Zitko and Cunningham[7]. In this procedure, fenitrothion (1 g) is dissolved in methanol (30 ml), iron filings are added, followed by methanolic hydrogen chloride (25 ml of 10% methanolic hydrogen chloride, added slowly in small portions), and the mixture is stirred for 2 h at room temperature. The mixture is then filtered, the filtrate is neutralized with solid sodium carbonate and extracted with chloroform (3 × 50 ml). The combined chloroform extracts are washed twice with distilled water, dried with anhydrous sodium sulphate, and evaporated to dryness on a rotary evaporator at 35°.

Apparatus

An automated gas chromatographic system was used which consisted of a Tracor Model MT-220 gas chromatograph mounted with a Hewlett-Packard Model 7671A automatic sampler. The sampler was interfaced to a Spectra Physics Autolab System I GC integrator with calculation accessory. A Melpar FPD (phosphorus mode) was connected with the flame gas inlets in the reverse configuration to prevent solvent flame-out. The detector was maintained at 185° and flame gases were optimized with flow-rates (ml/min) as follows: hydrogen, 80; oxygen, 10; air, 20. A 1.8 m × 4.0 mm I.D. U-shaped glass column packed with 4% (w/w) OV-101 and 6% (w/w) OV-210 on Chromosorb W AW DMCS, 80–100 mesh, was used. Nitrogen was used as carrier gas at a flow-rate of 70 ml/min. A column temperature of 195° sufficiently resolved fenitrooxon from its parent compound. The injection port temperature was set at 225°.

A Turner fluorometer, Model III (Turner Assoc., Palo Alto, Calif., U.S.A.) equipped with a Camag TLC scanner was used for all quantitative fluorometric measurements on thin-layer chromatograms.

Preparation of XAD-2 columns

The Amberlite XAD-2 resin (BDH, Toronto, Canada) was washed successively with portions of ethyl ether, acetone and methanol. A column (60 cm × 1.9 cm I.D.) with ground-glass joints (Johns Colonial Scientific) fitted with a coarse-porosity disc and a PTFE stopcock was filled with XAD-2 resin in a methanol slurry to a height of 10 cm. Air bubbles were removed by inverting the column several times, and a glass wool plug was placed on top of the resin. The column was then rinsed successively with 50 ml of acetone and methanol, and finally with 100 ml of distilled water. The column was filled with distilled water and stoppered before transportation into the field.

Collection of samples

The sampling sites were chosen within a forest area to be sprayed aerially with fenitrothion formulation at a rate of 115 g per hectare. The first site was located on the Cain's River, which is a tributary of the Southwest Miramichi River in New Brunswick (Canada). The river flows out of the spraying area and is *ca.* 25 m wide at the sampling site near its mouth. The second site was a small brook called Otter Brook, situated a few miles from the first site but deeper into the woods. It measures *ca.* 5 m wide and 1 m deep and flows out of the spray area.

Samples were collected at different time intervals in 4.5-l dark glass bottles by holding the spout of the bottle *ca.* 5 cm below the surface of the water. Two 1-l aliquots were measured and each poured into a dark 1-l bottle. Chloroform (50 ml) was added to one bottle and benzene (50 ml) to the other; the containers were shaken and capped tightly after the spouts were covered with clean pieces of aluminium foil. The samples were returned to the laboratory for analysis within the next few days. At the Otter Brook site, two 1-l samples of the remaining water were run through XAD-2 columns at a rate of 50 ml/min; the columns were capped and returned to the laboratory for analysis 3 days later. At the Cain's River site the sample was run through the column, which was immediately eluted in the field. The solvent was stored in a 250-ml Sovirel bottle and sent to the laboratory for analysis.

Methods

After a water sample was run through an XAD-2 column, the latter was eluted successively with three 30-ml portions of ethyl acetate. The composite organic extract was dried through a sodium sulphate column, evaporated and made up to an adequate volume with ethyl acetate for quantitation by GLC.

A 1-l water sample was extracted in a 2-l separatory funnel with two additional 50-ml portions of chloroform, which were collectively dried through an anhydrous sodium sulphate (50 g) column. The chloroform was replaced with ethyl acetate on a flash evaporator, carefully reduced to 4–5 ml and made up to the mark with ethyl acetate in a 10-ml volumetric flask.

Gas chromatography

The automatic sampler syringe mechanism was adjusted to inject a volume of 5 μl for GLC. The sample vials were loaded on the sampler tray with calibration mixtures after every third or fourth sample and injected in triplicate; the results were averaged. The calibration mixtures were made up in ethyl acetate at concentrations of 3.0, 1.0 and 5.0 ng/μl for aminofenitrothion, fenitrothion and fenitrooxon, respectively.

The Autolab System I integrator automatically measures the retention times and areas of respective peaks and calculates concentrations in the appropriate units, the detector response being linear at the levels analysed.

RESULTS AND DISCUSSION

In this study, aminofenitrothion was recovered from environmental water using an XAD-2 column; the results, given in Table I, indicate good recoveries at an average flow-rate of 153 ml/min. The relative error, *ca.* 10%, is normal at a concentration of 50 ppb* when using *in situ* fluorometry[3]. Under similar conditions, fenitrooxon can also be recovered with good yields.

TABLE I

RECOVERY OF AMINOFENITROTHION AND FENITROTHION FROM NATURAL WATER AT A CONCENTRATION OF 50 ppb

Method: TLC and *in situ* fluorometry; eluting solvent: hexane–acetone (6:1).

Aminofenitrothion		*Fenitrooxon*	
Experiment No.	*Recovery (%)*	*Experiment No.*	*Recovery (%)*
1	89	1	89
2	87	2	90
3	103	3	83
4	103		
5	103		
6	118		
7	98		
8	95		
Average	100	Average	87
Relative standard deviation	9.8%		

The procedure was adapted to the simultaneous analysis of the parent compound and its two derivatives by GLC. The data in Table II indicate that with XAD-2 resin, conditions such as flow-rate and column length are crucial to obtain good recoveries. If a 10 × 1.9 cm I.D. column is used the maximum flow-rate is limited to *ca.* 50 ml/min, which is easily sustained by gravity flow. In order to increase processing time using a vacuum, column length has to be increased[5].

* Throughout this article the American billion (10^9) is meant.

TABLE II

CALIBRATION OF XAD-2 COLUMNS FOR THE ANALYSIS OF FENITROTHION (F), FENITROOXON (FO) AND AMINOFENITROTHION (AF)

Method: GLC with FPD; F, 10 ppb; FO, 100 ppb; AF, 30 ppb.

Sample flow-rate (ml/min)	*Column length (cm)*	*Recovery (%)*		
		F	*AF*	*FO*
238	5	0	0	68
218	5	0	0	56
135	5	53	17	72
129	5	50	10	70
71	5	71	43	85
63	10	83	83	89
60	10	91	95	84
50	10	102	117	114

Very good recoveries are illustrated in Table III when using XAD-2 for extracting spiked lake water with the three compounds. Experiments carried out at concentration levels *ca.* 10 times lower yielded similar results, except for aminofenitrothion when low recoveries were obtained. These low values may be attributable to a determinate error and the cause is presently being investigated. Statistically, relative standard deviations of 5.1–6.4% are very good, considering that the reproducibility of the GLC automated system for fenitrothion at 1.0 ng/μl over a 3-h span is 1.7% relative standard deviation with calibration at the start only.

TABLE III

RECOVERY OF A MIXTURE OF FENITROTHION (F), FENITROOXON (FO) AND AMINOFENITROTHION (AF) AT VARIOUS CONCENTRATIONS FROM NATURAL WATER WITH XAD-2

Method: GLC with FPD; concentrations: F, 10 ppb; FO, 100 ppb; AF, 30 ppb.

Experiment No.	*Recovery (%)*		
	F	*FO*	*AF*
1	96	98	98
2	95	95	94
3	98	102	97
4	91	109	99
5	85	95	98
6	84	95	86
Average	91.5	99	95.3
Relative standard deviation (%)	6.4	5.6	5.1

The overall average recovery (99.7%) of the three compounds by the conventional serial solvent extraction procedure is somewhat better (Table IV) than by the XAD method (95.3%). Reproducibilities are all better for the exception of fenitrooxon, The concentration levels of aminofenitrothion and fenitrooxon were chosen because

TABLE IV

RECOVERY OF A MIXTURE OF FENITROTHION (F), FENITROOXON (FO) AND AMINOFENITROTHION (AF) FROM NATURAL WATER BY THE CONVENTIONAL SERIAL SOLVENT EXTRACTION PROCEDURE

Method: GLC with FPD; concentrations: F, 10 ppb; FO, 100 ppb; AF, 30 ppb.

Experiment No.	*Recovery (%)*		
	F	*FO*	*AF*
1	90	96	106
2	97	95	101
3	95	92	110
4	96	95	105
5	99	103	110
6	96	99	99
7	97	106	108
8	90	82	112
9	96	89	112
10	99	97	115
11	93	98	114
12	101	90	110
Average	95.7	95.1	108.5
Relative standard deviation (%)	3.5	6.7	4.5

of the relative response of these compounds on the FPD and not because of expected concentration levels in water.

Another experiment was carried out to determine the stability in the column of fenitrothion and the two degradation products fenitrooxon and aminofenitrothion following recovery from water using XAD-2. The data in Table V demonstrate that all three components can be recovered quantitatively from a column that is left standing at room temperature for 6 days. Additional data indicate that all three compounds will remain stable in a column for a prolonged time, as was the case with fenitrothion[5] alone.

An evaluation of the XAD-2 method of sample collection was made on site after an aerial application of fenitrothion over a large forest lot situated in the

TABLE V

PERCENTAGE RECOVERIES OF FENITROTHION AND SOME BREAKDOWN PRODUCTS WITH TIME

Method: Two-dimensional TLC and *in situ* fluorometry; concentration 50 ppb. The thin layer was developed first in benzene–ethyl acetate (4:1) and then in carbon tetrachloride–methanol (10:1).

Compound	*Time (h)*						
	0	*24*	*48*	*72*	*90*	*120*	*144*
F	98	97	100	98	93	107	107
AF	82	108	104	86	104	104	102
FO	91	102	83	89	103	87	88

Miramichi River area. Table VI illustrates the results monitored at two different locations. At both sites, samples were split into three sub-samples; two 1-l sub-samples were preserved with chloroform and benzene, respectively, and analysed at the laboratory later. The remaining sub-sample from Otter Brook was extracted and eluted from the column at the site by the XAD procedure; the extract was properly stored and analysed later at the laboratory. The remaining Cain's River aliquot was extracted onto the XAD column, which was then immediately capped and shipped to the laboratory for analysis.

TABLE VI

ANALYSIS OF BROOK AND RIVER WATER AFTER A FOREST SPRAYING OPERATION WITH FENITROTHION

Method: GLC with FPD; A, field extraction on XAD-2 and elution three days later at laboratory; B, 1 l sub-sample preserved in bottle with chloroform; C, 1 l sub-sample preserved with benzene; D, extraction and elution from XAD-2 in field; E, 1 l sub-sample preserved with chloroform; F, 1 l sub-sample preserved with benzene; N.D., not detected.

Fenitrothion concentration (ppb)					
Otter Brook			*Cain's River*		
A	*B*	*C*	*D*	*E*	*F*
16.9	11.3	12.0	8.0	9.3	
10.5	9.4	13.6	10.5	11.0	10.9
8.4	8.3	6.3	4.5	6.2	6.9
7.3	8.8	6.0	5.5	6.0	5.4
6.7	6.5	6.2	5.5	5.0	4.7
6.7	8.3	5.3	4.0	3.8	3.1
4.5	4.5	—	2.0	2.0	—
4.5	4.8	—	3.5	4.0	3.4
4.0	3.9	5.3	0.3	0.3	—
2.5	2.3	2.5	0.1	0.1	—
3.0	2.7	—	N.D.	N.D.	—

Among some sub-samples, the data are somewhat scattered. The most probable cause is that the whole sample was not homogeneous when it was sub-sampled, the carrier (oil) floating on the surface did not disperse evenly enough even after the sample was vigorously shaken. According to the data, the carrier does not appear to pose any problems relating to the efficacy of the XAD-2 method. Addition of organic solvents to preserve samples is not new, and this work seems to confirm its effectiveness in the case of fenitrothion. Samples that are suspected of containing phosphamidon should be preserved with hexane instead and analysed as soon as possible according to Ripley's method[1], because on certain GLC columns (*i.e.* OV-101 + OV-210) the isomers of phosphamidon co-elute with fenitrothion.

Degradation products are not expected to be found just a few hours after spraying in a rapidly flowing stream, and samples extracted by XAD-2 in the field confirm their absence. The respective limits of detection for fenitrothion, amino-fenitrothion and fenitrooxon by GLC were 0.01, 0.01 and 0.05 ppb.

Because of the unavailability of analytical standards at the time it was impossible to assess the methods for other degradation products that could possibly be found in water.

CONCLUSION

The XAD-2 extraction technique and the conventional method are adapted to include two possible degradation products, namely aminofenitrothion and fenitrooxon. This study demonstrates that XAD-2 will produce reliable data whether it is applied in the field or in the laboratory.

Extraction of 1 l of water in the field takes about 25 min and, because of the preserving ability of the resin, analyses can be performed at a later date without any loss of the three compounds under study. Results indicate that adding chloroform or benzene to a water sample in the field is also an adequate way of stabilizing fenitrothion. No data are available for the two derivatives, but it is suspected that aminofenitrothion might not be stable even though an organic solvent is added.

There is one drawback with XAD-2; processing time in the field (and in the laboratory) is relatively long: *ca.* 25–30 min. Any attempt to increase the flow-rate results in a loss of sample. Recent experiments indicate that this problem may be overcome if other resins are used. It is also expected that other XAD-resins could be used to recover additional degradation products of fenitrothion. Research is presently in progress in this area.

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