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Note

Recovery of fenitrothion from water using Amberlite resin XAD-7

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This study follows a continuing evaluation of Amberlite XAD-resins for the recovery from water of fenitrothion and some of its major degradation products. Fenitrothion, O,O-dimethyl O-(3-methyl-4-nitrophenyl) phosphorothioate, is an organophosphorous insecticide sprayed heavily in Eastern Canada to control spruce budworm (*Chloristoneura Fumiferana Clemens*) infestations. There is need for a faster and more reliable analytical technique that will enable the chemist to determine the parent compound and the metabolites present in water at a particular time without further loss by degradation.

Amberlite XAD-resins are basically porous polymer beads that vary in chemical composition from being essentially non-polar to varying degrees of polarity. They are also different in terms of porosity, *i.e.*, specific surface contact area. They have been used successfully to recover organic contaminants[1] including pesticides[2,3] from environmental water.

An earlier study with Amberlite XAD-2 columns[4] revealed that fenitrothion can be recovered quantitatively from environmental water and that the insecticide remains stable in a column for a reasonable length of time, thus acting as a means of preservation. The applicability of using XAD columns in the field to recover fenitrothion and two important metabolites, was then verified[5]. It was found that using XAD-2 columns is as efficient as a preservation technique than the conventional procedure of adding an organic solvent to the sample.

Recently, another study[6] was completed with Amberlite XAD-4, also a polystyrene considered non-polar but with a greater surface area than Amberlite XAD-2. It was found that XAD-4 has more capacity and consequently is more adaptable to experimental variations, such as increase in the flow-rate or volume of water processed. A slight disadvantage with XAD-4 is that gravity flow is twice as slow as with XAD-2 but the flow-rate can be increased such that one litre of water may be processed in less than two minutes without loss in recovery, which is not the case with XAD-2. The resin also acts as a preservative and columns may be regenerated many times.

In this study it was intended to evaluate Amberlite XAD-7, an acrylic ester polymer resin, for the recovery of fenitrothion from water and compare its per-

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formance with Amberlite XAD-2 and XAD-4. The final goal is to select the most appropriate resin or mixture of resins that will be best suitable to extract fenitrothion and its major metabolites, from environmental water and other substrates.

EXPERIMENTAL

Details regarding materials, apparatus and experimental procedures are the same as those already published for resin XAD-2 (refs. 4, 5).

Unless otherwise specified the standard conditions used were as follows: 50 μg of fenitrothion per litre of distilled water (50 ppb); a flow-rate of 113 ml of water per minute, elution of Amberlite XAD-7 column with 3 $\times$ 30 ml of ethyl acetate; analyses performed by thin-layer fluorimetry[7].

RESULTS AND DISCUSSION

The Amberlite resins studied previously namely XAD-2 and XAD-4, are polystyrenes, thus basically non-polar, differing mainly from each other because of surface contact area[8]. Amberlite XAD-7 is considered of intermediate polarity because it is an acrylic ester type of polymer with a surface contact area in-between that of XAD-2 and XAD-4. But considering both factors of surface contact area and polarity it should behave more like XAD-4.

Under standard conditions, that is, similar to those used previously with XAD-2 and XAD-4, the recoveries obtained with Amberlite XAD-7 are comparable (Table I). Variation in the data is attributed mainly to the quantitative technique which in this case was *in situ* fluorimetry on thin-layer chromatogram. The technique requires spraying the thin layer with fluorescamine which produces fluorescence with the amino group resulting from the chemical reduction of fenitrothion with stannous chloride. Ordinarily an average relative standard deviation of 9% can be expected[7]. When using gas–liquid chromatography with a flame-photometric detector the reproducibility is usually better.

If the flow-rate is increased above 113 ml/min a loss in recovery occurs after 450 ml/min as was the case with XAD-4 (ref. 6; Table II). This means that a 1-l

TABLE I

RECOVERY OF FENITROTHION FROM DISTILLED WATER UNDER STANDARD CONDITIONS

Experiment No.	*Recovery (%)*
1	95
2	89
3	91
4	94
5	94
6	87
Average	92
Average standard deviation (%)	3.7

TABLE II

RECOVERY OF FENITROTHION FROM WATER: EFFECT OF FLOW-RATE

Experiment No.	*Flow-rate (ml/min)*	*Recovery (%)*
1	113	94
2	155	95
3	284	94
4	567	72

sample can be processed in about 2 min without too much loss in recovery. The quantity of resin in a column as expressed by a column length in Table III suggests that only 4 cm of resin (in a glass column 1.9 cm I.D.) is sufficient to yield quantitative recoveries. This seems to be slightly better than XAD-4 which gave only 58% recovery under those conditions.

TABLE III

RECOVERY OF FENITROTHION FROM WATER: EFFECT OF QUANTITY OF RESIN

Experiment No.	*Quantity of resin (column length, cm)*	*Recovery (%)*
1	12	94
2	10	97
3	8	80
4	6	79
5	4	75

The data in Table IV indicate that the insecticide is stable in an XAD-7 column up to 148 h. This is less than was obtained with either Amberlite XAD-2 or XAD-4 (refs. 4 and 6). Amberlite XAD-4 did not show any loss before 336 h. The loss may be due to chemical interaction of the pesticide with water in the more polar XAD-7 resin resulting in chemical degradation.

TABLE IV

RECOVERY OF FENITROTHION FROM WATER: PRESERVATION

Experiment No.	*Time (h)*	*Recovery (%)*
1	6	94
2	24	100
3	48	93
4	72	92
5	96	89
6	144	95
7	148	95
8	240	78
9	720	62

The data in Table V allow a better comparison between Amberlite XAD-7 and two resins already studied, namely XAD-2 and XAD-4. Under standard con-

TABLE V

RELATIVE PERFORMANCE OF AMBERLITE XAD-7 AS COMPARED WITH XAD-2 AND XAD-4

Parameter	*Recovery (%)*		
	XAD-2	*XAD-4*	*XAD-7*
Recovery of fenitrothion from distilled water	94	99	93
Recovery of fenitrothion from environmental water	92	83	85
Preservation of fenitrothion in the column (environmental water)	92 left after 840 h	—*	62 left after 720 h

* Data not available.

ditions using distilled water the recoveries are all very good. When environmental water containing large amounts of suspended solids is used the recovery with XAD-7 seems less good. This is again attributed to the greater polarity of XAD-7 which undeniably retains most of the particles in suspension while XAD-2 in particular does not retain them very well. These suspended particles which are actually sediments in suspension would retain fenitrothion more strongly which would explain a loss in recovery during the elution step.

The actual mechanism of preservation in the resins is not known but it is anticipated that since fenitrothion is a very labile compound, the less interaction it has with a substrate the better. It is thought that since XAD-2 is essentially non-polar, chemical interactions are minimized thus the greater preservation power (see Table V). However, porosity or surface contact area has something to do with it since XAD-4 does not preserve as well as XAD-2.

CONCLUSION

The data in this study suggest that Amberlite XAD-7 is suitable to recover fenitrothion from environmental water. It seems to retain fenitrothion more strongly than either XAD-2 or XAD-4 which may be an advantage when metabolites have to be recovered also. Overall its performance is much better than XAD-2 since experimental conditions can be varied without causing great losses in recovery, and it behaves very similarly to Amberlite XAD-4. Like the latter it takes longer than XAD-2 to process one litre of water by gravity flow but the flow-rate can be increased tremendously with good recoveries. Its preserving abilities are obviously not as good as with Amberlite XAD-2, however the latter may not be suitable for some metabolites of fenitrothion as it has been mentioned before[5].

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