Journal of Chromatography, 172 (1979) 388–393

CHROM. 11,681

Note

Evaluation of Amberlite XAD-4 for the recovery of fenitrothion from water

VICTORIN N. MALLET*, J. M. FRANCOEUR and G. VOLPÉ
Department of Chemistry, Université de Moncton, Moncton, New Brunswick (Canada)
(Received December 12th, 1978)

Amberlite XAD resins have been used to recover pesticides and other related chemicals, *e.g.*, chlorinated insecticides[1], polychlorinated biphenyls[2] and organophosphorous compounds[3], from water with excellent results.

In an earlier paper[4], Amberlite XAD-2 was used for the quantitative recovery of fenitrothion from water. Good recoveries were obtained for 50 ppb** solutions and it was found that the pesticide remained stable in a column for a reasonable length of time. In addition, there was the added advantage that the XAD column could be regenerated and used again many times without loss in efficacy.

More recently a comparative study[5] was made of the use of XAD-2 and conventional solvent extraction for the analysis of water for fenitrothion and some derivatives. The technique was evaluated directly in the field immediately after aerial application of the formulated insecticide and it was found that results obtained with XAD-2 compared very favourably with those obtained by the conventional approach.

In this study, it was intended to evaluate thoroughly another Amberlite resin, XAD-4, for the recovery of fenitrothion from water. Amberlite XAD-4 is also a polystyrene resin considered to be non-polar, but it is more porous than XAD-2. Thus, it should have a greater capacity to retain fenitrothion under a variety of experimental conditions.

EXPERIMENTAL

Details of the apparatus, chemicals and experimental procedures were given earlier[4]. Unless otherwise stated, the height of the adsorbent in the column (30 × 1.9 cm I.D.) was 12 cm.

For regeneration, the column was washed with 50 ml of diethyl ether, 30 ml of methanol and 1 l of distilled water to remove trace amounts of organic solvents. A vacuum was used when necessary to accelerate the flow.

RESULTS AND DISCUSSION

Both Amberlite XAD-2 and XAD-4 are polystyrenes and are considered to be non-polar resins. The difference between the two is the greater porosity of XAD-2

* To whom correspondence should be addressed.
** Throughout this article the American billion (10^9) is meant.

For instance, the surface area is 750 m^2/g for XAD-4 but only 330 m^2/g for XAD-2[6]. Thus, Amberlite XAD-4 should have a greater capacity to retain a substrate and therefore should be less affected than Amberlite XAD-2 by the experimental conditions. In an earlier study[4] with XAD-2, a decrease in recovery was usually observed with an increase in the flow-rate of water or a decrease in the amount of resin used.

Fenitrothion was recovered from distilled water under experimental conditions analogous to those used with XAD-2 (Table I). The results indicate that recovery is complete at an average flow-rate of 113 ml/min. It should be emphasized that by gravity flow it takes approximately 20 min to process 1 l of water with XAD-2, but it may take as long as 45 min with XAD-4. This aspect is important in field applications whereas one might require the use of a vacuum apparatus with XAD-4. Nevertheless, both resins give excellent recoveries under gravity flow.

TABLE I

RECOVERY OF FENITROTHION FROM WATER USING XAD-4

Experiment No.	*Flow-rate (ml/min)*		*Recovery (%)**
1	106		94
2	113		100
3	115		104
4	115		99
5	110		98
6	119		99
Average:	113	Relative standard deviation:	3.0%

* Method: gas–liquid chromatography (GLC) with flame-photometric detector (FPD).

However, with XAD-4 the flow-rate can be greatly accelerated before any significant decrease in recovery is noted (Table II). In fact, 1 l of water can be processed in only a few minutes without loss. This is not so with XAD-2, where an increase in flow-rate to greater than 150 ml/min results in a proportional loss in recovery. This is to be expected when one considers the lower adsorption capacity of XAD-2.

The amount of resin in the column is important, as illustrated by the results in Table III. As was observed with XAD-2[4], a significant loss of sample occurs if the height of the resin in the column is decreased to below 10 cm. It was earlier expected that this effect would not be as important with XAD-4 as it has a greater retaining power.

Various experiments related to the concentration of fenitrothion in water were performed. In the experiment reported in Table IV, the amount of fenitrothion per litre of water was kept constant (50 μg/l) and the effect of passing successively (not continuously) up to 5 l of spiked water was observed. The percentage recoveries increase systematically with the number of litres processed or with the total amount of fenitrothion. The results were confirmed by thin-layer chromatography and *in situ* fluorescence spectroscopy.

An explanation for this phenomenon is that the regeneration procedure is not as effective when more than 50 μg of fenitrothion are processed so that when the same column is used repeatedly with increasing amounts of fenitrothion, an increase in recovery is observed. Such experiments should be useful for the proper sampling of a

TABLE II

EFFECT OF FLOW-RATE ON RECOVERY OF FENITROTHION FROM WATER USING XAD-4

Experiment No.	*Flow-rate (ml/min)*	*Recovery (%)* *
1	106	94
2	113	99
3	122	99
4	142	99
5	154	99
6	170	100
7	189	99
8	212	94
9	242	93
10	284	97
11	341	96
12	450	75
13	567	77

* Method: GLC with FPD.

TABLE III

EFFECT OF COLUMN LENGTH ON RECOVERY OF FENITROTHION FROM WATER USING XAD-4

Experiment No.	*Flow-rate (ml/min)*	*Column length (cm)*	*Recovery (%)* *
1 (6)	154	12	99 (–)
2 (7)	164 (112)	10	81 (90)
3 (8)	154 (115)	8	78 (80)
4 (9)	127 (112)	6	77 (75)
5 (10)	127 (110)	4	58 (64)

* Recoveries in parentheses were obtained by thin-layer chromatography (TLC) and *in situ* fluorometry; those without parentheses were obtained by GLC with FPD.

TABLE IV

EFFECT OF SUCCESSIVE EXTRACTIONS ON RECOVERY OF FENITROTHION (50 μg/l) FROM WATER USING XAD-4

Experiment No.	*Flow-rate (ml/min)*	*Volume (l)*	*Absolute amount (μg)*	*Recovery (%)* *	
				GLC	*TLC*
1	154	1	50	99	–
2	179	2	100	101	84
3	179	3	150	106	91
4	176	4	200	110	100
5	176	5	250	113	110

* The results by TLC were obtained using different samples to those obtained by GLC.

body of water in order to obtain a more representative sample, particularly when the concentration is low.

In another set of experiments (Table V), the absolute amount of fenitrothion was kept constant (50 μg) but the volume was varied; water was passed continuously

TABLE V

EFFECT OF VOLUME OF WATER ON RECOVERY OF FENITROTHION (50 μg) FROM WATER USING XAD-4

Experiment No.	*Flow-rate (ml/min)*	*Volume of water (l)*	*Recovery (%)**
1	115	1	99
2	160	2	95
3	159	3	98
4	122	4	93
5	128	5	96
6	164	8	92

* Method: GLC with FPD.

through the column. The results indicate that the passage of up to 8 l of water does not significantly affect the percentage recovery for 50 μg of fenitrothion. This could be advantageous in the field as the detection limit could be increased 10-fold by processing 10 l instead of 1 l of water.

An increase in the amount of fenitrothion does not affect the percentage recovery when the volume of water is also increased. This is shown in Table VI, which gives the results of an experiment in which up to 5 l of water (50 ppb maintained constant) were passed continuously through a 12-cm column of resin. Similarly, the percentage recoveries are not affected by an increase in concentration at least up to 500 μg/l, as shown in Table VII. These results illustrate the potential of XAD-4 because it is adaptable to a variety of experimental conditions without significant changes in percentage recovery.

TABLE VI

EFFECT OF VOLUME AND AMOUNT ON RECOVERY OF FENITROTHION FROM WATER USING XAD-4

Average flow-rate = 120 ml/min.

Experiment No.	*Volume (l)*	*Amount (μg)*	*Recovery (%)**
1	1	50	99
2	2	100	97
3	3	150	98
4	4	200	97
5	5	250	99

* Method: GLC with FPD.

The results in Table VIII show the effect of increasing the flow-rate of the eluting solvent on the recovery of fenitrothion from the column. In all, three 30-ml portions of ethyl acetate were passed successively through the column. The gravity flow-rate was *ca.* 3 ml/min, but it could be increased to 14 ml/min without any significant loss in recovery. An increase in flow-rate of the elution solvent is desirable as the total time needed for processing a water sample is then reduced.

Finally, the technique was tested on real water samples, some of which were very turbid owing to sediments in suspension. The recoveries were very good (above [illegible]%) and consequently no particular problem is foreseen with this type of substrate.

TABLE VII

EFFECT OF CONCENTRATION ON RECOVERY OF FENITROTHION FROM WATER USING XAD-4

Average flow-rate = 118 ml/min.

Experiment No.	*Concentration (μg/l)*	*Recovery (%)**
1	5	97
2	50	100
3	100	97
4	150	97
5	200	103
6	250	100
7	300	96
8	500	103

* Method: experiments 1–5, GLC with FPD; experiments 6–8, TLC and *in situ* fluorescence.

TABLE VIII

EFFECT OF ELUTION SOLVENT FLOW-RATE ON RECOVERY OF FENITROTHION (50 ppb) FROM WATER USING XAD-4

Experiment No.	*Flow-rate of water (ml/min)*	*Flow-rate of solvent (ml/min)*	*Recovery (%)**
1	170	3	88
2	181	4	86
3	159	5	89
4	170	7	91
5	163	14	89

* Method: GLC with FPD.

CONCLUSION

In an earlier study[4] it was shown that Amberlite XAD-2 can be used to recover fenitrothion quantitatively from water under optimal conditions of flow-rate of water and amount of resin.

With XAD-4 the flow-rate can be greatly accelerated such that 1 l of water can be processed in less than 2 min. Significantly, the flow-rate of the elution solvent can also be increased without a loss in recovery. In addition, the concentration of fenitrothion can be varied together with the total volume of water and successive extractions can be carried out without affecting the percentage recovery substantially.

It is felt that Amberlite XAD-4 would be more suitable for recovering fenitrothion from water, particularly in field applications when the experimental parameters, such as the volume of water, have to be varied. A disadvantage is that more time is required to process a sample under gravity flow, but if a vacuum apparatus is available Amberlite XAD-4 is far superior.

In addition, it is thought that because of its greater retaining capacity XAD-4 might be more useful than XAD-2 when it becomes desriable to analyse for fenitrothion and some of its degradation products. Work along those lines is currently in progress.

Finally, it should be emphasized that Amberlite XAD-4 columns can be regenerated and re-used many times. Some of our columns have been used over 20 times. In addition, as with XAD-4, fenitrothion remains stable in the column for a prolonged time period, so that the technique is of interest for preservation purposes prior to analysis.

ACKNOWLEDGEMENTS

The authors thank Environment Canada and the Conseil de Recherche of this University for financial support.

REFERENCES

1 P. R. Musty and G. Nickless, *J. Chromatogr.*, 89 (1974) 185.
2 G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz and G. V. Calder, *J. Chromatogr.*, 99 (1974) 745.
3 G. G. Daughton, D. G. Crosby, R. L. Garnos and D. D. Hsieh, *J. Agr. Food Chem.*, 24 (1976) 236.
4 K. Berkane, G. E. Caissie and V. N. Mallet, *J. Chromatogr.*, 139 (1977) 386.
5 V. N. Mallet, G. L. Brun, R. N. MacDonald and K. Berkane, *J. Chromatogr.*, 160 (1978) 81.
6 *Amberlite Polymeric Absorbents*, Rohm & Haas, Philadelphia, Pa., 1972.