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Strategies for the analysis of chlorobenzenes in soils using solid-phase microextraction coupled with gas chromatography–ion trap mass spectrometry.

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Abstract

Solid-phase microextraction (SPME) was examined as a possible alternative to Soxhlet extraction in the analysis of chlorobenzenes at high concentrations (up to 65 $\mu g\,g^{-1}$) in soils. Gas chromatography–ion trap mass spectrometry (GC–IT-MS) was used and different strategies were tested in order to obtain suitable responses for chlorobenzenes. Two headspace SPME methods, using fibres coated with polydimethylsiloxane (PDMS) as stationary phase, in splitless and split injection modes, respectively, and a direct SPME method using 100-μm PDMS fibre were studied. For headspace SPME, 7-μm and 100-μm PDMS fibres were used and good sensitivity was obtained by adding 200 μl of water to the soil, at a sampling temperature of 30°C and absorption times of 40 and 60 min, respectively. For direct SPME, which involves extraction of chlorobenzenes from stirred soil solutions using a 100-μm PDMS fibre, the effect of the addition of different organic solvents, such as methanol or acetone, on the sensitivity and the extraction time was evaluated. The shortest time to reach equilibrium (50 min) was achieved when a mixture acetone–water (30:70) was added to the sample. Repeatabilities lower than 8% were obtained for headspace and direct SPME with 100-μm PDMS fibre, whereas for 7-μm PDMS fibre, repeatabilities were slightly higher (between 7 and 11%). The SPME methods were applied to the analysis of chlorobenzenes in an industrially contaminated clay soil, CRM-530, which is a candidate reference material. Chlorobenzenes in this soil were quantified by standard addition, which led to good reproducibility (R.S.D. between 2 and 10%) for headspace and direct SPME with the 100-μm PDMS fibre and acceptable detection limits (30 to 100 $pg\,g^{-1}$ of soil). The results were consistent with those obtained in a European intercomparison exercise.

Keywords: Soil; Solid-phase extraction; Environmental analysis; Headspace analysis; Sample handling; Chlorobenzenes

1. Introduction

Chlorobenzenes are used in large quantities as industrial solvents, pesticides, dielectric fluids, deodorants and chemical intermediates. This wide usage of chlorobenzenes has resulted in contamination of the environment, where these compounds tend to persist [1], so they are prevalent in water [2], soils [3,4], sediments [5,6], sewage sludges [7,8] and aquatic biota [9]. Chlorobenzenes have been included as priority pollutants in the United States Environmental Protection Agency (US EPA) and the European Union (EU) lists. In particular, hexachlorobenzene, used as wood preservative and fungicide in agriculture, is widely distributed as an environmental and food contaminant, and it is known to be a human carcinogen [10]. Most of the methods used for the analysis of chlorobenzenes in solid

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matrices, e.g. soils, sediments and sludges, are based on classical technologies, such as the common Soxhlet or sonication extraction methods [11]. These traditional sample extraction methods use large quantities of toxic organic solvents and multi-step procedures, which may cause loss of volatile compounds, and are typically time consuming,

Solid-phase microextraction (SPME) developed by Pawliszyn and co-workers [12–16] is a new and practical solvent-free alternative for the extraction of organic compounds from solid samples. SPME can integrate sampling, extraction, concentration and sample introduction in a single step and is a fast, inexpensive and easily automated technique. SPME uses coated fused-silica fibres to extract analytes from gaseous and liquid phases. After equilibrium is reached or after a well-defined extraction time, the absorbed compounds are thermally desorbed by exposing the fibre in the injection port of a gas chromatograph, or redissolved in an organic solvent if coupled to HPLC [16].

SPME has been mainly applied to the analysis of organic compounds in aqueous samples; for analysing volatile and semivolatile compounds in solid samples, such as soils, sediments and sludges, headspace SPME has often been used [14]. So far, headspace SPME has been used to determine aromatic and polyaromatic hydrocarbons (PAHs) in spiked sand and clay matrices [17,18]; volatile organic compounds in landfill soils [19]; organometallic compounds in sediments [20] and chloro- and nitrobenzenes and chloro- and nitroanilines in a broad variety of soils [21,22]. Generally, the sensitivity of the headspace SPME procedure can be improved by manipulation of the matrix (e.g. water addition) or by optimization of the extraction conditions (e.g. fibre coating material, temperature, stirring and extraction time). For instance, the effect of high temperatures and water addition has been reported to be of major importance for the analysis of low-volatile analytes, such as PAHs in soils [17].

In the literature different procedures have been described for quantitative analysis of solid samples, such as soils, sediments and sludges, by headspace SPME. For instance, Moens et al. [20] obtained good results for the analysis of organometallic compounds in a reference sediment material using spiked water solutions for calibration. Nevertheless, matrix effects due to soil characteristics, especially the organic carbon and the clay content, which can strongly adsorb the analytes, can affect the quantitative analysis of solid samples [21]. Therefore, calibration has frequently been performed by standard addition within the linear range of both the headspace SPME procedure and the detector [19,21,22]. In a previous paper, the reliability of headspace SPME for the analysis of chlorobenzenes in a sandy soil by standard addition was evaluated [22].

Although headspace SPME allows the extraction of analytes from polluted matrices, avoiding contact with the sample, direct SPME has also been used to analyse pesticides, alkylbenzenes, aromatic amines and PAHs in soils [23–26], organometallic compounds in sediments [27] and alkylphenol ethoxylate surfactants in sludges [28]. The analysis by direct SPME is performed by immersion of the fibre in solid solution [24,27,28] or in the aqueous extract of the solid [23,25,26]. Generally, quantification is performed using external calibration and spiked aqueous solutions, assuming that the matrix does not significantly interfere with the extraction. However, Boyd-Boland and Pawliszyn [28] reported that the matrix interferes with the analysis of alkylphenols in sewage sludges, and suggested that the use of the standard addition method would overcome this problem. Nevertheless, quantitation of analytes in soil samples by standard addition and direct SPME has not been frequently reported.

In this paper, SPME–GC–ion trap (IT)-MS was applied to the analysis of soil samples containing high concentrations of chlorobenzenes (up to 65 $\mu g\ g^{-1}$). Different strategies, such as headspace and direct SPME using polydimethylsiloxane fibres (7-μm and 100-μm), were tested to adjust the high concentrations in the soil to the linear dynamic range of the ion trap detector by reducing the amount of compound absorbed in the fibre or injected in the GC system. After optimization of the extraction conditions, the methods were applied to the analysis of chlorobenzenes in a candidate reference material, CRM-530. Finally, the SPME methods were evaluated by comparing the results with those obtained in a European intercomparison exercise organised by the Community Bureau of Reference (BCR).

2. Experimental

2.1. Standards and reagents

The semivolatile organic compounds studied in this work were obtained at a purity higher than 98% from the following sources: 1,3,5-trichlorobenzene, 1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenzene and pentachlorobenzene from Merck (Darmstadt, Germany); 1,2,3,5-tetrachlorobenzene and 1,2,4,5-tetrachlorobenzene from Riedel-de Haën (Seelze, Germany); 1,2,4-trichlorobenzene from Carlo Erba (Milan, Italy) and 1,3,5-tribromobenzene, used as internal standard, from Fluka (Buchs, Switzerland). The solvents acetone, *n*-hexane and methanol, of residue analysis grade, were supplied by Merck.

For headspace and direct SPME studies, individual stock standard solutions of each compound between 500 and 20 000 mg l^{-1} were prepared in acetone. A secondary standard mixture was prepared by dilution in acetone of the primary standard solutions to give concentrations between 20 and 4000 mg l^{-1}. For quantification, acetone–water (HPLC grade) (2.5:7.5) standard solutions, which contained all the compounds at concentrations between 0.16 μg l^{-1} and 95 μg l^{-1}, were prepared from the secondary standard solution.

2.2. Chromatographic conditions

Gas chromatography was carried out with a Varian 3400 CX GC capillary gas chromatograph coupled with a Saturn 3 GC–MS ion trap mass spectrometer (Sugar Land, TX, USA). A DB-5 MS (5% phenyl-, 95% methylpolysiloxane) fused-silica capillary column (30 m×0.25 mm I.D.) (J and W Scientific, Folsom, CA, USA) with 0.25 μm film thickness was used with helium as carrier gas at a linear velocity of 31 cm s^{-1}. The temperature was held isothermally at 50°C for 1 min, raised to 90°C at 20°C min^{-1}, then to 150°C at 3°C min^{-1} and finally to 280°C at 25°C min^{-1}, which was held for 5 min. For studies with 7-μm polydimethylsiloxane (PDMS) fibre, the injector was maintained at 280°C and splitless injection mode was used, whereas in the case of 100-μm polydimethylsiloxane (100-μm PDMS), the temperature was 250°C in both split and splitless mode.

The ion trap mass spectrometer was operated in the electron impact ionization (EI) positive mode using automatic gain control (AGC). The electron multiplier, emission current and modulation amplitude were set at 1650 V, 25 μA and 2.5 V, respectively, using perfluorotributylamine (FC-43) as reference. The transfer line and the ion trap manifold were set to 280°C and 220°C, respectively. The mass range was from m/z 60 to m/z 400 at 0.8 s/scan. For quantification, the two most abundant ions of the molecular cluster of each chlorobenzene were selected (m/z 180/182 for trichlorobenzenes, m/z 214/216 for tetrachlorobenzenes and m/z 248/250 for pentachlorobenzene). Saturn version 5.2 software was used for data acquisition. Linear dynamic ranges of the GC–IT-MS system were determined by conventional injection of standard mixtures of the seven chlorobenzenes at concentrations between 20 ng ml^{-1} and 80 μg ml^{-1} for each compound in *n*-hexane using 1,3,5-tribromobenzene as internal standard.

2.3. Solid-phase microextraction procedure

SPME was performed with commercially available 100-μm and 7-μm film thickness PDMS fibres housed in its manual holder (Supelco, Bellefonte, PA, USA).

Two sampling techniques were investigated. One technique involved headspace above a soil slurry using 100-μm and 7-μm fibres. In the other technique, a 100-μm PDMS fibre was immersed in a soil solution. Before use, PDMS fibres of 7-μm and 100-μm were conditioned for 2 h in the GC injector port at 320°C and 250°C, respectively. Possible carryover of unknown compounds was removed by keeping the fibre in the injector for an additional time with the injector in the split mode (purge on). Moreover, blanks were run periodically during the analysis to confirm the absence of contaminants.

In the preliminary study, a headspace SPME method described elsewhere was used [22]. Briefly 200 μl of water was added to 0.1 g of soil placed in 40 ml screw-cap glass vials with silicone–PTFE septa and a 100-μm PDMS fibre was exposed to the

headspace above the soil slurry. An exposure time of 25 min, a desorption time of 1 min (splitless injection) and an extraction temperature of 30°C were used. Several parameters were consecutively modified, such as the the soil amount (from 0.1 to 0.03 g), the water added to the soil (up to 1 ml) and the extraction temperature (50°C).

For the subsequent headspace experiments, 200 μl of water were added to the soil (0.03 to 0.1 g) placed in 40 ml screw-cap glass vials with silicone–PTFE septa and extracted at 30°C with a 100-μm PDMS fibre and split injection mode (split ratio of 1:35). For headspace with 7-μm fibre, the soil was extracted at the same conditions, but using splitless injection mode. In both cases, the vial was placed in a thermostatic water bath and after 10 min the needle was introduced in the vial and plunged into the headspace above the slurry. After setting a well-defined absorption time, the fibre was again withdrawn into the needle and the syringe was removed from the vial and introduced into the injection port of the gas chromatograph for 1 min at 250°C (100-μm PDMS) and 280°C (7-μm PDMS).

The direct SPME experiments were performed by immersing the 100-μm PDMS fibre in a soil solution of 0.03 g of soil mixed with the desired amount of water (between 30 and 45 ml) continuously agitated with a 3 mm-diameter×8 mm-long stirring bar and a magnetic stirplate at stirring speed of 1000 rpm and extracted for 25 min at 30°C. The vial was placed in a thermostatic water bath as for headspace SPME experiments and the needle was plunged directly into the aqueous soil solutions. Finally, and after the extraction process, the fibre was desorbed in the injection port of the gas chromatograph for 1 min at 250°C in splitless injection mode. To decrease the signal, the effect of organic solvents on extraction sensitivity was studied by preparing a series of soil solutions that contained methanol–water or acetone–water mixtures at percentages of organic solvent from 0% (v/v) to 30% (v/v). In both cases, the absorption time profiles were determined between 1 and 70 min at percentages of solvent that gave adequate responses for all compounds.

To calculate the detection limits of the method, 0.1 g of soil and 200 μl of water, extraction temperature and absorption time, 30°C and 25 min, respectively, headspace SPME with 100-μm PDMS fibre and splitless injection mode were used [22]. For this purpose, an agricultural soil without detectable quantities of chlorobenzenes was spiked overnight with 200 μl of chlorobenzene standard solutions and the compounds were then extracted.

2.4. Soil analysis

The sample used in this study was an industrial clay soil, CRM-530, candidate reference material, supplied by the Measurement and Testing Programme (M&T-BCR) of the Union of the European Communities (Brussels). This soil contained tri-, tetra- and pentachlorobenzenes, with concentrations for 1,2,4-trichlorobenzene and 1,2,3,4-tetrachlorobenzene higher than 65 and 20 $\mu g\,g^{-1}$ respectively, and also chlorophenols (concentrations between 0.4 and 85 $\mu g\,g^{-1}$), hexachlorocyclohexanes (HCH up to 2 $mg\,g^{-1}$), chlorinated dibenzo−*p*-dioxins and dibenzofurans (from 5 to 5000 $\mu g\,g^{-1}$) as possible interferences. Duplicate analyses of four samples of soil were carried out by standard addition, spiking the samples at different concentration levels 0, 30, 60 and 90% of the concentration in the soil sample. After spiking the soil with 30 μl of chlorobenzene standard solutions, the sample was equilibrated overnight at 4°C and then extracted at the optimized conditions for each procedure.

3. Results and discussion

3.1. SPME optimization.

In the preliminary study using headspace SPME, an overloading of the signal on the ion trap detector was observed due to the high concentration of some chlorobenzenes in the clay soil CRM-530 (up to 65 $\mu g\,g^{-1}$). In order to decrease the signal, the amount of soil and the water added were optimized. In addition the effect of increasing temperature which can adversely affect the absorption of analytes through the coating [29] was also studied. Although the soil mass was reduced to 0.03 g, and the water volume added to the soil and the extraction temperature were increased up to 1 ml and 50°C, respectively, peak areas, especially for 1,2,4-trichlorobenzene

and 1,2,3,4-tetrachlorobenzene, were higher than the upper limit of the linear dynamic range of the ion trap detector. Furthermore, the variability obtained in the responses of the most volatile compounds was between 8 and 15% at 50°C, whereas it was lower than 4% at 30°C. Subsequent studies were thus performed at 30°C.

In order to obtain appropriate responses, different strategies for the analysis of chlorobenzenes in the CRM-530 soil were studied in an attempt to reduce the amount of compound absorbed in the fibre or the amount introduced in the GC. Two headspace SPME methods using 7-μm PDMS and 100-μm PDMS fibres with splitless and split injection modes, respectively, were used. In addition, direct SPME of aqueous soil solutions was also studied.

In headspace SPME procedures, the amount of sample, the exposure time of the PDMS fibres in the headspace and the desorption time in the GC injection port were optimized. The weight of soil to be extracted was determined taking into account the linear dynamic range of the ion trap detector. For headspace SPME with 7-μm PDMS and splitless injection mode, 0.03 g of soil was adequate, whereas for headspace SPME with 100-μm PDMS fibre and split injection mode with a split ratio of 1:35, a mass of 0.045 g gave good responses for all compounds.

The time required to reach the equilibrium between the fibre stationary phase and the soil sample at 30°C was determined. As an example, Fig. 1 shows the absorption time profiles for four chlorobenzenes using a 100-μm PDMS fibre. Different responses were found for the compounds, according to volatilities, distribution constants and the concentration of each compound in the soil. The equilibration time for chlorobenzenes was 40 min, except for pentachlorobenzene, which required 60 min to reach equilibrium. Using a 7-μm fibre, 40 min were enough to achieve equilibrium for all compounds.

Desorption time was also studied and as an example, the desorption time profiles for four chlorobenzenes in optimum extraction conditions for the 7-μm PDMS fibre are shown in Fig. 2. As can be seen, quantitative desorption was achieved in less than 1 min.

The first direct SPME experiments with 0.03 g of soil and 30 ml of water gave responses for 1,2,4-

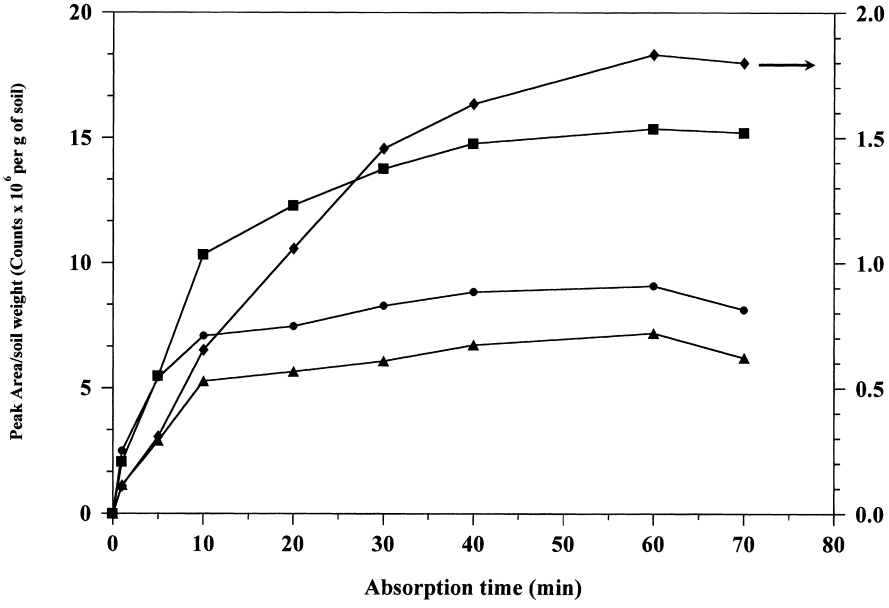

Fig. 1. Absorption time profiles for ● 1,2,3-trichlorobenzene, ■ 1,2,3,4-tetrachlorobenzene, ▲ 1,2,4,5-tetrachlorobenzene and ♦ pentachlorobenzene in CRM-530 soil by headspace SPME–GC–IT-MS using a 100-μm PDMS fibre [0.045 g of soil; 200 μl of water; sampling temperature 30°C; split injection mode (ratio 1:35)]. For pentachlorobenzene the scale is shown on the right.

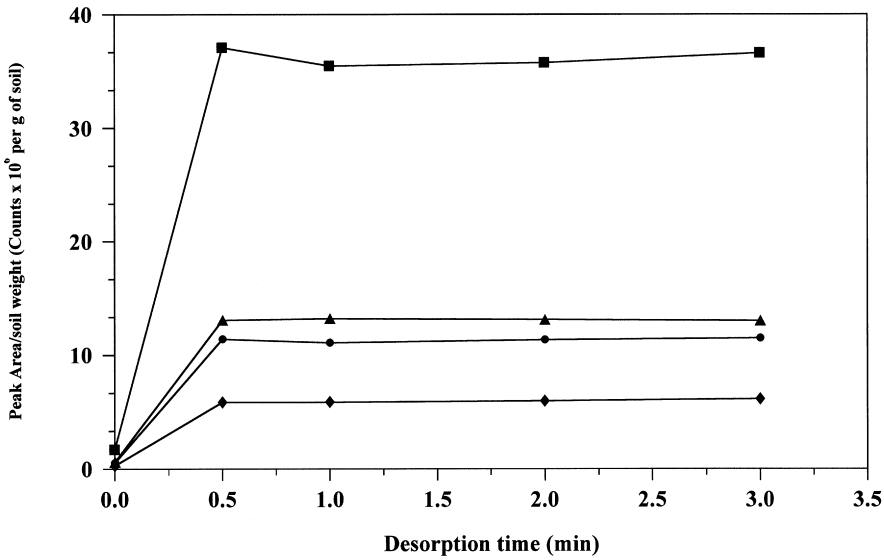

Fig. 2. Desorption time profiles for ● 1,2,3-trichlorobenzene, ■ 1,2,3,4-tetrachlorobenzene, ▲ 1,2,4,5-tetrachlorobenzene and ♦ pentachlorobenzene by headspace SPME–GC–IT-MS using a 7-μm PDMS fibre (0.030 g of CRM-530 soil; 200 μl of water; sampling temperature 30°C; exposure time 40 min; splitless injection mode).

trichlorobenzene and 1,2,3,4-tetrachlorobenzene beyond the upper limit of the linear dynamic range of the detector. Water addition up to 40 ml allowed the decrease of the signals for all the compounds, except 1,2,4-trichlorobenzene, which was present at very high concentration in the sample (>65 μg g^{-1}). In an attempt to decrease the signal, the effect of the addition of organic solvents to the aqueous soil solution was studied [12]. An example of the effect of the addition of methanol on the absorption time profiles for some chlorobenzenes using the 100-μm PDMS fibre is shown in Fig. 3. The SPME absorptivity of the compounds decreased when methanol was present at percentages greater than 5%. At 10% methanol, responses for all compounds were low enough to be in the linear dynamic range of the detector, but equilibrium was not reached in 70 min, as can be seen in Fig. 4A where absorption time profiles for pentachlorobenzene are given. To decrease the extraction time, higher amounts of methanol were tested, but using 30% methanol, no equilibrium was reached for the tetrachlorobenzenes or pentachlorobenzene. So, the effect of adding another solvent of higher elutropic strength, such as acetone, was evaluated and good results were obtained when the soil solution contained 30% acetone. Under these conditions, the equilibrium was achieved in 30 min for trichlorobenzenes, 45 min for tetrachlorobenzenes and 50 min for pentachlorobenzene (Fig. 4B).

3.2. Quality parameters

Linear dynamic ranges of the GC–IT-MS system were established from the fitted curves of each chlorobenzene obtained by plotting relative areas per amount of compound $[(A_i/A_{IS})/\text{pg injected}]$ versus relative mass (m_i/m_{IS}), and were from 100 to 30 000 pg injected for all the compounds. Detection limits, defined as the concentration of the analytes in the sample that produces a peak with a signal-to-noise ratio (S/N) of 3, and calculated, as has been described in the experimental section, using an agricultural soil without detectable quantities of chlorobenzenes, are given in Table 1 and ranged from 30 pg g^{-1} for 1,2,3-trichlorobenzene to 100 pg g^{-1} for pentachlorobenzene.

To determine repeatability of the proposed SPME–GC–IT-MS procedures, five replicates of the soil sample were consecutively analyzed using the PDMS fibres at the optimized conditions. In Table 1 are listed the mean and the relative standard deviations (R.S.D., %) of the peak areas/soil mass

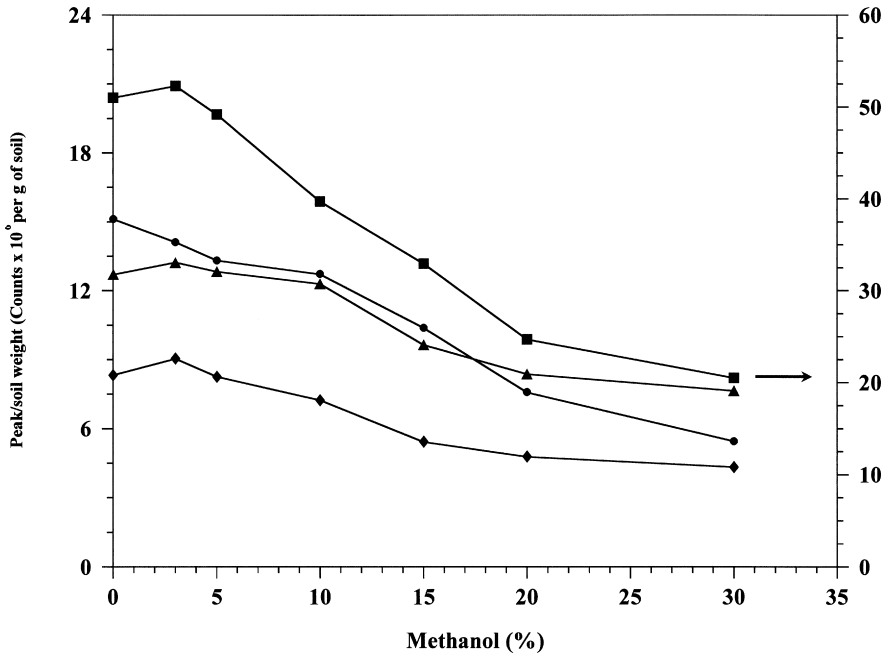

Fig. 3. Effect of methanol on absorption of ● 1,2,3-trichlorobenzene, ■ 1,2,3,4-tetrachlorobenzene, ▲ 1,2,4,5-tetrachlorobenzene and ♦ pentachlorobenzene by direct SPME–GC–IT-MS with a 100-μm PDMS fibre (0.030 g of CRM-530 soil; 40 ml of water–organic solvent; stirring-speed 1000 rpm.; sampling temperature 30°C; exposure time 25 min; splitless injection mode). For 1,2,3,4-tetrachlorobenzene the scale is shown on the right.

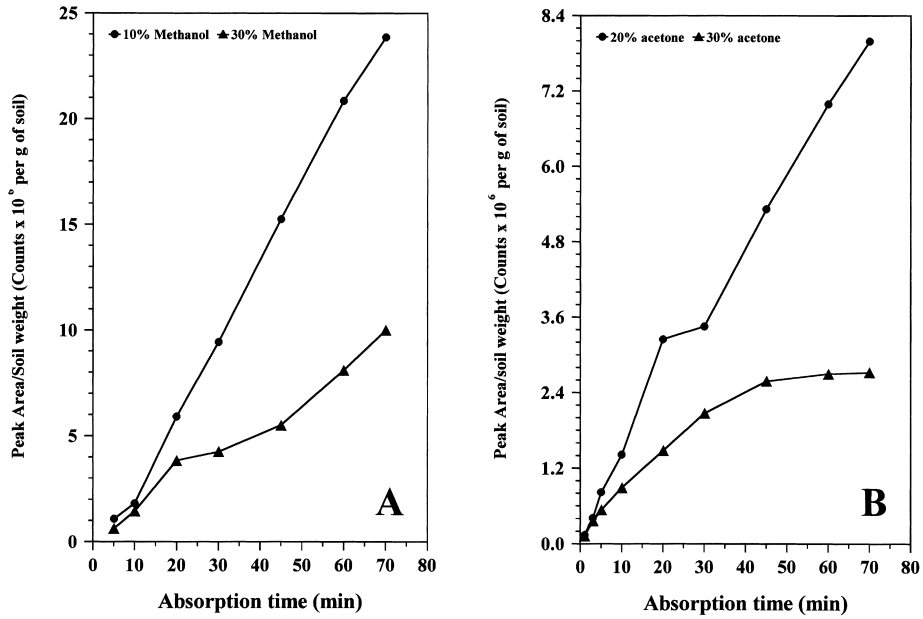

Fig. 4. Effect of (A) methanol and (B) acetone on the absorption time profile of pentachlorobenzene by direct SPME–GC–IT-MS using a 100-μm PDMS fibre. Conditions as in Fig. 3.

Table 1
Detection limits and repeatability of the proposed SPME procedures ($n=5$)

Compound	Headspace SPME 100-μm PDMS fibre[a]:	Headspace SPME 7-μm PDMS fibre[a]		Headspace SPME 100-μm PDMS fibre[b]		Direct SPME 100-μm PDMS fibre[c]	
	L.O.D[d] (pg g^{-1})	Mean[e] (counts g^{-1})	R.S.D. (%)	Mean[e] (counts g^{-1})	R.S.D. (%)	Mean[e] (counts g^{-1})	R.S.D. (%)
1,3,5-Trichlorobenzene	55	1.3×10^{5}	10	6.6×10^{4}	8	4.8×10^{4}	8
1,2,4-Trichlorobenzene	46	5.7×10^{7}	8	4.3×10^{7}	8	9.7×10^{6}	6
1,2,3-Trichlorobenzene	30	1.1×10^{7}	8	8.3×10^{6}	5	1.2×10^{6}	7
1,2,3,5-Tetrachlorobenzene	36	5.8×10^{6}	11	2.7×10^{6}	4	1.2×10^{6}	5
1,2,4,5-Tetrachlorobenzene	51	1.3×10^{7}	10	6.7×10^{6}	5	3.2×10^{6}	6
1,2,3,4-Tetrachlorobenzene	40	3.5×10^{7}	7	1.6×10^{7}	4	6.1×10^{6}	5
Pentachlorobenzene	100	5.8×10^{6}	8	1.7×10^{6}	2	2.0×10^{6}	5

[a] 200 μl of water added, splitless injection mode.
[b] 200 μl of water added, split injection mode.
[c] 40 ml of water–acetone (70:30) added, splitless injection mode.
[d] LOD=Limit of detection.
[e] Peak area/soil mass.

obtained sampling the analytes by headspace SPME and direct SPME. Generally, standard deviations lower than 8% for all the compounds and with non significant differences for both headspace SPME and direct SPME using 100-μm PDMS fibre (confirmed with *F*-test at the 95% confidence level), were obtained. For headspace SPME with the thinner fibre, 7-μm PDMS, significantly higher relative standard deviations were obtained.

3.3. Analysis of CRM-530 soil

Both, headspace SPME and direct SPME procedures were used to determine seven chlorobenzenes in the clay soil, CRM-530. GC–IT-MS total-ion chromatograms obtained by headspace SPME with split injection and by direct SPME with splitless injection (100-μm PDMS fibre), as well as the single-ion chromatograms selected for chlorobenzenes are given in Figs. 5 and 6. As can be seen, headspace and direct SPME–GC–IT-MS are highly selective procedures for the analysis of chlorobenzenes in contaminated soils, showing no interferences from other compounds potentially present in the sample matrix. However, the chromatograms obtained using headspace (Fig. 5) were cleaner than those obtained using direct SPME (Fig. 6).

The results obtained in the SPME analysis of CRM-530 soil with the three strategies proposed are given in Table 2, where the mean values and the standard deviation (S.D.) of 1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenzene and pentachlorobenzene in soil CRM-530 obtained in the certification exercise are also given. The results with both headspace and direct SPME agreed with the mean values reported by the European laboratories, most of whom used Soxhlet extraction. The analytical significance of the mean values of the SPME strategies was statistically studied using a *t*-test. In case of obtaining unequal variances (*F*-test), the Cochran's test was applied. The significance values (*P*) obtained comparing the three procedures are given in Table 2. Generally, no significative differences were observed when comparing the methods, except for 1,3,5-trichlorobenzene and 1,2,4,5-tetrachlorobenzene ($P<0.05$). Moreover, the results obtained using the *F*-test (at the 95% confidence level) showed no significant differences in the standard deviations between headspace SPME with 100-μm PDMS fibre (split injection) and direct SPME. For headspace SPME with 7-μm PDMS fibre procedure, significantly higher standard deviations (between 18% and 24%) were observed, except for pentachlorobenzene. Headspace SPME showed some advantages over direct SPME, such as the longer durability of the fibres, because direct contact between the fibre and polluted samples was avoided. Furthermore, the presence of a high concentration of organic solvent in the soil solution

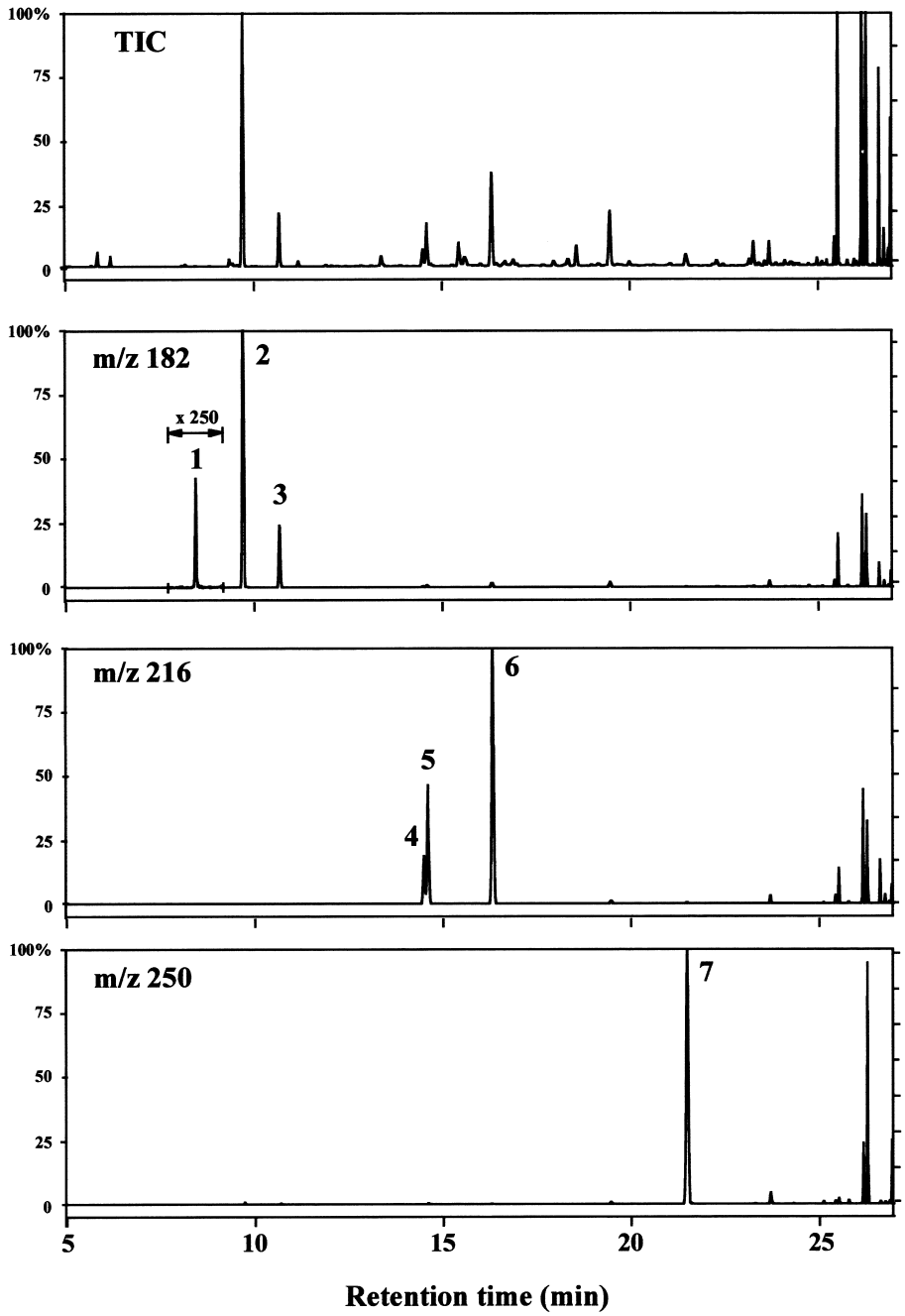

Fig. 5. Headspace SPME–GC–IT-MS total-ion chromatogram and single-ion chromatograms of chlorobenzenes from CRM-530 soil with 100-μm PDMS fibre and split injection. Peaks: 1=1,3,5-trichlorobenzene; 2=1,2,4-trichlorobenzene; 3=1,2,3-trichlorobenzene; 4=1,2,3,5-tetrachlorobenzene; 5=1,2,4,5-tetrachlorobenzene; 6=1,2,3,4-tetrachlorobenzene; 7=pentachlorobenzene.

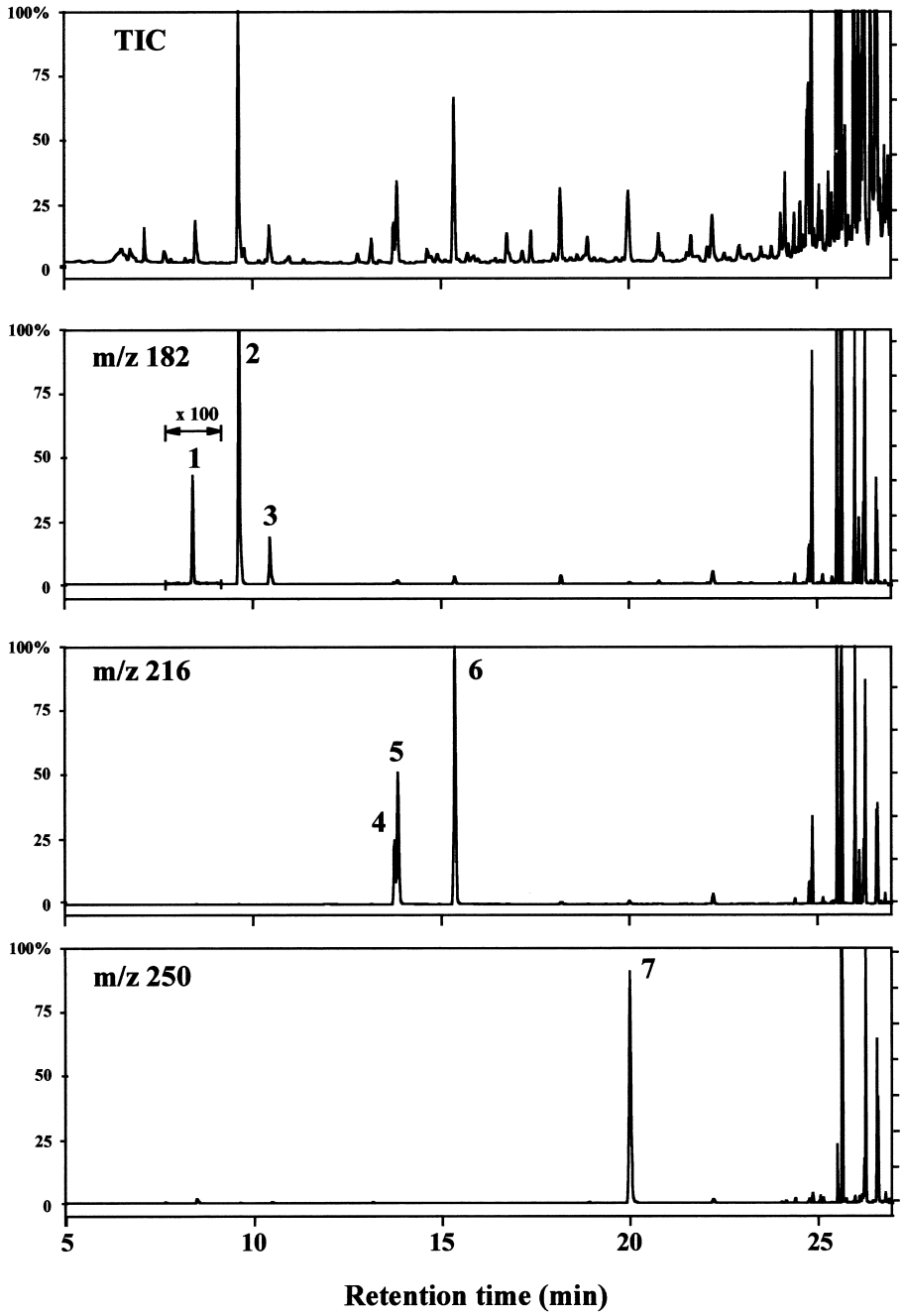

Fig. 6. Direct SPME–GC–IT-MS total-ion chromatogram and single-ion chromatograms of chlorobenzenes from CRM-530 soil with 100-μm PDMS fibre and splitless injection. Peaks as in Fig. 5.

Table 2
Analysis of chlorobenzenes in the clay CRM-530 soil

Compound	Concentration ($\mu g\ g^{-1}$ of soil)									Significance level (P-value)[b]			Intercomparison exercise[c]	
	Headspace–SPME 7-μm PDMS fiber[a] (A)			Headspace–SPME 100-μm PDMS fibre[a] (B)			Direct-SPME 100-μ PDMS fiber[a] (C)							
	Mean	S.D.	R.S.D.(%)	Mean	S.D.	R.S.D.(%)	Mean	S.D.	R.S.D.(%)	A vs. B	B vs. C	A. C	Mean	S.D.
1,3,5-Trichlorobenzene	0.253	0.051	20	0.194	0.028	15	0.278	0.026	9	0.033	0.011	0.320		
1,2,4-Trichlorobenzene	80.05	14.91	19	71.44	7.09	10	67.09	11.43	2	0.337	0.319	0.183		
1,2,3-Trichlorobenzene	14.63	3.59	24	13.17	1.26	10	13.04	0.51	4	0.471	0.876	0.446	14.32	1.39
1,2,3,5-Tetrachlorobenzene	5.352	1.242	23	4.088	0.306	7	24.366	0.328	7	0.143	0.300	0.247		
1,2,4,5-Tetrachlorobenzene	13.33	2.85	21	10.92	0.58	5	9.779	0.300	3	0.195	0.029	0.048		
1,2,3,4-Tetrachlorobenzene	27.12	4.80	18	23.51	0.72	3	24.41	0.71	3	0.234	0.164	0.346	25.31	4.43
Pentachlorobenzene	4.514	0.474	10	4.267	0.364	8	4.513	0.410	9	0.440	0.439	0.998	4.370	0.413

[a] $n=4$.[b] Significant differences between procedures for $P<0.05$ (at the 95% confidence level).[c] $n=9$ laboratories $\times 5$ replicates $=45$ results.

that was in direct contact with the fibre may have reduced its lifetime.

4. Conclusions

SPME–GC–IT-MS was applied to the analysis of soil samples containing high concentrations of chlorobenzenes. Different strategies which involve headspace and direct SPME techniques were proposed to prevent overloading of the signal of the ion trap detector. Good repeatabilities (R.S.D. between 2 and 8%) were obtained for headspace SPME with 100-μm PDMS fibre using split injection mode and an extraction time of 50 min, whereas for headspace SPME with 7-μm PDMS fibre, significantly higher relative standard deviations, from 7 to 11%, were obtained. For direct SPME procedure, the addition of organic solvent to the aqueous soil solution, such as methanol and acetone, was used to reduce the sensitivity. The addition of 30% acetone to the soil solution allowed equilibrium to be reached in 50 min. In these conditions, repeatabilities lower than 8% were obtained.

The optimized SPME–GC–IT-MS procedures were applied to the analysis of chlorobenzenes in CRM-530 soil, which is a candidate reference material. The results with the three SPME procedures were in good agreement with those obtained in a European intercomparison exercise. However, headspace SPME and direct SPME–GC–IT-MS procedures using 100-μm PDMS fibre were found to be more precise (R.S.D. between 2 and 15%) than headspace SPME with the 7-μm PDMS fibre (R.S.D. up to 24%). In conclusion, headspace SPME as well as direct SPME with 100-μm PDMS fibre are suitable methods to analyse chlorobenzenes in contaminated soil, with the advantage that no clean-up steps or long extraction times were needed, compared with conventional extraction procedures, i.e. Soxhlet extraction, thus considerably reducing the analysis time.

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