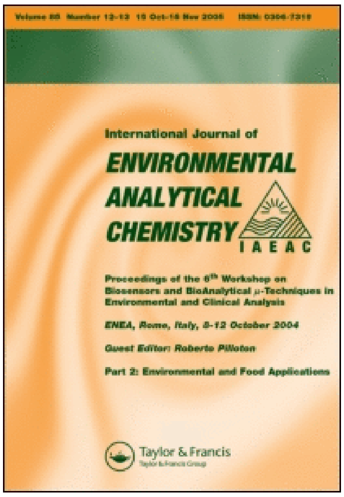

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Determination of Dimethoate in Waste Water, Soil and Sediment Using Gel Permeation Chromatography for Sample Clean-up[†]

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A method for the determination of trace amounts of the organophosphorus insecticide dimethoate in waste water, soil and sediment is presented. Sediment and soil samples are extracted by soxhlet with acetone/hexane followed by partition of the extract between methylene chloride and water. Separation of dimethoate from other compounds is carried out using gel permeation chromatography with Bio-Beads SX-3. Dimethoate is determined by capillary gas chromatography with a nitrogen-phosphorus detector.

Detection limits are 10, 30 and 130 ppt for surface water, waste water and soil/sediment respectively. Recoveries are 70.6–75.2% with standard deviations between 5.4 and 9.2%.

KEY WORDS: Dimethoate, gel permeation chromatography, gas chromatography, waste water, sediment.

INTRODUCTION

Dimethoate (0,0-dimethyl-S-(N-methylcarbamoylmethyl)phosphorodithioate) is a contact and systemic insecticide effective against a broad range of insects on a wide range of crops.

[†] Presented at the 14th Annual Symposium on the Analytical Chemistry of Pollutants, Barcelona, November 21–23, 1984.

Dimethoate is a polar compound (sol. in water: 25 g/l at 21°C) and rather stable in aqueous media at acidic or neutral pH[1]. As a result of its mobility[2] it may be found not only in waste water and surface waters but also in soil and groundwater. In sediments dimethoate probably only occurs near effluents from pesticide manufacturing plants.

A number of methods for the simultaneous determination of organophosphorus pesticides in environmental samples or foodstuffs have been proposed.[3,4,5] However, these procedures often give poor results for dimethoate and other polar pesticides. Though gel permeation chromatographic systems have been reported for clean-up of environmental samples[3,6,7] none of them seems to be selective for a single compound. Dimethoate has not been thoroughly studied in any of these procedures.

This paper demonstrates a selective method for the determination of dimethoate in complex environmental samples at ppt-level.

EXPERIMENTAL

Materials

Pesticide standards: Dimethoate (99.5%) was purchased from Cheminova A/S (Harboøre, Denmark) and dichlorvos (99.4%) from Dansk Shell A/S (Copenhagen, Denmark). All solvents: Acetone, hexane, methylene chloride, isopropanol and cyclohexane were of HPLC-grade quality from Rathburn Chemicals Ltd. (Walkerburn, Scotland). Bio-Beads SX-3 was purchased from Bio-Rad Laboratories (Richmond, CA, U.S.A.). The gel material was allowed to soak in cyclohexane for 24 hours and was then transferred to a glass tube of 25 cm × 1.5 cm I.D. The column was washed with 50 ml of cyclohexane before the clean-up of samples.

Extraction and clean-up procedure

Samples of soil and sediment were homogenized and an aliquot (~20 g dry weight) was transferred to an extraction thimble, acidified with 1 ml of 4 M hydrochloric acid and extracted overnight by soxhlet with 200 ml acetone/hexane (4:1).

The extract was concentrated to 25 ml and transferred to a separatory funnel with 25 ml of methylene chloride. 100 ml deionized water was added and pH was adjusted to 5–6 with 0.5 M sodium hydroxide. The aqueous phase was partitioned with a total of 3 × 25 ml methylene chloride that were dried with anhydrous sodium-sulfate and evaporated to dryness. Water samples (0.5 l) were partitioned directly with 2 × 50 ml and 1 × 25 ml methylene chloride. The residue was transferred to a tube (25 cm × 1.5 cm I.D.) with 20 cm Bio-Beads SX-3 by means of 2 ml cyclohexane and eluted with cyclohexane at 2 ml/min.

The first 110 ml were discarded while the fraction from 110–150 ml containing the dimethoate was concentrated to 1 ml and added the internal standard (dichlorvos at a concentration of 100 ng/ml).

1 μl of the extract was subjected to gaschromatographic analysis.

Gas chromatography

A Packard Model 433 gas chromatograph with a nitrogen-phosphorus detector and a Packard Model 612 PND-Controller were used.

The column was a 25 m fused-silica capillary column (0.20 mm I.D.; 0.33 μ filmthickness) coated with 5% phenyl methyl silicone (SE-54) (Hewlett-Packard Gmbh, Böblingen, F.R.G.).

Temperature programming: 0.7 min. at 75°C followed by 8°/min. to 225°C and 20°/min. to 275°C. This temperature was held for 2 minutes. 1 μl was injected splitless in 0.7 min.

RESULTS AND DISCUSSION

The method has been tested on waste water, surface water, soil and sediment samples that were spiked with a solution of dimethoate in isopropanol. Recoveries are in the range from 70.6–75.2% and as standard deviations are low precise quantitative determinations of dimethoate can be performed even at very low levels in samples of complex composition (Table I). Chromatograms of waste water and sediment samples are shown in Figure 1 and 2. Detection limits are in the range 10–130 ppt depending on the matrix. The values shown in Table I are estimated by extrapolation of the data obtained in the recovery-study.

The excellent selectivity of the method is due to the fact that dimethoate elutes separately from other organophosphorus pesticides

TABLE I
Recovery and detection limit for dimethoate in environmental samples

matrix	spike-level	recovery (%)	SD (%)	detection limit[a]
waste water[b]	100 ppt	75.2	7.8	30 ppt
surface water[b]	20 ppt	72.3	9.2	10 ppt
soil/sediment[c]	5 ppb	70.6	5.4	130 ppt

[a] Stated for a signal:noise ratio of 3.
[b] Based on 0.5 l samples.
[c] Based on samples of 20 g dry weight. The detection limit is estimated from experiments at 1 ppb level ($n = 4$).

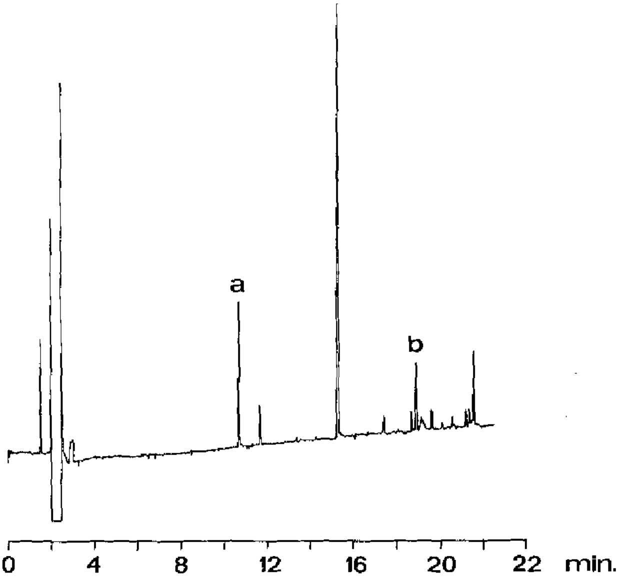

FIGURE 1 0.5 l waste water spiked with 50 ng of dimethoate. Peak a is dichlorvos (internal standard, 100 pg/μl) and peak b is dimethoate. Injection volume: 1 μl. Clean-up of sample and chromatographic conditions as described in the text.

and related compounds in the gel permeation chromatographic system being used here.

The pesticides dichlorvos, ethion, fenitrothion, malathion, parathion-Me, parathion and sulfotep have been found to elute much earlier from the column than dimethoate. The same result was

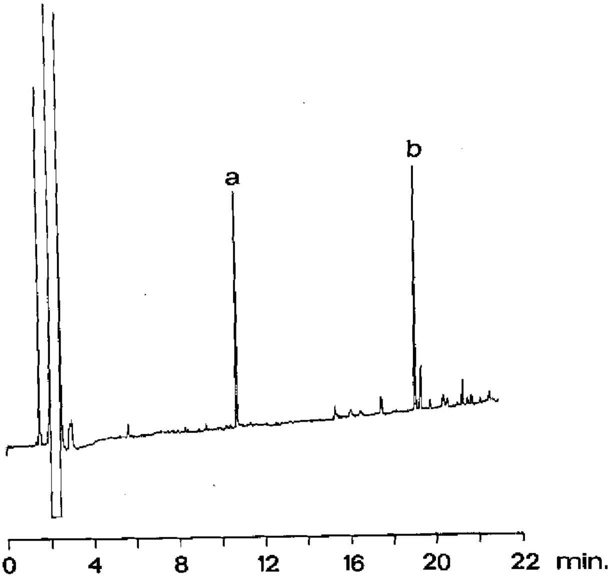

FIGURE 2 20 g marine sediment spiked with 100 ng of dimethoate. Peak a is dichlorvos (internal standard, 100 pg/μl) and peak b is dimethoate. Injection volume: 1 μl. Clean-up of sample and chromatographic conditions as described in the text.

obtained for 4 related triesters of phosphoric-, thio- and dithiophosphoric acid. Elution profiles for selected compounds are shown in Figure 3.

Soil and sediment samples were extracted wet as investigations at our laboratory have shown no improvement of the extraction efficiency of the compounds in question by freezedrying of the samples before extraction.[8] The same study revealed that extraction by partition was most efficient at pH = 5–6. This pH was chosen here as well.

A number of factors influence the elution profile of dimethoate on Bio-Beads SX-3 why a spike-test using an aliquot of the sample in question should be performed in order to determine the optimal fraction for collection. Batch number of gel material, manufacturer and quality of solvent and co-solutes present in the extract should be mentioned as important variables influencing the gel chromatographic separation.

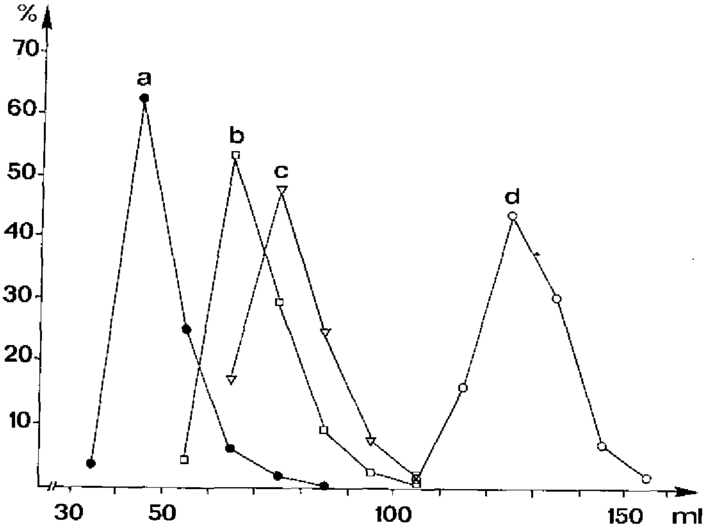

FIGURE 3 Elution profiles for selected organophosphorus compounds on Bio-Beads SX-3 using cyclohexane as eluent at 2 ml/min.

Compound a is triethyldithiophosphate, b is 0,0-diethyl-S-methylthiophosphate, c is malathion and d is dimethoate.

Of 12 compounds examined 11 eluted in one group while the last eluted separately (dimethoate). a was the first of these, b was in the middle and c was the last. The values at the y-axis are the percentages of the total amount of the compound eluted in each fraction.

References

1. C. R. Worthing (Ed.), *The Pesticide Manual* (The British Crop Protection Council, Croydon, 1983), 7th ed., p. 4880.
2. B. Schultz, S. Lind, J. Kjølholt and P. Kjeldsen, yet unpublished results.
3. J. A. Ault, C. M. Schofield, L. D. Johnson and R. H. Waltz, *J. Agric. Food Chem.* **27**, 825 (1979).
4. A. Ambrus, E. Hargitai, G. Károly, A. Fülöp and J. Lantos, *J. Assoc. Off. Anal. Chem.* **64**, 743 (1981).
5. G. L. LeBel, D. T. Williams, G. Griffith and F. M. Benoit, *J. Assoc. Off. Anal. Chem.* **62**, 241 (1979).
6. J. Pflugmacher and W. Ebing, *J. Chromatog.* **93**, 457 (1974).
7. J. Askew, J. H. Ruzicka and B. B. Wheals, *Analyst*, **94**, 275 (1969).
8. J. Kjølholt, *J. Chromatog.* (submitted for publication).