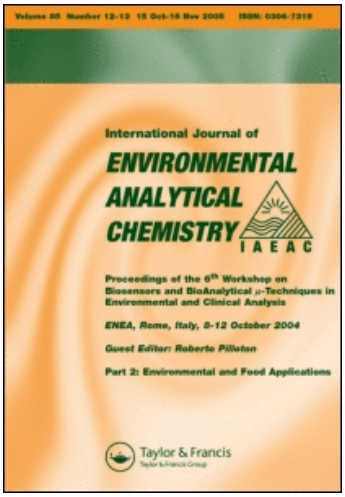

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DETERMINATION OF O,O-BIS(2-ETHYLHEXYL)PHOSPHORODITHIOIC ACID IN WATER AT THE ppt LEVEL BY GC/ECD AFTER REACTIVE EXTRACTION AND PRE-COLUMN DERIVATIZATION

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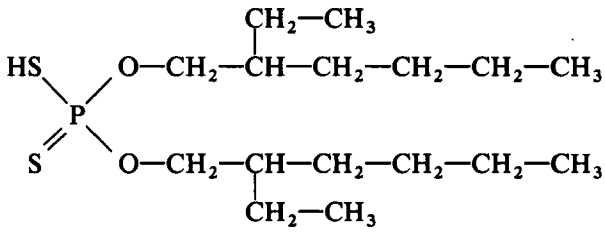
A procedure for the determination of O,O-bis(2-ethylhexyl)phosphorodithioic acid (EPDTH) in water has been developed. It includes the extraction of the analyte as its Bi(III) complex followed by derivatization with pentafluorobenzylbromide and subsequent GC separation and electron capture detection. The formation of a Bi(III) complex of EPDTH ensures quantitative extraction and derivatization also at very low concentrations, whereas the use of a reagent leading to a halogen-containing derivative allows the application of the highly sensitive and selective ECD. The good linearity is characterized by a value of 0.9993 of the linear correlation coefficient in the 0.05–1000 ppb analyte concentration range. The mass detection limit for the pentafluorobenzylester of EPDTH is 1 pg for a signal-to-noise ratio of 3. With this method, the determination of EPDTH below the maximum admissible concentration of 100 ppt established for organophosphorous compounds in drinking water is possible.

Non-contaminated groundwater samples from different areas were analysed. It was demonstrated that no matrix compounds are present that can interfere with the determination of the analyte in a concentration above 20 ppt. In a contaminated groundwater sample 50 ppt EPDTH were found.

KEY WORDS: Water pollution, dialkylphosphorodithioic acid, GC/ECD, reactive extraction, pre-column derivatization.

INTRODUCTION

Thioorganophosphorous compounds have found widespread application. Especially dialkylphosphorodithioic acids are commonly used, e.g. as flotation reagent (Aerofloat), as extreme-pressure additive in lubricating oils, as reagent in the liquid–liquid extraction of metal ions from aqueous solutions or as starting material for the synthesis of insecticides.[1–11] One of the most widely used dialkylphosphorodithioic acids is O,O-bis(2-ethylhexyl)phosphorodithioic acid (EPDTH) having the following structure:



It is a strong acid with a pK_a value of 1.25 (ref. 12). Its ability to form very stable complexes with many metal ions leads to its application as an extractant. The partition coefficients between organic and aqueous phases of these complexes are much higher than 1000 over a wide pH range.[3–5] Its high stability against hydrolysis compared to other complexing agents like dialkyldithiocarbamates is of great advantage since in most cases the extracting conditions are highly acidic. Hydrolysis of the complex increases significantly, however, at higher temperature.[13]

The toxicity of EPDTH compared to trialkyldithiophosphates used as insecticides like thimet, malathion, parathion and many others,[11] is relatively low: the LD_{50} value was found to be 2140 mg/kg[14] for rats (oral application). Because of the much higher toxicity for other organophosphorous species a maximum admissible concentration of 100 ppt has been defined for this class of compounds in drinking water.[15] Due to fire at an industrial plant in Austria in 1987, EPDTH was accidentally emitted into a river, making its control in groundwater necessary.

Analytical methods for the determination of EPDTH described in the literature include iodometric titration,[1] potentiometric titration with a sulphur-selective or silver-selective electrode[16,17] and photometric detection after extraction of EPDTH as a metal complex.[1,18] These methods allow the determination of EPDTH only in the absence of interfering compounds.

High-performance liquid chromatography (HPLC)[19–21] and gas chromatography (GC)[22–24] are described in the literature as analytical methods suitable for mixtures. They were applied for the determination of the length of the alkyl chains of dialkylphosphorodithioic acids used as additives for lubricating oils. No method is described, however, for the determination of EPDTH at trace level. Therefore an appropriate method had to be worked out combining a high-performance separation technique with a highly sensitive and selective detection method, which makes it possible to determine EPDTH in groundwater down to a concentration of 100 ppt, as required by EEC regulations.[15]

EXPERIMENTAL

Chemicals

The chemicals used were of analytical grade (E. Merck, Darmstadt, FRG), except pentafluorobenzylbromide (purum, Fluka, Buchs, Switzerland). The analytes O,O-bis(2-ethylhexyl)phosphorodithioic acid and O,O-dioctylphosphorodithioic acid (OPDTH) were of technical grade (kindly provided by Hoechst, Frankfurt/Main, FRG). Pure water was prepared by double distillation in a quartz apparatus.

Apparatus

Gas chromatography For the determination of the halogen-containing derivatives a gas chromatograph (Model 3400, Varian, Walnut Creek, USA) equipped with a split injector (split ratio 1:20) and an electron capture detector (ECD) was used. The separations were carried out with a fused silica capillary column (15 m length; 0.32 mm i.d.; coated with polydimethylsiloxane OV 101 of 0.1 μm film thickness). Carrier gas was nitrogen of 99.999% v/v purity (Messer Griessheim, Düsseldorf, FRG) at a flow rate of 1 ml/min. The oven temperature was 240 °C isothermal; the injector and detector temperature were 300 °C. The make-up gas for the ECD was nitrogen at a flow of 30 ml/min.

Mass spectrometry The measurements were carried out on a quadrupole instrument with electron impact ion source (Model HP 5990A, Hewlett Packard, Palo Alto, USA). The temperature of the ion source was 280 °C; the ionization energy was 70 eV.

Procedures

Extraction The analyte EPDTH is extracted from water as $Bi(EPDT)_3$. An aqueous sample (100 ml) containing EPDTH is mixed with 5 ml concentrated sulphuric acid and about 10 mg $Bi(NO_3)_3 . 5H_2O$ are added to the mixture. This solution is mixed with 10 ml hexane for 3 min, the organic layer is separated and the solvent evaporated under vacuum to dryness.

Derivatization The evaporation residue of the extract is dissolved in 1 ml acetone containing 40 mg pentafluorobenzylbromide (PFBBr) and heated overnight on a water bath at about 56 °C. Then the solvent and excess PFBBr are removed under vacuum at 70 °C during 15 min. The residue is dissolved in 100 μl hexane and an aliquot (1 μl) is used for GC analysis.

RESULTS AND DISCUSSION

To eliminate interferences due to matrix components a high-performance separation technique is needed for the determination of EPDTH as pollutant in water. HPLC was studied in our laboratory as a possible separation method for this analysis.[25] In these experiments the free acid EPDTH could not be determined at low levels due to formation of complexes with metals present in low concentrations in water or in the reagents used. An attempt was made to solve this problem by converting the analyte into a single, well-defined, stable complex and determining this complex by HPLC with UV detection after extraction from the aqueous phase.

The use of capillary GC as separation method offers the advantage of a higher column efficiency, compared to HPLC. This could result in a better separation of the analyte from interfering matrix compounds. As EPDTH still has a free acidic SH group, the GC determination of the underivatized compound was not successful. Because of the low volatility of EPDTH thermolysis can be expected at the high temperature required for the gas chromatographic separation. Further-

more the strong interactions between the free acidic group of the analyte and adsorptive sites, occasionally present in the GC system, can lead to asymmetrical peaks resulting in a deterioration of the resolution as well as of the detection limit. Therefore it was decided to improve the gas chromatographic characteristics of EPDTH by converting the acidic SH group into a less polar ester group.

A simple and widely used approach for derivatization in GC is the conversion of an acid group into the corresponding methyl ester by reaction with diazomethane. When applying this method to derivatize EPDTH, the yield of the ester decreased at concentrations of EPDTH below 1 ppm, especially when drinking water was used instead of pure water. This effect may be explained by the formation of highly stable complexes of EPDT with metal ions, which are always present as trace impurities in water and the reagents, especially in the acids. These metal complexes probably interfere with the derivatization procedure, leading to irreproducible results and a higher detection limit.

To overcome the difficulties in the derivatization with diazomethane at low concentrations of EPDTH, another type of conversion was worked out, based on the reaction between a salt of EPDTH, formed by reactive extraction, and an alkyl halide.

Reactive Extraction

In reactive extraction the analytes are converted to compounds which are better extractable. Complex formation was used as chemical reaction for EPDTH. As complexing metal ion Bi^{3+} was chosen, because it is known from the literature that the Bi(III) complex of the analogous O,O-dibutylphosphorodithioic acid has one of the highest partition coefficients of all metal complexes of this compound in organic–aqueous liquid–liquid systems.[4] For EPDTH itself the partition coefficient of its Bi(III) complex is much higher than 1000 in the concentration range of 0.1 to 10 mol/l of sulphuric acid.[26]

When extracting EPDTH as a Bi(III) complex, the rate-determining step seems to be the complex formation at the interface of the two liquid phases.[27] The complex was found to be extracted quantitatively after 3 min.

The equation for the reactive extraction is given by

$$(Bi^{3+})_a + 3(EPDTH)_o \rightleftharpoons (Bi(EDPT)_3)_o + 3(H^+)_a \quad (1)$$

The suffixes a and o indicate the aqueous and the organic phases, respectively.

Pre-column Derivatization

The complex formed by reactive extraction can be converted with an alkyl halide to give the corresponding alkyl ester. Other metal ions present in the solution, which are also able to form extractable complexes with EPDTH will not disturb this procedure, since the complexes with such metal ions will react with the halide reagent in the same manner and give the same ester derivative, following the scheme

$$Me^{n+}(EPDT^{-})_n + R-X \rightleftharpoons nR-EPDT + Me^{n+}X_n \quad (2)$$

where R = alkyl group, Me = metal ion, and X = halogen.

The reaction of the Bi(III) complex with ethyl iodide was expected to lead to the corresponding ethyl ester. In contrast to the derivatization with diazomethane, the yield of this procedure was found to be independent of the concentration of EPDTH, but the detection limit, using a flame ionization detector, was only 1.5 ppb at a signal-to-noise ratio of 3. Since the required maximum admissible concentration of EPDTH in drinking water is 100 ppt, the above procedure was modified such that a reagent was used forming halogen-containing derivatives, because in this case the more sensitive ECD can be used for the measurement of the products. For this purpose PFBBr was chosen as reagent since it contains five fluorine atoms, so that a high response of the ECD can be expected for this derivative. Furthermore, it was assumed that the volatility of the corresponding ester is still high enough so that it can be determined by GC without decomposition. As solvent for the reaction acetone was used as recommended in the literature.[28]

In order to optimize the derivatization yield the influence of the temperature and of the reagent concentration was studied. For this purpose EPDTH was extracted as its Bi(III) complex as described. Aliquots containing 100 μg EPDTH each (as Bi complex) were reacted with PFBBr at different concentrations, ranging from 0.4 to 400 mg/ml at two different temperatures, viz., 20 °C and 56 °C, the latter being the boiling point of acetone. After a reaction time of about 15 h the amount of derivative was determined by GC as described. The results of this study are shown in Figure 1. The peak areas are normalized, the largest peak area being regarded to correspond to a yield of 100%. It can be seen that at a temperature of 20 °C the reaction is complete only when using a reagent concentration of 400 mg/ml, that is a 5000-fold excess compared to the analyte. At a lower concentration of PFBBr, e.g. at a 20-fold excess, the yield decreases drastically to a few per cent. By increasing the temperature to 56 °C a yield of more than 90% is already reached at a reagent concentration of 40 mg/ml, which is only a tenth of the concentration needed for a complete reaction at a temperature of 20 °C. Therefore for all further studies a concentration of 40 mg/ml of PFBBr and a temperature of 56 °C were used. From thermodynamic and kinetic points of view it can be assumed that a quantitative reaction will also occur when real samples containing lower concentrations of EPDTH are analysed.

GC and GC/MS

The GC analysis of the reaction mixture resulting from the derivatization of the Bi(III) complex of EPDTH with PFBBr shows that this type of derivatization leads mainly to a single product. A chromatogram obtained for EPDTH and O,O-dioctylphosphorodithioic acid (OPDTH) dissolved in pure water and treated by the procedure described is shown in Figure 2. The isomer OPDTH was added as an internal standard for better quantitation.

For identification, mass spectra of the two analyte peaks in the gas chromato-

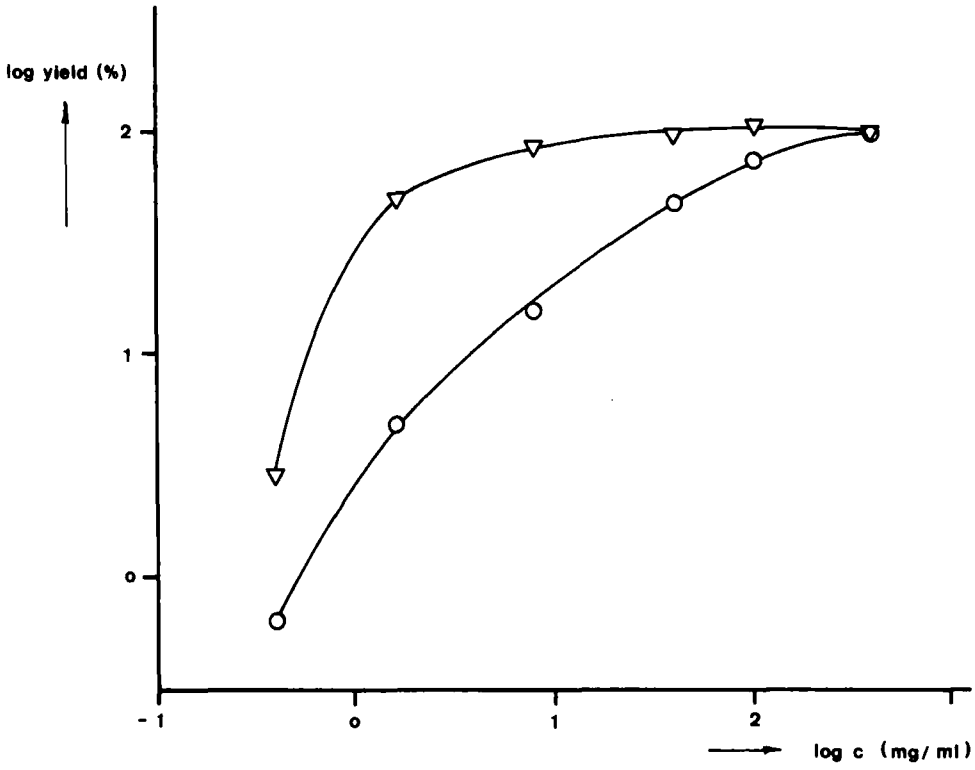


Figure 1 Dependence of the yield of derivatization on reagent concentration and temperature. ○, 20 °C, ▽, 56 °C, c, concentration of pentafluorobenzylbromide in the reaction solution.

gram in Figure 2 were recorded. They are shown in Figure 3. One can see that the two positional isomers exhibit nearly identical mass spectra. In both spectra no molecular ion at m/z 534 occurs. The peak with the highest m/z value of 423 results from the loss of one 2-ethylhexyl or octyl group, respectively. The peak at m/z 311 is caused by the elimination of the second alkyl group. The peak at m/z 181 corresponds to the pentafluoro group. From the MS data one can conclude that the extraction of EPDTH as its Bi(III) complex and its derivatization with PFBBr leads indeed to the corresponding ester.

Validation of the Method for Quantitative Analysis

Linearity The calibration curve obtained with pure as well as with drinking water in the concentration range between 0.05 and 1000 ppb is shown in Figure 4. The peak areas are given relative to the internal standard, the pentafluorobenzyl-ester of OPDTH, which was added just before the GC determination. At all concentration levels identical results were obtained within the statistical error for both types of matrices. The linearity described by the linear correlation coefficient

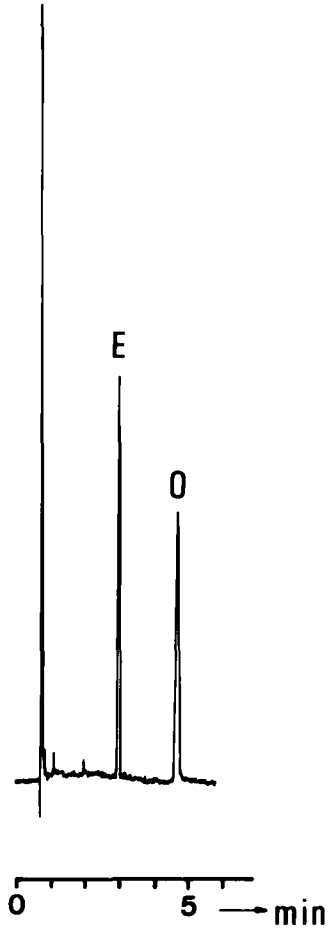


Figure 2 Gas chromatogram of a test solution of EPDTH (E) and OPDTH (O) after their conversion into the pentafluorobenzyl esters. The phosphorodithioic acids were dissolved in pure water, and the sample was pretreated as described in the experimental section. Chromatographic conditions: stationary phase, dimethylsiloxane OV 101; carrier gas, nitrogen; flow rate, 1 ml/min; column length, 15 m, i.d. 0.32 mm; temperature, 240 °C isothermal; split injection (1:20), EC detector.

is 0.9993. From the results it can be seen that no losses or artefacts occur in the determination of the analyte in drinking water compared to pure water.

Selectivity In order to study a possible interference of matrix compounds at the trace level, pure water and groundwater from different areas were analysed according to the method described above. Corresponding gas chromatograms are shown in Figure 5. No other compound with the same retention time as the analyte is present at a concentration above the detection limit of the method. Other peaks found in the chromatograms are probably caused by impurities in the

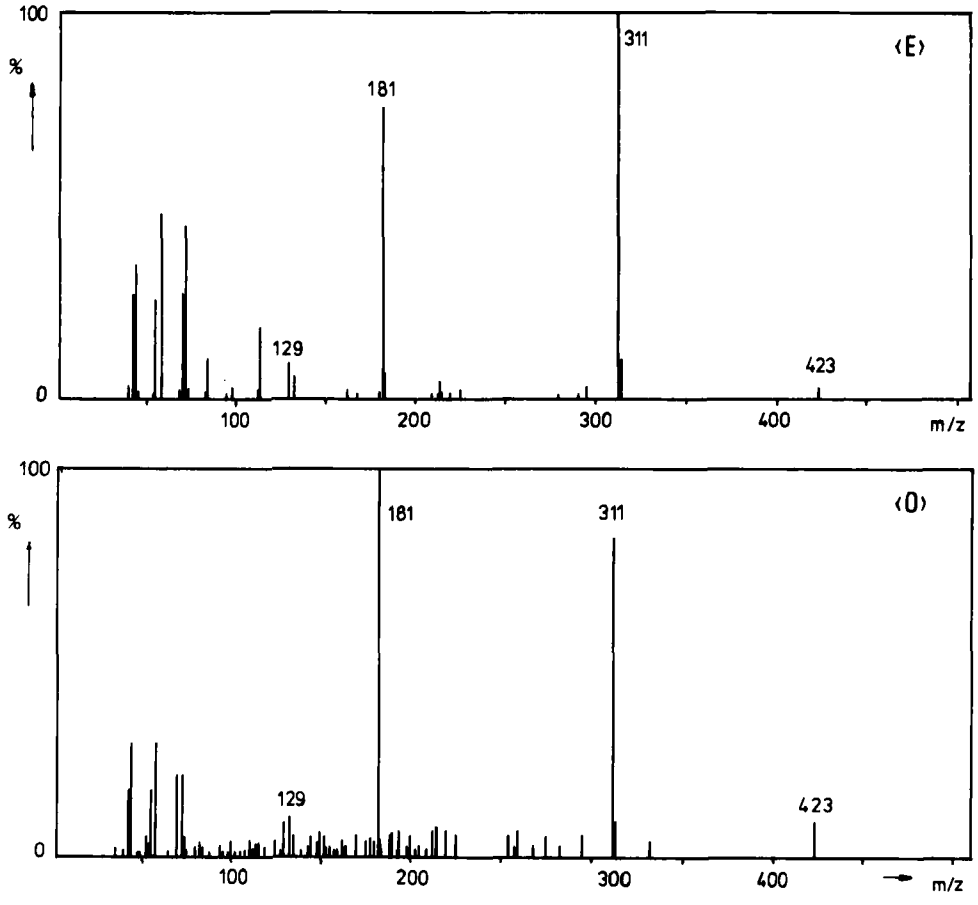


Figure 3 Mass spectra of the pentafluorobenzyl esters of EPDTH (E) and OPDTH (O). The spectra were recorded from the GC peaks shown in Figure 1. m/z, mass-over-charge ratio; %, relative abundance.

reagents used because these peaks occur with constant retention times and peak heights, independent of the type of water.

When spiking these groundwater samples with 0.1 ppb and 1 ppb of EPDTH and applying the above procedure, a peak of the expected height could be detected in the chromatogram at the position of the analyte as can be seen in Figure 6.

Precision and analysis of variance The precision of the single steps of the total procedure, including extraction, derivatization and GC determination, was evaluated at a concentration within the optimal range by means of variance analysis. For this purpose five aliquots of a solution, each containing the same concentration of 200 ppb EPDTH were extracted with hexane and each organic phase was divided into two equal parts. The resulting ten samples were reacted with PFBBr and then the concentration of the EPDTH derivative was determined in

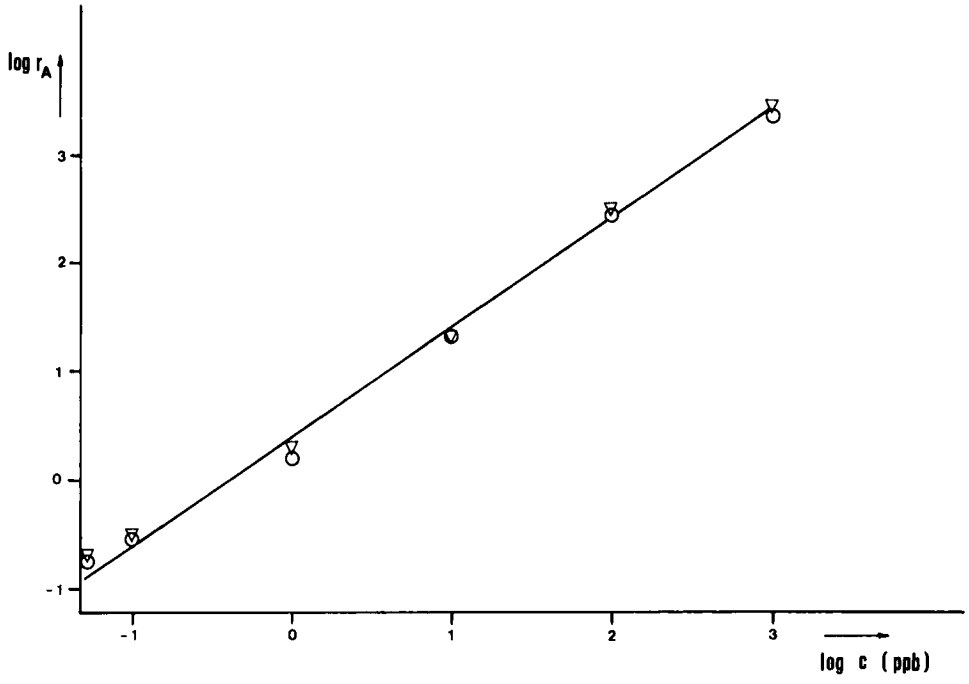


Figure 4 Calibration curve of EPDTH for GC with electron-capture detection after derivatization with pentafluorobenzylbromide. c, analyte concentration; r_A, ratio of peak areas of EPDTH and OPDTH (internal standard). ▽, bidistilled water; ○, drinking water.

duplicate in each sample by GC. The pentafluorobenzyl ester of OPDTH was added as an internal standard before the GC determination. The resulting data are shown in Table 1. Peak areas are given relative to the peak area of the internal standard. The result of the variance analysis (Table 2) shows that the contributions of the single steps—extraction, derivatization and GC analysis—to the total variance are of the same order of magnitude. The relative mean standard derivation of the whole procedure is 5.8%, which was considered to be satisfactory, so that no further optimization of the single steps was undertaken.

Detection limit The mass detection limit for the pentafluorobenzyl ester of EPDTH was found to be 1 pg at a signal-to-noise ratio of 3. The mass detection limit of the total method including extraction and derivatization was found to be about 20 pg corresponding to a sample concentration of 20 ppt.

Analysis of Ground and Drinking Water from a Contaminated Area

Ground and drinking water samples from 13 sources in the contaminated areas were taken. In the majority of the samples no pollution above the detection limit was found. The chromatogram of the sample with the highest concentration of

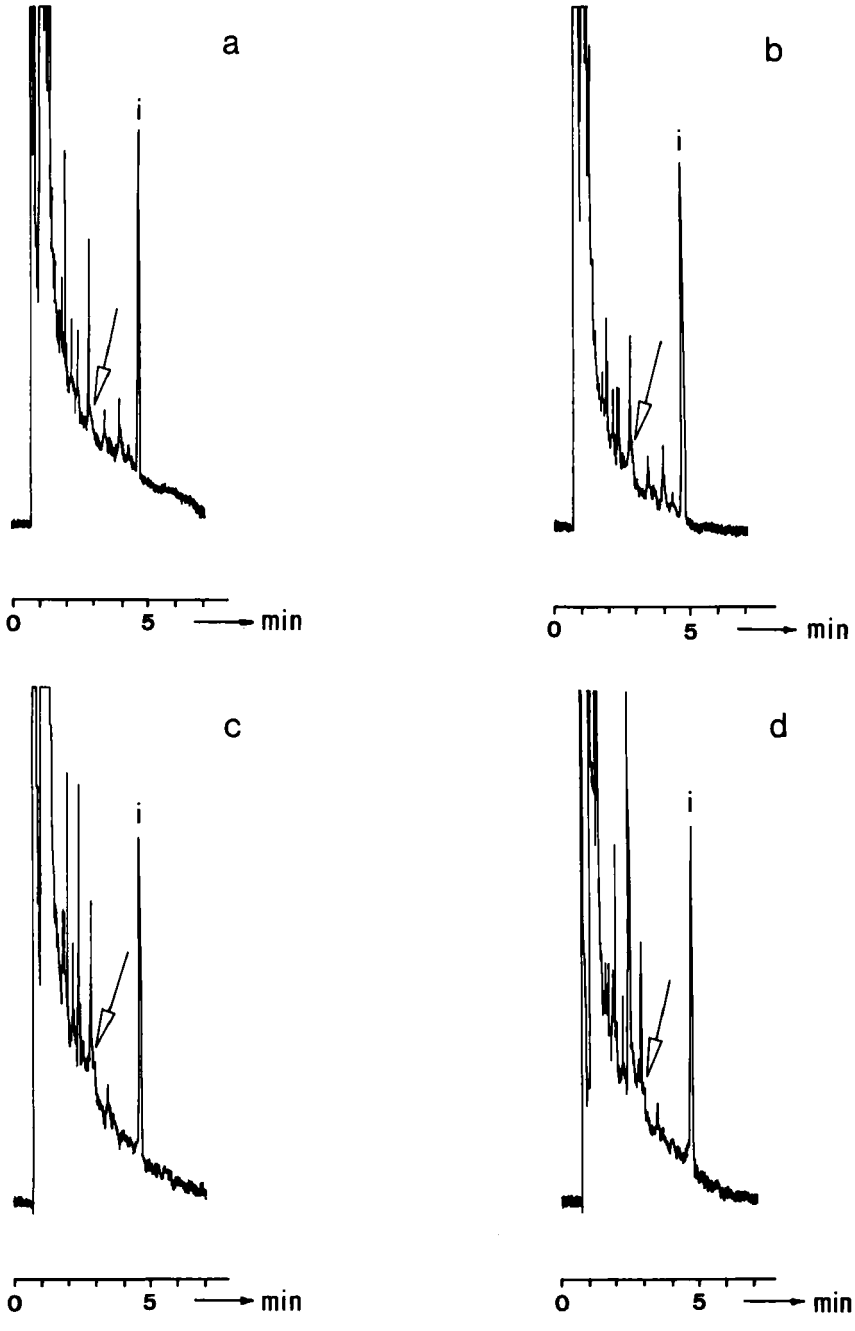


Figure 5 Gas chromatograms of drinking and groundwater samples originating from a non-contaminated area. Sample pretreatment as described in the experimental section. The position of the pentafluorobenzylester of EPDTH is indicated by an arrow. (a) pure water (reference); (b) drinking water from the municipal water supply, Vienna; (c) groundwater from Katzelsdorf, Lower Austria; (d) groundwater from Ternitz, Lower Austria; i = internal standard. Chromatographic conditions as in Figure 1 and the experimental section.

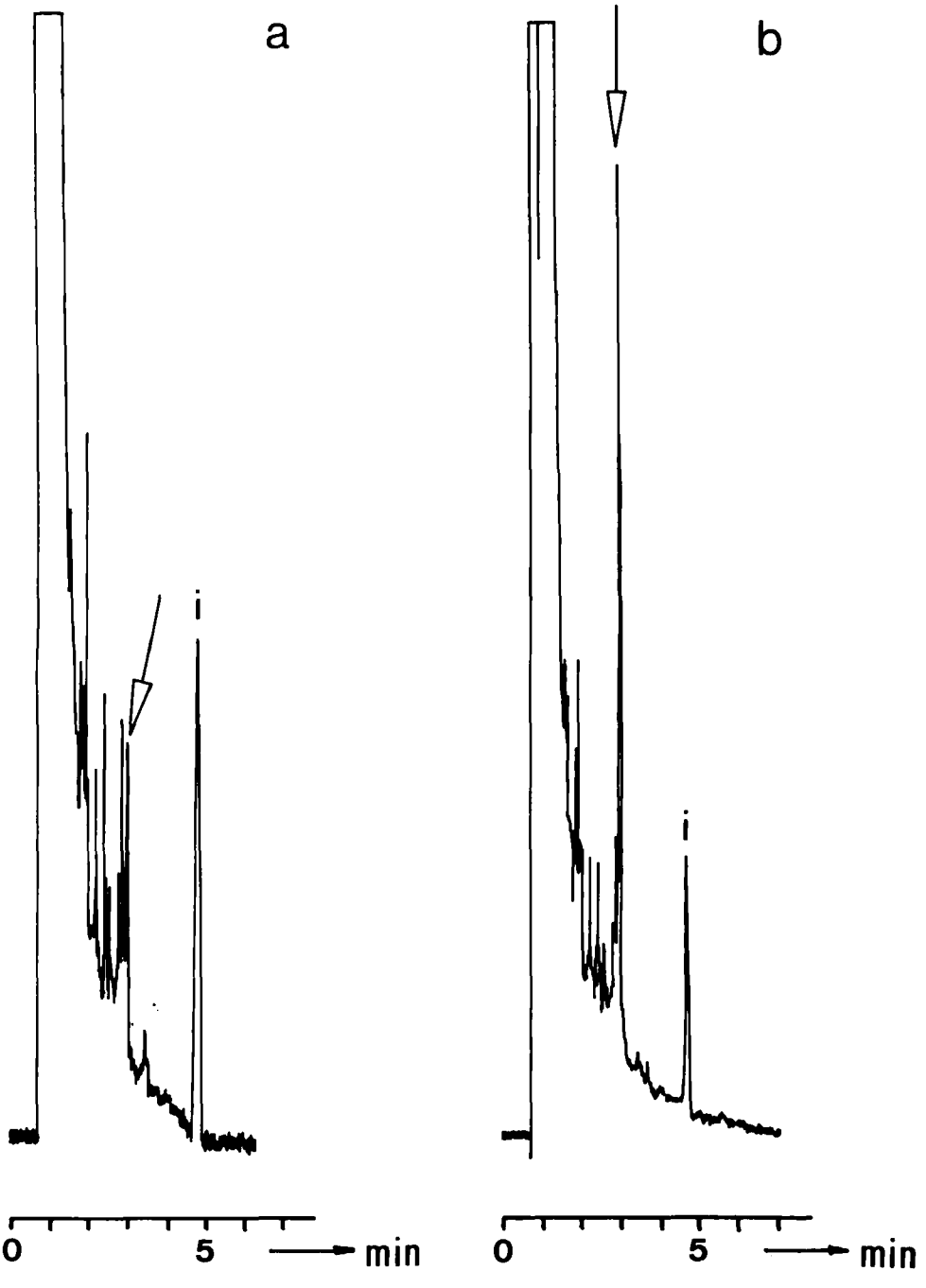


Figure 6 Gas chromatograms of spiked groundwater samples. The chromatogram of the corresponding (unspiked) groundwater is shown in Figure 5d. (a) 0.1 ppb and (b) 1 ppb EPDTH spiked. Sample pretreatment, see experimental section. The position of the pentafluorobenzyl ester of EPDTH is indicated by an arrow; i = internal standard. Chromatographic conditions as in Figure 1 and the experimental section.

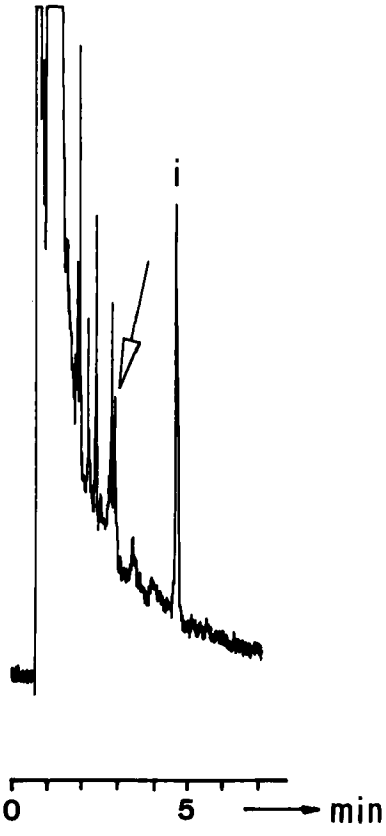


Figure 7 Gas chromatogram of a contaminated sample. Groundwater from Grafenbuch, Upper Austria. The position of the pentafluorobenzyl ester of EDPTH is indicated by an arrow; i = internal standard. Sample pretreatment and chromatographic conditions as in Figure 1 and the experimental section.

Table 1 Precision of analysis. Data are peak area ratios, r_A of EPDTH relative to the internal standard OPDTH. Five samples with each two aliquots were measured in duplicate

Measurements	*1*		*2*		*3*		*4*		*5*	
	1.1	*1.2*	*2.1*	*2.2*	*3.1*	*3.2*	*4.1*	*4.2*	*5.1*	*5.2*
1	1.350	1.381	1.387	1.231	1.391	1.457	1.264	1.420	1.457	1.475
2	1.344	1.344	1.329	1.232	1.489	1.436	1.357	1.436	1.493	1.467

Table 2 Analysis of variance. The data from Table 1 were used

Analysis step	*Variance*	*Mean standard deviation*	*Relative mean standard deviation*
Extraction	0.00360	0.0600	4.3%
Derivatization	0.00238	0.0488	3.5%
GC analysis	0.00126	0.0355	2.6%
Total procedure	0.00654	0.0809	5.8%

EPDTH is shown in Figure 7. In this sample, EPDTH was found at a level of 50 ppt (with a confidence limit of about 20% relative). This value is below the maximum admissible concentration of 100 ppt required by the EEC drinking water guideline.[15]

References

1. H. Bode and W. Arnswald, *Z. Anal. Chem.* **185,** 99 (1962).
2. H. Bode and W. Arnswald, *Z. Anal. Chem.* **185,** 179 (1962).
3. T. H. Handley, R. H. Zucal and J. A. Dean, *Anal. Chem.* **35,** 1163 (1963).
4. T. H. Handley and J. A. Dean, *Anal. Chem.* **34,** 1312 (1962)
5. J. Shibata and S. Nishimura, *Proc. Symp. Solvent Extr.* (1982), pp. 45–50.
6. H. Nedjate and J. L. Sabot, *C.R. Hebd. Seances Acad. Sci., Ser. C* **285,** 141 (1977).
7. V. F. Toropova, R. G. K. Budnikov and N. A. Ulakhovich, *Talanta* **25,** 263 (1978).
8. G. Marcu, M. Curtui and I. Haiduc, *J. Inorg. Nucl. Chem.* **39,** 1415 (1977).
9. J. L. Sabot and D. Bauer, *J. Inorg. Nucl. Chem.* **40,** 1129 (1978).
10. A. J. Bridgewater, J. R. Dever and M. D. Sexton, *J. Chem. Soc., Perkin Trans. II* 1006 (1980).
11. R. Wegler, *Chemie der Pflanzenschutz- und Schaedlingsbekaempfungsmittel* (Springer-Verlag, Berlin, Heidelberg, 1970), Vol. 1.
12. T. F. Rodina, V. I. Varentsova, A. N. Kolyshev and I. S. Levin, *Isv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **6,** 14 (1973).
13. G. Cote and D. Bauer, *Anal. Chem.* **56,** 2153 (1984).
14. *Safety Information Sheet (DIN)* (Hoechst AG, June 1986).
15. Council of the European Community, Council Directive of July 15, 1980, relating to the quality of water intended for human consumption, Directive 80/778/EEC, *Off. J. Eur. Comm.* **L229,** 11 (1980).
16. D. Haberland and W. Treichler, *Chem. Tech.* **34,** 195 (1982).
17. J. L. Sabot and D. Bauer, *Analusis* **6,** 441 (1978).
18. M. H. Jones and J. T. Woodcock, *Anal. Chem.* **58,** 1845 (1986).
19. T. Ohnishi, A. Nakanishi and M. Miwa, *Sekiyu Gakkaishi* **27,** 214 (1984).
20. K. Musha, C. Nagata and S. Tanaka, *Bunseki Kagaku* **34,** T26 (1985).
21. B. Kachlik-Olasinska, *Nafta* **36,** 161 (1980).
22. V. Zimmermann, J. Kempe and G. Jaeger, *Chem. Tech.* **35,** 359 (1983).
23. P. J. Marriot and T. J. Cardwell, *J. Chromatogr.* **234,** 157 (1982).
24. T. J. Cardwell, P. J. Marriott and P. S. McDonough, *J. Chromatogr.* **193,** 53 (1980).
25. J. F. K. Huber and H. Ruth, *Abstract, 2nd Toxicol. Seminar, Vienna, Nov. 1988*; to be published in *Intern. J. Environ. Anal. Chem.*
26. I. S. Levin, Yu. M. Yukhin, I. A. Bykhovskaya, I. A. Vorsina and V. V. Sergeeva, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **5,** 83 (1973).
27. S. A. Sedova and Yu. B. Kletenik, *Izv. Sib. Otd. Akad. Nauk, SSSR, Ser. Khim. Nauk* **5,** 73 (1976).
28. K. Blau and G. S. King, *Handbook of Derivatives for Chromatography* (Heyden, London, 1978).