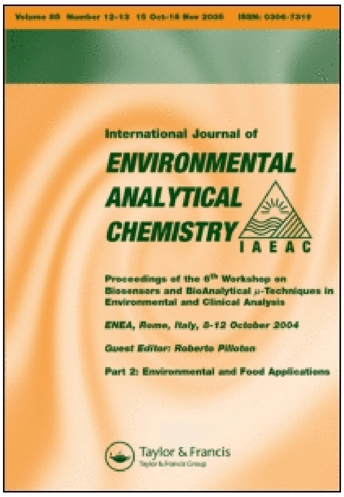

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Development of an Analytical Method for Fenitrothion and Five Derivatives in Water using XAD Resins and Gas Liquid Chromatography (GLC)

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The recovery from water of fenitrothion and five possible metabolites was studied using Amberlite XAD-4 and −7 resins followed by GLC analysis. Details are given for the syntheses of *s*-methylfenitrothion, formylfenitrothion, aminofenitrothion and hydroxymethylfenitrothion.

The results show that fenitrothion and three derivatives namely aminofenitrothion, fenitrooxon and *s*-methylfenitrothion may be recovered from water using either XAD-4 or 7 with expected recoveries over 90%.

However both formylfenitrothion and hydroxymethylfenitrothion were poorly recovered under the same conditions. The individual recovery of hydroxymethyfenitrothion could be improved to over 90% when the compound was alone and the concentration was reduced. The technique of GLC using a flame photometric detector in the phosphorous mode proved to be efficient for the separation of a mixture of six components. The detection limits were 0.5 to 3.5 ng per injection.

INTRODUCTION

Fenitrothion, 0,0-dimethyl 0-(3-methyl-4-nitrophenyl) phosphorothioate is currently used in Eastern Canada to control the spruce budworm (Choristoneura Fumiferana Clemens) and research is continuing to estab-

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lish a multi-residue analytical technique for the parent compound and some of its metabolites in environmental water.

Gas liquid chromatography (GLC) using a flame photometric detector (FPD) is the technique of choice for detecting small quantities (sub-nanogram) of fenitrothion (F)[1–3] and some derivatives such as fenitrooxon (FO) and aminofenitrothion (AF) which contain phosphorus. But *in situ* fluorometry[4] has also been used in the past for the simultaneous determination of F, FO, AF and nitrocresol (NC) on thin-layer chromatograms.

The extraction of fenitrothion and some degradation products from water is usually accomplished by liquid-liquid partition[5] with solvents such as methylene chloride or chloroform. Recently, Amberlite polymeric adsorbents, such as XAD-2, XAD-4 and XAD-7 have been used successfully.[5–8] In addition, XAD resins also provide a way to preserve the sample for a few weeks prior to analysis.[5]

In this study it was intended to evaluate the most promising resins,[5,8], namely XAD-4 and 7, for the simultaneous recovery of fenitrothion and up to five derivatives in water. It was also intended to optimize GLC parameters to obtain maximum sensitivity and resolution. The derivatives studied were FO, *s*-methylfenitrothion (SMF), formylfenitrothion (FF), hydroxymethylfenitrothion (HMF) and AF.

EXPERIMENTAL

Chemicals

All the organic solvents used were “pesticide grade”. Silica gel H and G used for preparative thin layer chromatography were obtained from Brinkman Instruments (CANADA) Ltd.

Starting chemicals for the syntheses were: Chromous (II) chloride solution (Fisher Scientific No SO-C-169); dimethyl chlorothiophosphate and 5-hydroxy-2-nitrobenzaldehyde (Aldrich Chem.); sodium hydride (alfa Inorganics Centron); sodium borohydride (J. T. Baker Chemical Co.).

Stock solutions of 1 μg/μl (1000 ppm) were prepared for fenitrothion (Forest Protection Limited, Fredericton, N.B.), fenitrooxon (Chemagro, Kansas City, U.S.A.), and the synthesized products, namely AF, SMF, FF and HMF. The names and structures of these chemicals are given in Table I.

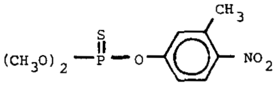
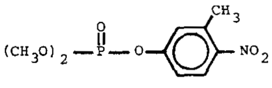
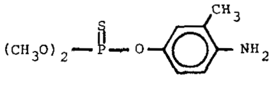
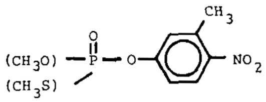
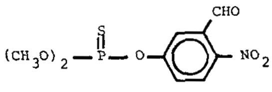
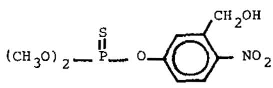
Apparatus

A gas-liquid chromatograph (Perkin Elmer 3920) equipped with a flame photometric detector (FPD) and a glass column (6 mm I.D. × 1.8 m) containing 3.6% OV-101 and 5% OV-210 on CHROMOSORB W DMCS 80/100, was used.

An infrared spectrophotometer (Perkin Elmer 467), an NMR spectrometer Varian T-60A and a gas-liquid chromatograph (Perkin Elmer 990) coupled to a mass spectrometer (Hitachi Perkin-Elmer RM-50) were used for identification of the synthesized products.

TABLE I

CHEMICAL STRUCTURES OF COMPOUNDS STUDIED

COMMON NAME	STRUCTURE
FENITROTHION (F)	
FENITROOXON (FO)	
AMINO FENITROTHION (AF)	
S-METHYL FENITROTHION (SMF)	
FORMYL FENITROTHION (FF)	
HYDROXYMETHYL FENITROTHION (HMF)	

Synthesis of fenitrothion derivatives

(1) *Aminofenitrothion*

The procedure was according to Forbes *et al.*[9] Fenitrothion (1 g) was dissolved in 10 mL of acetone and 10 mL of the chromous chloride solution were added under a nitrogen atmosphere. The reaction vessel was maintained in a water bath for 3 h at 60°C. After cooling to room temperature, the mixture was transferred to a separatory funnel and 300 mL of distilled water were added. The aqueous layer was extracted successively with 3 portions of 30 mL of benzene and the organic portion was dried with anhydrous sodium sulfate. The yield of the reaction was 70 % as measured by GLC.

Purification was done by preparative thin-layer chromatography (500 μm) using silica gel H. The mobile phase was carbon tetrachloride: methanol (100:8). Aminofenitrothion was recovered from the thin-layer with benzene and was 97 % pure as revealed by GLC.

(2) *s-Methylfenitrothion*

The procedure was according to Kovacicova *et al.*[10] Fenitrothion (5 g) was added dropwise to a potassium hydrosulfide solution; this solution was prepared by dissolving 1 g of potassium hydroxide in 8.8 mL of methanol and saturating the solution with hydrogen sulfide for 45 min. The mixture was refluxed for 5 h while stirring. The methanol was evaporated and 50 mL of water were added. The unreacted fenitrothion was removed by washing successively with five portions of 10 mL of benzene. The potassium salt was converted to SMF by adding 2 to 3 g of dimethyl sulfate while stirring. Impure SMF was separated in a separatory funnel. The brown layer (SMF) was dissolved in 30 mL of benzene and extracted with 3 × 10 mL of water. Thus *s*-methylfenitrothion was obtained 97 % pure as established by GLC. The yield was 40 %.

(3) *Formylfenitrothion*

The procedure was according to Greenhalgh and Marshall.[11] A solution of dimethyl chlorothiophosphate (0.75 mL) in dry acetone was added dropwise to a solution of 5-hydroxy-2-nitrobenzaldehyde (1 g) in benzene, containing 1.1 equivalent of sodium hydride. Initially the reaction vessel was cooled with ice while under a nitrogen atmosphere until the reaction subsided. Then the mixture was refluxed for 8 h. The benzene layer was removed and the residue was submerged in water and extracted with 3 portions of 30 mL of chloroform. The combined extract was dried with anhydrous sodium sulfate. The reaction yield was 35 %.

The compound was purified by preparative thin-layer chromatography (500 μm) using silica gel G. The elution system was hexane and ethyl acetate (3:2). The product was 96 % pure as established by GLC.

(4) *Hydroxymethylfenitrothion*

The synthetic procedure was according to Greenhalgh and Marshall.[11] A solution of sodium borohydride was prepared by dissolving 0.30 g in 55 mL of absolute ethanol. This solution was added dropwise to a solution of formylfenitrothion (1.0 g in absolute ethanol) at 0°C. When the reaction was completed, the solvent was evaporated, a little water was added and the derivative was extracted with chloroform. The yield was 40%.

The purification was done by preparative thin-layer chromatography (500 μm) on silica gel G. The eluant was hexane and ethyl acetate (3:2). The purity of the product was 96% as established by GLC.

Analysis of fenitrothion and/or derivatives from water using XAD columns and GLC

The columns were prepared as described earlier.[5,6] A water sample containing known amounts of fenitrothion and the derivatives was passed through either by gravity flow or with a vacuum.

The compounds were eluted from the column with an organic solvent such as ethyl acetate or methylene chloride usually three portions of 30 mL. The eluate was concentrated to 10 mL.

Each sample was analysed by GLC by injecting 5 μl. A calibration curve was established from stock solutions of one, five and 10 ppm of the parent compound or derivatives.

Column regeneration

The regeneration procedure has already been reported.[5,6]

RESULTS AND DISCUSSION

Most organophosphorus pesticides are analysed at present by GLC using a flame photometric detector (FPD) which is very selective and sensitive to phosphorus containing compounds such as those studied here. In the past fenitrothion has been analysed by GLC with FPD on several occasions[1-3] and in most cases it was extracted from water using organic solvents. But there is only very limited information[1] on the quantitative determination of fenitrothion and derivatives by GLC. In one particular study,[6] the extraction of fenitrothion, fenitrooxon and aminofenitrothion from water using Amberlite XAD-2 resin and subsequent analysis by GLC was successful. However, to our knowledge, the simultaneous extraction and analysis of fenitrothion and five possible degration products using XAD resins and GLC, respectively, has never been reported.

In this study a GLC column containing OV-101 and OV-210 was used for the separation of fenitrothion from its derivatives and the experimental conditions were optimized to obtain maximum sensitivity. Detection limits and retention times for a mixture of fenitrothion and five derivatives are given in Table II. The detection limits varied from 0.5 ng per injection for fenitrothion to 3.5 ng per injection for hydroxymethylfenitrothion. Under the operating conditions it was possible to separate all six compounds as indicated by the individual retention times and as illustrated in Figure 1.

The mixture was separated in approximately 21 min. The resolution was considered good overall although it was difficult to achieve complete separation between F and FO and between FF and SMF. An oven temperature of 185°C was critical to achieve separation but at the detriment of detection. Better detection limits (by a factor of 10) can sometimes be achieved with single compounds such as fenitrothion.

TABLE II
Simultaneous determination of fenitrothion and five derivatives by GLC

Compound	Rentention time (min.)	Detection limit (ng/5 μl)
AF	4.4	1.0
F	8.1	0.5
FO	8.4	3.0
FF	14.4	1.0
SMF	15.0	1.5
HMF	21.3	3.5

Operating conditions: column: 3.6% OV-101, 5% OV-210, 1.8 m, T = 185°C

Injection port and detector: T = 250°C

Gases: N_2 60 ml/min
H_2 28 ml/min
H_2 50 ml/min

The reproducibility of the detection technique was verified with fenitrothion for which a coefficient of variation of 2% was obtained over a three hour period with 10 injections of 5 μl at a concentration of 10 ppm. Also a linear calibration curve was obtained between 0.1 and 100 ppm by injecting 5 mL aliquots. In practice, similar results have been anticipated for all derivatives of fenitrothion.

The resins[12] evaluated in this study were Amberlite XAD-4 and XAD-7. Amberlite XAD-4 is a polystyrene and is considered nonpolar with a surface area of 750 m^2/g while XAD-7 is a poly(acrylic)ester of medium polarity with a surface area of 450 m^2/g. Previous studies[7,8] had revealed that both resins had a high capacity of adsorption for fenitrothion and were readily adaptable to experimental changes such as increase in flowrate or volume of processed water.

In order to better evaluate the recovery potential of Amberlite XAD-4, each derivative was studied with fenitrothion as internal reference. The results are summarized in Table III. Different concentrations for the derivatives were necessary to take into account variations in the detection limits. Very good recoveries were obtained for aminofenitrothion, fenitrooxon and *s*-methylfenitrothion. Unfortunately only 27% and 34% recoveries were obtained with formylfenitrothion and hydroxymethylfenitrothion, respectively.

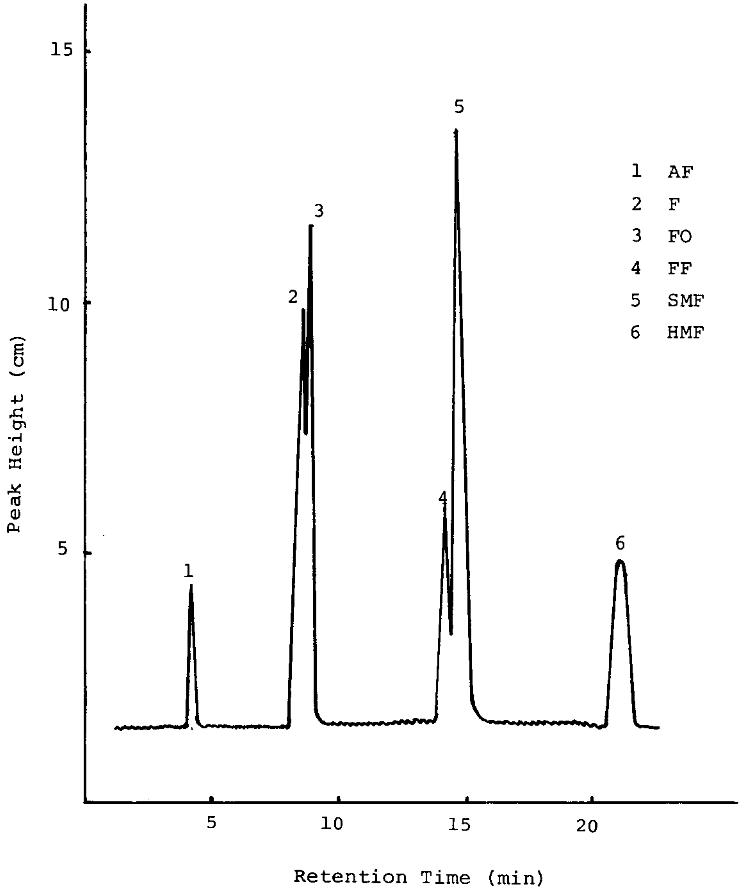


FIGURE 1 GLC chromatogram of fenitrothion and five derivatives.

An attempt to improve the recovery for FF and HMF was partly successful. With FF, an increase from 27 to 51% was observed when the concentration was reduced to 50 ppb but a further reduction in concentration did not improve recovery (Table IV). The same experiment with HMF gave an increase in recovery from 34 to 89%. In fact when the concentration of HMF alone was varied from 250 to 10 ppb, the recovery increased to 98%. The results with HMF seem to indicate in part that the capacity of the resin to retain such compounds is limited. But the results with FF are difficult to interpret since the recovery does not increase at lower concentrations than 50 ppb. Further attempts to improve recoveries using different eluants or by varying the volume of eluant were not successful.

TABLE III
Recovery from distilled water of fenitrothion and one derivative with Amberlite XAD-4

Mixture	Concentration (ppb)	Recovery (%)* F	Recovery (%)* Derivative
F+AF	50	96	86
F+FO	500	97	92
F+SMF	250	95	91
F+FF	250	94	27
F+HMF	500	96	34

*Mean of three recoveries using 3 × 30 mL of ethyl acetate for elution.

TABLE IV
Recovery from distilled water of FF with Amberlite XAD-4
Effect of concentration

Compound	Concentration (ppb)	% Recovery*
F, FF	10, 50	99, 51
F, HMF	5, 50	96, 89
HMF	250	57
HMF	100	72
HMF	50	90
HMF	10	98

*Average of three determinations, with 3 × 30 mL of methylene chloride.

Considering the partial success obtained with particular derivatives attempts were made to recover a mixture of six components from distilled water at concentrations between 5 and 50 ppb (Table V). As expected results were very good for fenitrothion, fenitrooxon, s-methylfenitrothion and aminofenitrothion but with FF and the hydroxymethylfenitrothion in particular the recoveries were similar to those given in Table IV, which leads us to believe in the phenomenon of site saturation in presence of a mixture of compounds (matrix effect) and consequently that XAD-4 can only hold so much of FF and HMF (compare results of Table IV and V).

TABLE V
Recovery from water of a mixture of fenitrothion and five derivatives with Amberlite XAD-4.

	Recovery (%)*					
Experience #	F (5 ppb)	AF (10 ppb)	FO (50 ppb)	SMF (50 ppb)	FF (25 ppb)	HMF (50 ppb)
1 (distilled water)	95	81	92	98	35	28
2	99	84	99	86	37	30
3	97	82	90	83	33	29
4 (polluted environmental water)	98	101	100	87	43	41

*Recovery with 3 x 30 mL of methylene chloride.

TABLE VI
Recovery from distilled water of a mixture of fenitrothion and five derivatives with Amberlite XAD-7 resin.

	Recovery (%)*					
Experience #	F (5 ppb)	AF (10 ppb)	FO (50 ppb)	SMF (50 ppb)	FF (25 ppb)	HMF (50 ppb)
1	99	100	98	84	28	26
2	103	100	100	85	26	21
3	97	97	96	81	23	22
	$\bar{x} = 100$	99	98	83	26	23

*Recovery with 3 x 30 mL of methylene chloride.

Experiments were performed with a polluted environmental water sample containing many organic and biological contaminants and having excessive turbidity.

The chromatogram was clear with no indication of interferences. During the procedure, it was noted that the resin (XAD-4) retained only very little suspended solids. The results also presented in Table V indicate very good recoveries except for FF and HMF, as expected. However, an increase in recovery is noticeable with FF and HMF when using polluted environmental water. The phenomenon remains unexplained.

Using the same experimental conditions as with Amberlite XAD-4, a series of experiments were performed to evaluate Amberlite XAD-7. The data are given in Table VI. In general, all the recovery data were similar to those obtained with XAD-4.

From all the experiments carried out in this study it has been possible to calculate coefficients of variation for each of the compounds with a minimum of six recoveries in each case. The data as presented in Table VII illustrate that good reproducibility is obtained at particular concentrations for all the individual compounds even though for FF and HMF the % recoveries are not expected to be very good at such high concentrations. But since reproducibility usually varies depending on the concentration used in an analytical technique, the data in Table VII should only serve to indicate that the reproducibility of the technique is expected to be good.

TABLE VII
Reproducibility of the method using Amberlite XAD-4 and GLC

Compound	Mean recovery* (%)	Concentration (ppb)	Coefficient of variation (%)
F	97	50	3.1
AF	98	50	2.9
FO	95	500	3.4
SMF	90	500	3.2
FF	27	250	5.3
HMF	32	500	4.0

*Mean of six recoveries using 3 × 30 mL of methylene chloride.

CONCLUSION

The results of this study demonstrate the capacity of Amberlite resins XAD-4 and 7 to recover quantitatively from water fenitrothion and three derivatives, namely AF, FO, and SMF. Two other derivatives namely FF and HMF could not be recovered successfully when present in mixtures although the recovery of HMF could be increased above 90% when the concentration was 50 ppb or less. On the other hand, it was shown that GLC may be used to separate all six chemicals in one single step with satisfactory detection limits.

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