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Analysis of chlorinated 1,3-butadienes by solid-phase microextraction and gas chromatography–mass spectrometry

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Abstract

Hexachloro-1,3-butadiene, as well as some of its dechlorinated degradation products, is known to be an antifungal agent and a by-product of the manufacture of chlorinated hydrocarbons. We analysed 1,1,4,4-tetrachloro-1,3-butadiene (TCBD), 1,1,2,4,4-pentachloro-1,3-butadiene (1,1,2,4,4-PCBD), *cis*-1,1,2,3,4-pentachloro-1,3-butadiene (*cis*-1,1,2,3,4-PCBD) and hexachloro-1,3-butadiene (HCBD) in water by solid-phase microextraction (SPME) and gas chromatography–mass spectrometry (GC–MS). We optimised the analytical technique, considering the efficiency of the desorption and extraction under different experimental conditions. The linearity and the sensitivity was tested. The lower concentrations detected were 25–50 ng/l and the linearity of the absorption was verified in the range 0.1–200 μg/l. The method has been applied to polluted ground-water samples.

Keywords: Sample preparation; Water analysis; Environmental analysis; Butadienes; Chlorinated butadienes

1. Introduction

Hexachloro-1,3-butadiene (HCBD) is a toxic compound, with a high bioaccumulating potential, that is included in the U.S. Environmental Protection Agency (EPA) list of the 129 priority pollutants. It does not occur as a natural product in the environment; it has been used as a heat-transfer fluid in transformers and it arises chiefly as a by-product of chlorinated hydrocarbon manufacture. Moreover, it was used as an antifungal agent in the former Soviet Union [1,2]. Its reductive dechlorination products have been investigated recently [2] and some of its less chlorinated analogs seem to be intermediates, or end-products, under particular environmental conditions. These compounds, such as tetrachloro-1,3-butadiene and pentachloro-1,3-butadiene are toxic too.

Recently 1,1,3,4-tetrachloro-1,3-butadiene was found in river water in Slovakia [3]. In spite of their toxicity and their occurence in the environment, very little information is available regarding their analysis in environmental samples.

HCBD and related compounds (Fig. 1) have been found in ground-water samples near Milan. Samples came from a highly industrialised area where a factory that produced paint materials and has been closed for many years, is deemed to be responsible for the pollutants coming into ground-water. Indeed in this area a lot of chemicals, many of them unknown, are dispersed into the soil, or stored in basins and tanks.

The purpose of this study was to investigate use of SPME for the GC–MS analysis of these compounds in ground-water samples coming from this area. SPME is an extraction technique that allows a fast, solvent-free and simple extraction of organic compounds [4–11]. It uses a coated fiber, within a

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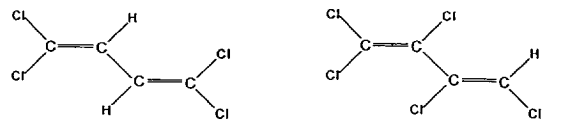
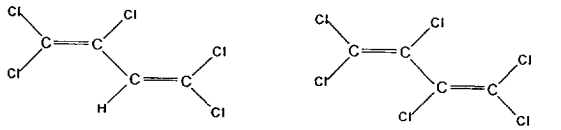


1,1,4,4-Tetrachloro-1,3-butadiene

cis-1,1,2,3,4-Pentachloro-1,3-butadiene



1,1,2,4,4-Pentachloro-1,3-butadiene

Hexachloro-1,3-butadiene

Fig. 1. Chemical formulae of polychlorobutadienes.

modified syringe, that is exposed directly to the sample, or in the headspace above the liquid or solid matrix, until equilibrium of the analytes absorbed to the coating phase and those in the sample matrix is reached. Analytes are then thermally desorbed into the injector of gas chromatograph, and subsequently analysed.

2. Experimental

2.1. Materials

TCBD, 1,1,2,4,4-PCBD and *cis*-1,1,2,3,4-PCBD were synthetised in the laboratories of the Institute of Physical Organic Chemistry, Minsk, Belarus, as these componds are not commercially available. Some of their physico-chemical characteristics are as follows: TCBD, purity 91%, b.p. 60°C at 1333 Pa, ^{1}H NMR ($CDCL_3$) δ: 6.60; 1,1,2,4,4-PCBD, purity 97%, b.p. 80°C at 1333 Pa, ^{1}H NMR ($CDCL_3$) δ: 6.7; *cis*-1,1,2,3,4-PCBD, purity 95%, b.p. 80°C at 1333 Pa, ^{1}H NMR ($CDCL_3$) δ: 6.52.

HCBD was obtained from Sigma-Aldrich, (St. Louis, MO, USA), while the internal standards (2,2,3,3-tetrachloro-hexafluoro-butane, 1,1,3,4-tetrachloro-hexafluoro-butane and 1,3,5-trichloro-2,4,6-trifluorobenzene) were from Fluorochem, (Derby, UK).

The SPME holders for manual sampling and the coating fibers were supplied by Supelco (Bellefonte, PA, USA). The modified syringe contains the coated fused-silica inserted and glued into a stainless steel tubing. During the extraction procedure, the fiber is withdrawn into the needle to penetrate the septum of the sample vial and then the plunger is pushed down and the fiber is exposed to the sample.

2.2. Instrumental analysis

The GC–MS analysis was carried out on a HP 5980 MSD 5971. The capillary column used was a CP Sil 8 (25 m × 0.25 mm I.D., with a 1.2-μm stationary phase), purchased from Chrompack (Middelburg, Netherlands). The injector was mantained at 200°C and the desorption time was 3 min. The temperature programme was: 60°C for 3 min, increasing by 12°C/min up to 200°C with a head pressure and a detector temperature of 40 kPa and 280°C, respectively. The GC–MS has been used in the selected ion monitoring (SIM) technique; for each compounds the selected masses (m/z) were: 190, 192 (TCBD); 189, 191 (1,1,2,4,4-PCBD and *cis*-1,1,2,3,4-PCBD); 225, 227 (HCBD); 234, 236 (1,3,5-trichloro-2,4,6-trifluorobenzene); 101, 103 (1,1,3,4-tetrachloro-1,2,2,3,4,4-hexafluorobutane); 151, 153 (2,2,3,3-tetrachloro-hexafluoro-butane).

3. Results

Fig. 2 shows the mass spectra of TCBD and 1,1,2,4,4-PCBD obtained in the electron ionization (EI) mode. The extracted ion chromatogram (Fig. 3) shows that each analyte is completely separated under these chromatographic conditions. We also tested negative ion chemical ionization on a Finnigan 4000 quadrupole mass spectrometer. The performance of the procedure was not improved compared to the EI mode, which was preferred. The negative ion mass spectra of the butadienes analysed (mass scan from 50 to 400 u) were as follows: m/z (relative abundance %): TCBD, 119 (100), 192 (33 - molecular ion); 1,1,2,4,4-PCBD, 71 (100), 190 (4); *cis*-1,1,2,3,4-PCBD, 71 (100), 190 (22); HCBD, 71 (100), 190 (7).

The polydimethylsiloxane fiber (PDMS), with a 100-μm thickness, was chosen after preliminary

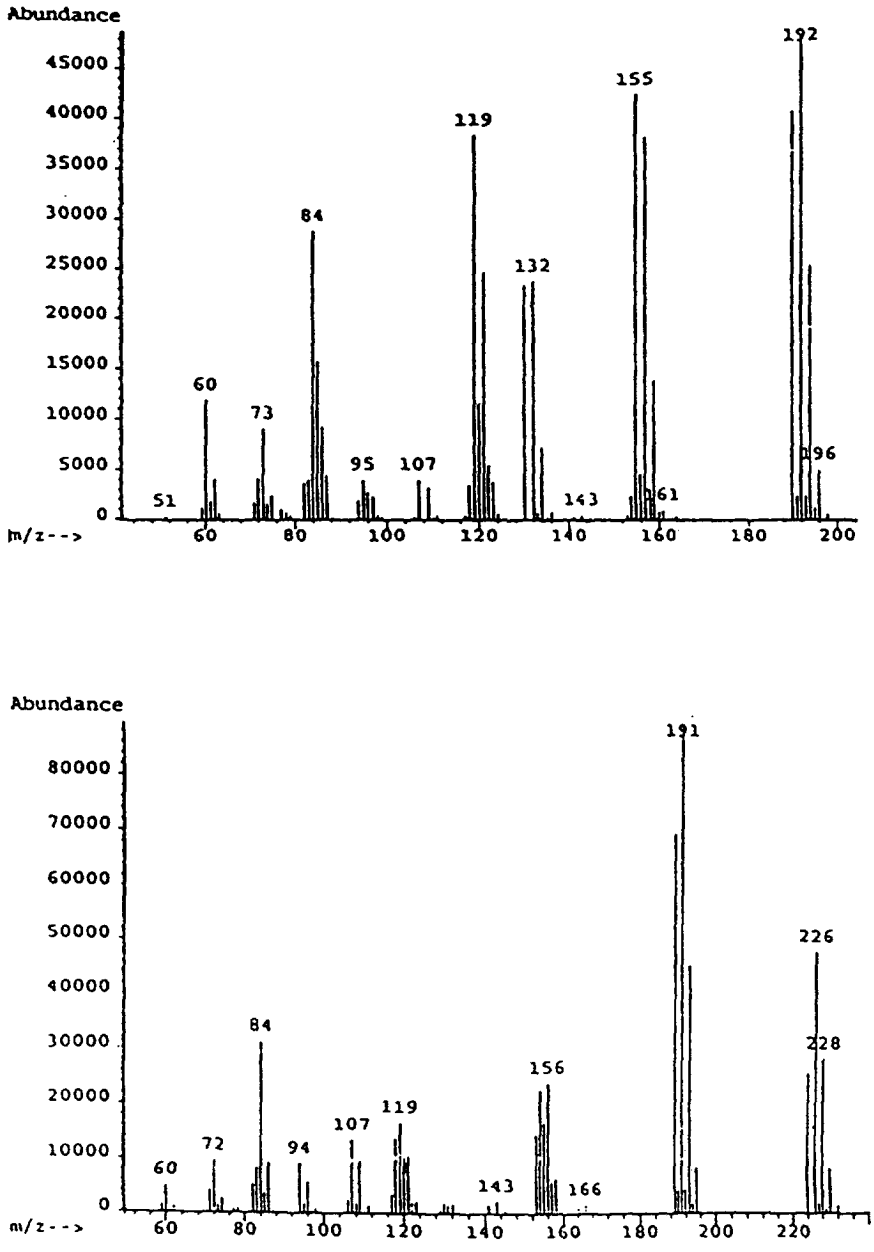


Fig. 2. Mass spectra of 1,1,4,4-TCBD (top) and 1,1,2,4,4-PCBD (bottom). The mass spectrum of *cis*-1,1,2,3,4-PCBD is identical to that of 1,1,2,4,4-PCBD.

tests concerning the sensitivity of different fibers of different thicknesses (PDMS 7 μm, polyacrylate 85 μm and carbon 80 μm) towards the analytes. In fact, PDMS is the most suitable fiber for non-polar compounds and the amount of the analytes extracted is directly proportional to the volume of the fiber, hence to the thickness. Nevertheless, thicker fibers need longer equilibration times.

To evaluate the extraction method, different parameters, such as absorption and desorption time profiles, linearity, sensitivity and reproducibility, were studied. In each test the sample volume was 2

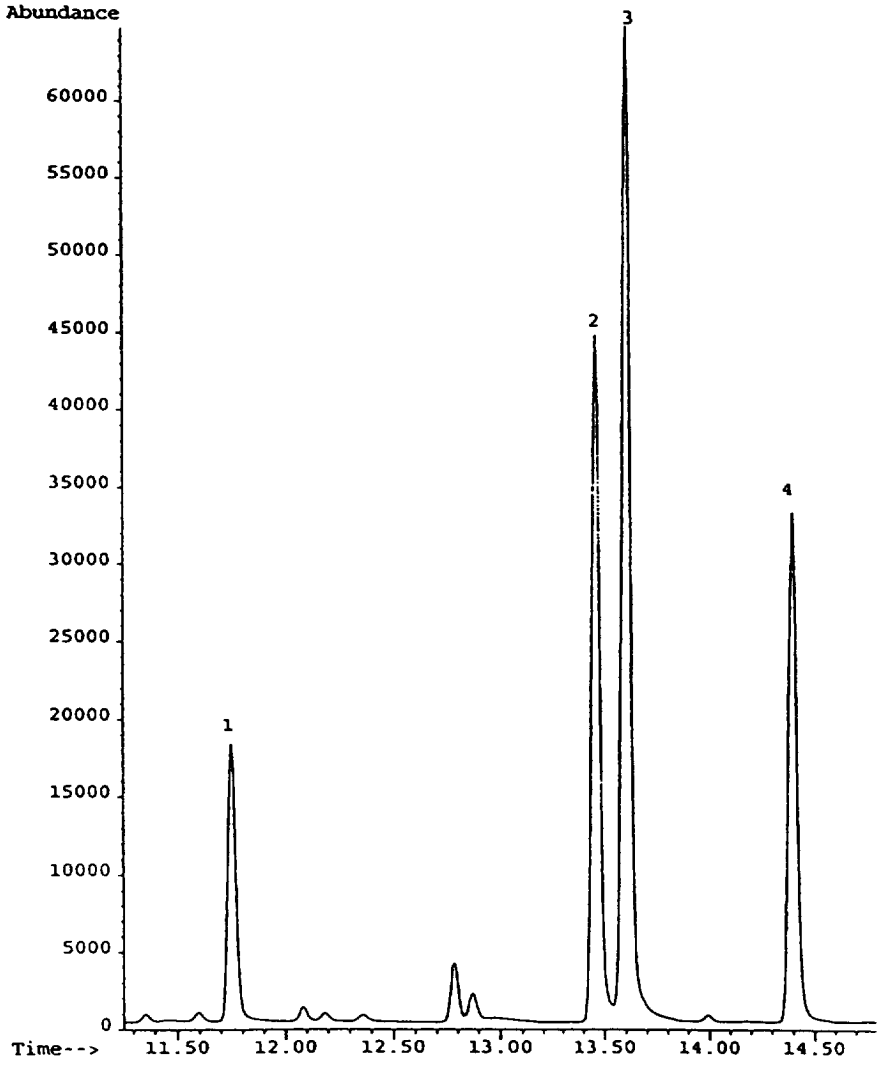


Fig. 3. Extracted ion chromatogram of a standard mixture of polychlorobutadienes: 1 = 1,1,4,4-TCBD; 2 = 1,1,2,4,4-PCBD; 3 = *cis*-1,1,2,3,4-PCBD; 4 = HCBD.

Table 1
Linearity, limit of detection and precision of the method

Compound	Coefficient of determination (r^2)		Limit of detection (μg/l)	Coefficient of variation (%) (n=4)	
	Without I.S.	With I.S.		With I.S.	Without I.S.
TCBD	0.996–1.000	0.999–1.000	0.05	5	12
1,1,2,4,4-PCBD	0.994–1.000	0.999–1.000	0.025	11	6
cis-1,1,2,3,4-PCBD	0.995–0.999	0.996–1.000	0.025	9	9
HCBD	0.996–1.000	0.999–1.000	0.05	19	6

ml, and during the extraction the sample was mixed using a stirring bar to shorten the extraction time. Different internal standards were tested. The best results were obtained with 1,3,5-trichloro-2,4,6-trifluorobenzene, whose chromatographic behaviour was most similar to the chromatographic behaviour of the analytes.

3.1. Absorption and desorption time profiles

The equilibration of the analytes between the aqueous phase and PDMS is time-dependent. For this test, a solution containing 10 μg/l of each compound was prepared and divided between four vials. By monitoring the area counts as a function of exposure time (Fig. 4), we concluded that the equilibrium was not reached after 60 min. It is not necessary to reach a complete equilibrium, however, if this condition is not verified, the exposure time must be exactly constant [4].

Desorption time was investigated between 3 and 10 min, by leaving the fiber in the injector for progressively longer periods of time and keeping the temperature of the injector at 200°C. After 3 min the analytes were fully desorbed and no memory effect was observed.

3.2. Precision and detection limit

Precision was tested under different conditions, keeping the temperature and time of extraction exactly constant. At room temperature, the reproducibility expressed as coefficient of variation (C.V.) of the fiber was between 6 and 12%. No improvement was observed using an internal standard (Table 1).

The limit of detection (LOD) was evaluated using a signal to noise ratio of about 3, and maintaining the extraction for 30 min (Table 1).

3.3. Linearity

Linearity (Fig. 5) was investigated at a range of concentrations (0.1–200 μg/l) for each compound. 1,3,5-trichloro-2,4,6-trifluorobenzene was used as the internal standard. The determination coefficient (r^2) varied between 0.997 and 1.000 (Table 1). In this

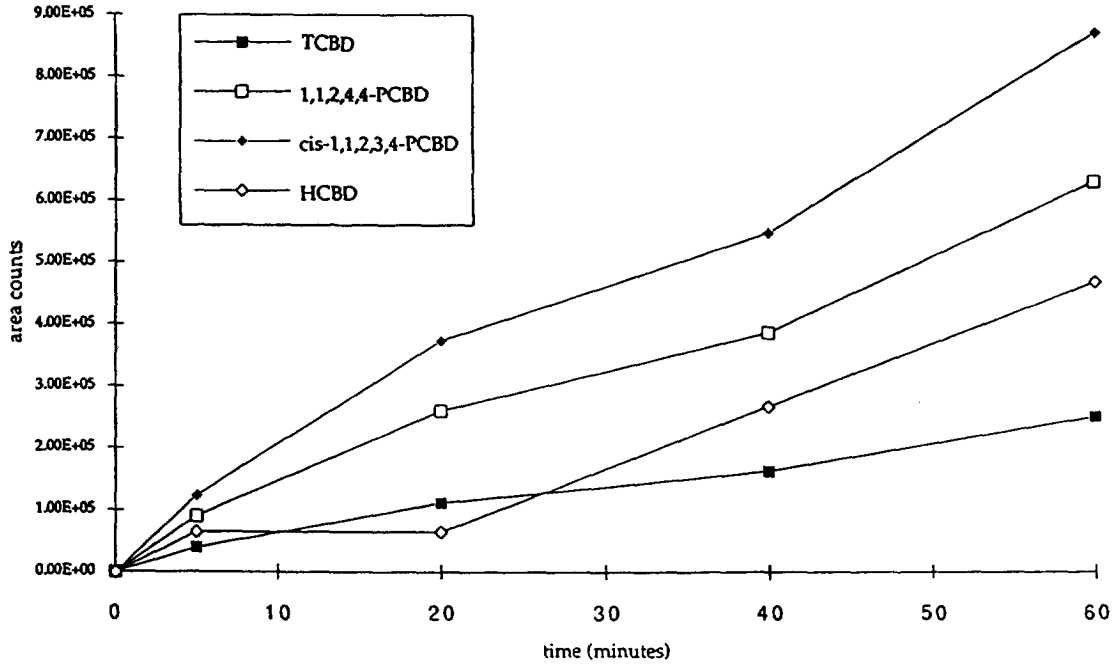


Fig. 4. Absorption–time profiles.

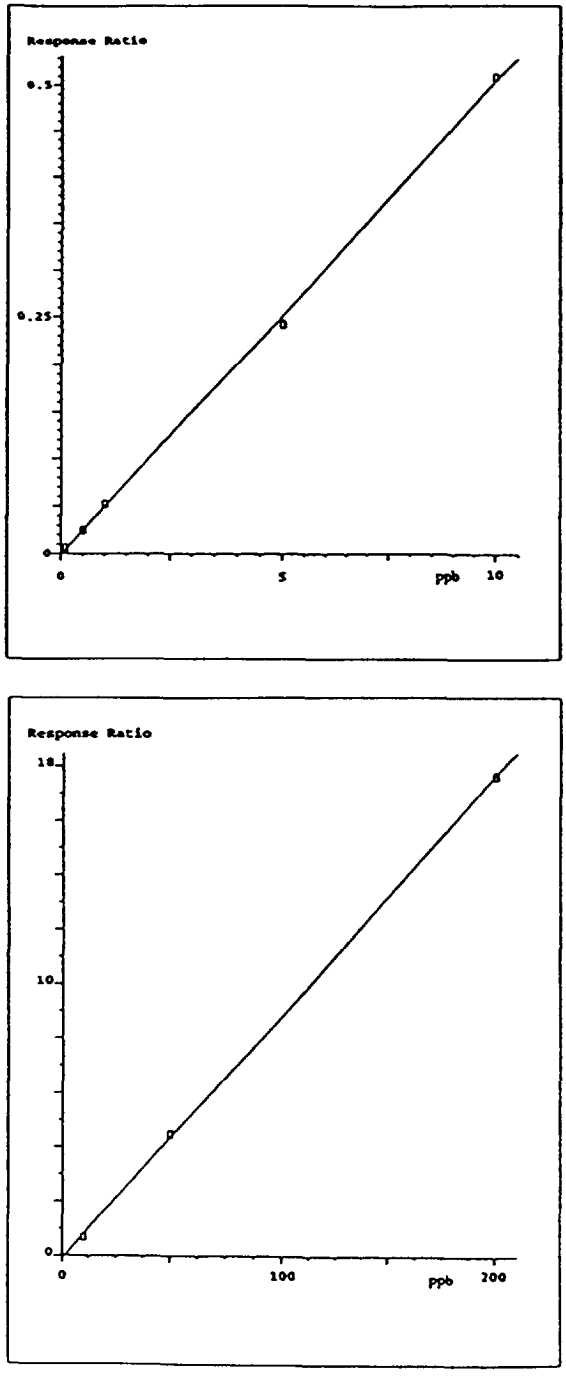


Fig. 5. Calibration curves of TCBD: linearity range, 0.1–10 ppb; r^2 = 0.999; linearity range, 10–200 ppb: r^2 = 1.000.

case also, there was no real improvement with the internal standard.

3.4. Real samples analysis

Ground-water samples coming from the investigated area described above were analysed in preliminary tests to identify the chlorinated-1,3-butadienes according to their retention times and mass spectra, recorded in the full scan mode. Afterwards the samples were analysed using SPME and the SIM technique applying the same instrumental conditions described in Section 2, except for the temperature chromatographic programme which was slightly faster. Fig. 6 shows the extracted ions chromatogram of raw ground-water (before treatment for potabilization) coming from a well affected by this kind of contamination. Concentrations of TCBD, 1,1,2,4,4-PCBD, *cis*-1,1,2,3,4-PCBD and HCBD were about 28, 1, 4 and 4 μg/l, respectively. Besides the chromatographic peaks related to these compounds, others peaks are present in the chromatogram, corresponding to unidentified isomers of TCBD, and an unidentified isomer of PCBD, according to their mass spectra. We did not quantify these compounds because their standards were not available.

4. Conclusion

SPME represents a good technique for the analysis of these compounds. Using the PDMS-coated fiber, quite good sensitivity and precision can be reached. Moreover, linearity was verified over a large range. The use of the internal standards tested did not improve the technique. This could be due to the difficulties in finding compounds with the same affinity to the fiber. A real improvement of the technique probably could be obtained using labelled compounds as the internal standards.

Acknowledgments

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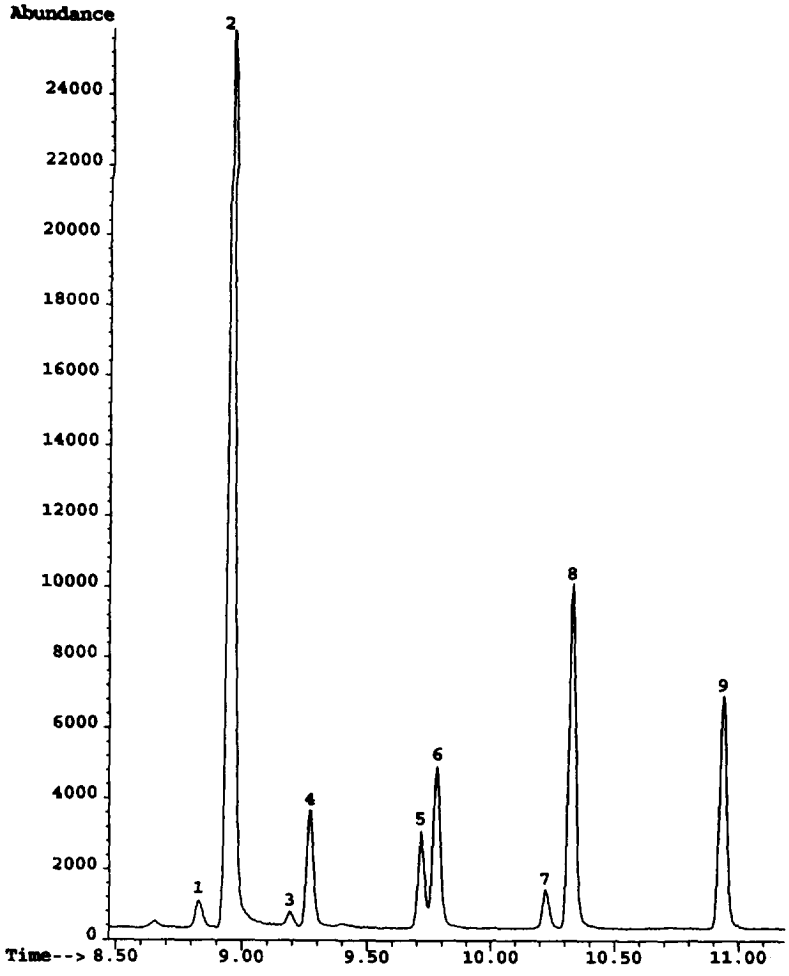

Fig. 6. Extracted ion chromatogram of a real sample of ground-water: 1, 3, 4, 5 = unidentified isomers of TCBD; 2 = TCBD; 6 = unidentified isomer of PCBD; 7 = 1,1,2,4,4-PCBD; 8 = *cis*-1,1,2,3,4-PCBD; 9 = HCBD.

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