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Analysis of chlorobenzenes in soils by headspace solid-phase microextraction and gas chromatography–ion trap mass spectrometry

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Abstract

Headspace solid-phase microextraction (SPME) with gas chromatography–ion trap mass spectrometry (GC–IT-MS) was investigated as a possible alternative to Soxhlet extraction in the analysis of chlorobenzenes in soils. A 100 μm polydimethylsiloxane fibre was used for the optimization studies. Maximum sensitivity was obtained at a sampling temperature of 30°C and with an absorption time of 25 min. The effect of the addition of solvents of different polarity was evaluated. Better repeatability (R.S.D. between 5 and 7%) and higher responses were obtained when water was added to the soil. The headspace SPME method was applied to the analysis of the chlorobenzenes, 1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenze and pentachlorobenzene, in an industrially contaminated sandy soil, CRM-529 (Candidate Reference Material). The chlorobenzenes in this soil were quantified by standard addition, which led to good reproducibility (R.S.D. between 3 and 5%) and adequate detection limits (0.03 to 0.1 ng g^{-1} of soil). The method was validated by comparing the results with those obtained in a European intercomparison exercise.

Keywords: Solid-phase microextraction; Soil; Chlorobenzenes

1. Introduction

Chlorobenzenes can be introduced into the environment as solvents, dielectric fluids, deodorants and chemical contaminants or as intermediates in the manufacture of other chemical products such as pesticides, phenols and dyestuffs [1]. They are prevalent in both solid and liquid industrial effluents and in atmospheric discharges. As a result of their widespread use over several decades, chlorobenzenes have become very common in the environment. They are found in water [2], soils [3–5], sediments [1,6,7], sewage sludges [7,8] and aquatic biota [9]. Chlorobenzenes have been listed as priority pollutants by the United States Environmental Protection Agency (U.S. EPA) and the European Community; and some of them, such as hexachlorobenzene, are known to be human carcinogens [10,11]. Analysis of these compounds in solid matrices, such as soils, sediments, sludges and hazardous wastes, requires several steps of extraction and preconcentration of the analytes, and complicated clean-up procedures. U.S. Environmental Protection Agency (EPA) Method 3540 (Soxhlet extraction) and EPA Method 3550 (sonica-

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tion extraction) are currently used for the extraction of semivolatile organic compounds such as chlorobenzenes [12]. These methods require extensive clean-up and evaporative concentration procedures, which may cause loss of the volatile compounds and are time-consuming. Moreover, these extraction methods need expensive and hazardous solvents, which are undesirable for health and disposal reasons [3].

Solid-phase microextraction (SPME), developed by Pawliszyn and coworkers [13–15], is an alternative to the above techniques. It is a rapid, inexpensive, solventless and easily automated technique for the isolation of organic compounds from gaseous and liquid samples. The SPME method uses a fine fused-silica fibre coated with a polymer (i.e., polydimethylsiloxane or polyacrylate) to extract organic compounds from their matrix. SPME fibre combines sampling and preconcentration in a single step. After a well-defined adsorption time the fibre is transferred to a standard split/splitless injector, where the organic compounds are thermally desorbed from the polymeric phase. So far, SPME has been used coupled with GC to analyse a wide range of organic compounds in aqueous samples [16], such as aromatic hydrocarbons [17,18], halogenated volatile organic compounds (VOCs) [19,20], polyaromatic hydrocarbons (PAHs) [21,22], polychlorinated biphenyls (PCBs) [22], pesticides [23–26], nitroaromatic compounds [27] and phenol and its derivatives [28,29]. The analysis of organic compounds using SPME in soils and sludges is not as widespread as in water and is commonly based on the analysis of a water soil solution. SPME with polyacrylate- or poly(dimethiylsiloxane)-coated fibres has been used to analyse organophosphorus, organochlorine organonitrogen pesticides and PAHs [23,25,30–32] in soils and alkylphenol ethoxylate surfactants in sludges [33]. Currently, SPME is optimized in water and is then used to determine the analytes in soils suspended in water, as long as the soil matrix does not significantly interfere in the extraction.

By sampling analytes from the headspace above the sample matrix, SPME can be extended to the analysis of volatile and semivolatile organic compounds in complex samples of soils and sludges [34–37]. Zhang and Pawliszyn demonstrated that the extraction times can be substantially reduced by using headspace, because the diffusion of analytes is many times greater in the vapour phase than in the aqueous phase [38]. The equilibrium of the analytes between the gas phase and the polymeric fibre is achieved in a few minutes, whereas in direct aqueous extraction, where the SPME fibre is directly introduced into the aqueous matrix, the sample must be stirred intensely in order to shorten the equilibration times. A further advantage of the headspace SPME approach is that samples from virtually any matrix can be analysed since the fibre is not in direct contact with the sample, although care should be taken to release analytes efficiently into the headspace. For volatile compounds, the main difficulty is the trapping and chemisorption of analytes in solid matrices, while for semivolatile analytes low volatility is an additional problem [39]. Thermal desorption or the addition of modifiers to the soil are two ways these problems could be overcome [34,40]. However, as absorption of analytes by the fibre is exothermic, an increase in temperature can adversely affect the absorption of analytes through the coating due to decrease in partition coefficients [18]. There are few applications of headspace SPME to the analysis of solid matrices. Nevertheless, it has been used to determine aromatic and polyaromatic hydrocarbons in spiked sand matrices [34,36]; and chloro- and nitrobenzenes and -anilines in a broad variety of spiked soils [37].

In this paper, headspace SPME for the analysis of chlorobenzenes in soils is optimized. Temperature effect, absorption time and the addition of solvents of different polarity are studied. The main objective of the study was to evaluate SPME as a routine alternative technique for classical soil extraction methods, so it was applied to the analysis of chlorobenzenes (1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenzene and pentachlorobenzene) in an industrially contaminated sandy soil, which is a candidate reference material (CRM). The results using SPME were compared with the results using Soxhlet extraction and with those of a European intercomparison exercise for the analysis of this candidate reference material, organised under the aegis of the Measurement and Testing (MAT) programme.

2. Experimental

2.1. Standards and reagents

The semivolatile organic compounds studied (1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenzene and pentachlorobenzene) were supplied at a purity higher than 98% by Merck (Darmstadt, Germany); 1,3,5-tribromobenzene, used as internal standard, was purchased from Fluka (Buchs, Switzerland).

For headspace SPME study, individual stock standard solutions of each compound at 5000 mg l^{-1} were prepared by weight in acetone for residue analysis (Merck). Secondary individual standard solutions were prepared, also by weight, in acetone–water (HPLC grade) (1:1) mixture from the primary standard solution to give concentrations of 100 mg l^{-1}. Water standard solutions for quantification, which contained all the compounds at concentrations between 80 ng l^{-1} and 240 ng l^{-1} for 1,2,3-trichlorobenzene and between 200 ng l^{-1} and 620 ng l^{-1} for 1,2,3,4-tetrachlorobenzene and pentachlorobenzene, were prepared from the secondary standard solutions by weight. For the extraction, 200 μl of this water standard solution were added to 0.1 g of soil which was placed in 40-ml screw-cap vials fitted with silicone–PTFE septa.

For Soxhlet extraction, *n*-hexane, isooctane and acetone for residue analysis were supplied by Merck. The purity of the solvents was determined by the concentration of a 100-ml volume to 1 ml and analysis with high-resolution GC with electron capture detection (HRGC–ECD). Florisil (600-100 mesh) and anhydrous sodium sulphate for residue analysis were purchased from Merck and Panreac (Barcelona, Spain), respectively. All glass materials were cleaned with AP-13 Extran alkaline soap (Merck) for 24 h, dried at 180°C and rinsed with high-purity solvents immediately prior to use. Standard solutions which contained all the compounds in isooctane were prepared by weight in order to calculate recovery by standard addition. The industrial sandy soil was provided by Institut Fresenius (Germany) and was candidate reference material, CRM-529.

2.2. Chromatographic conditions

For headspace SPME study, 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 (equivalent to a 5% phenyl, 95% methyl polysiloxane) fused-silica capillary column (30 m× 0.25 mm I.D.) (J&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 isothermically at 50°C for 1 min, raised to 90°C at 20°C min^{-1}, then raised to 150°C at 3°C min^{-1} and finally raised to 280°C at 25°C min^{-1} and held for 5 min. The injector was maintained at 250°C and splitless injection mode was used.

The ion trap mass spectrometer (IT-MS) was operated in the EI positive mode and tuned to perfluorotributylamine (FC-43) in line with the manufacturer's instructions for achieving optimal sensitivity when working with automatic gain control (AGC). The electron multiplier, emission current and modulation amplitude were set at 1800 V, 40 μA and 2.5 V, respectively. The transfer line and the ion trap manifold were set to 280°C and 170°C, respectively. The mass range scanned was from m/z 60 to 400 at 0.8 s/scan. For quantification, the two most abundant ions of the molecular cluster of each chlorobenzene were selected. Saturn version 5.2 software was used for data acquisition.

The extracts obtained after Soxhlet extraction and clean-up were analysed on a Carlo Erba 5300 Mega Series gas chromatograph (Milan, Italy), equipped with a ^{63}Ni electron capture detector (ECD). A DB-17 (50% phenyl, 50% methyl polysiloxane) 60 m×0.25 mm I.D. fused-silica capillary column (J&W Scientific) of 0.25 μm film thickness was used. The temperature was programmed from 60°C to 90°C at 20°C min^{-1} and then raised to 170°C min^{-1} at 1.5°C min^{-1}, maintained at 170°C for 1 min and finally programmed to 280°C at 10°C min^{-1}, keeping the final temperature for 15 min. For confirmation, a DB-5 (5% phenyl, 95% methyl polysiloxane) 60 m×0.25 mm I.D. fused-silica capillary column (J&W Scientific) of 0.25 μm film thickness was used. The temperature conditions were

the same as for the DB-17 column. Helium was the carrier gas at 30 cm s^{-1} and nitrogen the make up at 54 ml min^{-1}. Injector and detector temperatures were held at 250°C and 330°C, respectively. Chrom-Card version 1.3 software (Fisons Instruments Spain) was used for data acquisition.

2.3. Solid-phase microextraction procedure

The studies were carried out with a SPME device purchased from Supelco (Ontario, Canada). A polydimethylsiloxane microextraction fibre of 100-μm film thickness and a solid-phase microextraction syringe purchased from Supelco were used.

The headspace SPME procedure developed was very simple. Initially, 0.1 g of the soil and an adequate amount of water, between 10 and 300 μl (10–75% of water, w/w), were combined in a 40-ml sample vial. The vial was placed in a thermostatic water bath and after 10 min the stainless-steel needle of the syringe was used to penetrate the septum of the sample vial. When the needle was in the sample vial, the fibre was plunged into the headspace above the soil slurry. When equilibrium was reached, the fibre was again withdrawn into the needle and the syringe was removed from the vial. The last step was the thermal desorption of the analytes in the injection port of the gas chromatograph for 3 min at 250°C.

The fibre was conditioned at 250°C for 2 h in the GC injector port before use. After conditioning, a fibre blank was run to ensure that no contaminants were in the fibre coating prior to exposure of the fibre to a given sample. Blanks were run periodically during the analysis to confirm the absence of contaminants.

2.4. Soxhlet extraction procedure

A 3-ml volume of water was added to a 1.3-g portion of contaminated soil, which was then placed on top of 50 g of anhydrous sodium sulphate in a glass thimble and Soxhlet extracted with 180 ml of *n*-hexane–acetone (1:1) for 12 h. In order to remove sulphur and sulphur compounds, the solvent extract was in contact with 0.5 g of copper powder for 3 h. After addition of 10 ml of isooctane as a keeper, the extract was concentrated to ca. 10–12 ml using a rotary evaporator without heating. Sample was then cleaned using Florisil column chromatography. Glass columns (150 mm×10 mm I.D.) filled with 6.5 g of Florisil (activated at 675°C overnight) were used. After packing, the column was rinsed with *n*-hexane, the entire extract was placed at the top of the column and then eluted with 50 ml of *n*-hexane. The eluate was again concentrated after addition of 5 ml of isooctane to ca. 20 ml and diluted to a final volume of 25 ml; 800 μl of this solution, adjusted to 1 ml with the internal standard, was analysed by HRGC–ECD.

3. Results and discussion

3.1. Headspace SPME optimization

In order to develop a headspace SPME procedure for the analysis of chlorobenzenes in soil, the extraction temperature, the exposure time of the fibre in the headspace and the effect of the addition of organic solvents to the CRM-529 soil were optimized. First, in order to enhance the mass transfer process and increase the vapour pressure of the semivolatile analytes in the headspace, the extraction temperature was increased to between 30°C and 50°C. Using a sampling time of 30 min, a decrease in the SPME-GC–IT-MS responses was observed. For instance, for 1,2,3,4-tetrachlorobenzene at 50°C an area of only 40% of the corresponding area at 30°C was obtained. This is probably due to a decrease in the partition coefficients between the SPME fibre and the headspace that can no longer be offset by the increased concentration of the analytes in the headspace. These results agreed with those of Nilsson et al. [18] and Zhang and Pawliszyn [36]. These latter authors indicated that the use of an internally cooled SPME device enabled a high extraction temperature to be used.

As a second step, the time required to reach an equilibrium between the stationary phase and the soil sample at a temperature of 30°C was determined. Fig. 1 shows the absorption time profiles for chlorobenzenes absorbed on a 100 μm polydimethylsiloxane fibre from the CRM-529 soil. From this figure, it can be deduced that the time required to reach equilibrium was between 15 and 25 min for all the compounds. Different responses (peak area/soil

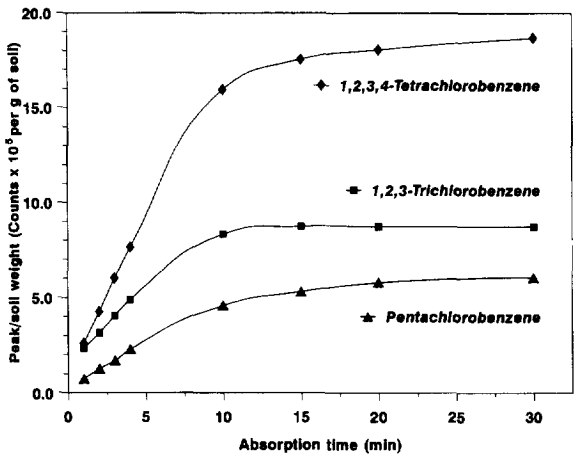

Fig. 1. Absorption time profiles for chlorobenzenes in CRM-529 soil using a 100 μm polydimethylsiloxane fibre at a sampling temperature of 30°C.

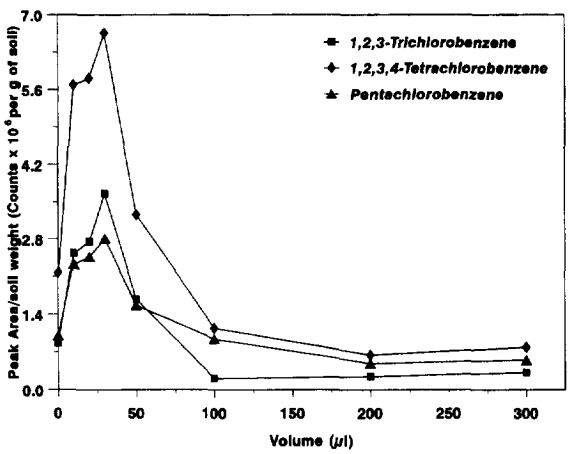

Fig. 2. Acetone effect on chlorobenzene response by headspace SPME-GC–IT-MS in optimized conditions (0.1 g of CRM-529 soil; sampling temperature, 30°C; exposure time, 25 min).

mass) were found for the three compounds, according to volatilities, distribution constants between headspace/fiber and headspace/soil and the concentration of each compound in the soil.

A solvent has to be used to spike the soil for quantification, so the effect of the addition of solvent to the soil has to be studied. In this study solvents of different polarity, such as ethanol, methanol, dichloromethane and acetone, in which chlorobenzenes are soluble, were added to the soil. The responses obtained for the three compounds, using headspace SPME-GC–IT-MS procedure after adding 100 μl of each solvent to 0.1 g of soil and extracting for 25 min at 30°C, with the response for each compound with ethanol used as reference (100), are given in Table 1. Maximum sensitivity for 1,2,3-trichlorobenzene was achieved when dichloromethane was used, whereas the maximum response for 1,2,3,4-tetrachloro- and pentachlorobenzene was achieved with acetone. Therefore, acetone seemed to be the most adequate organic solvent for spiking the soil.

The volume of solvent added to the soil is another parameter affecting the adsorption of the analytes on the fibre. The effect of adding acetone to the CRM-529 soil up to 70% (w/w) (300 μl) was studied and the headspace SPME-GC–IT-MS responses for the three chlorobenzenes studied are given in Fig. 2. Whereas the addition of small amounts of acetone (between 10 and 30 μl) progressively improved the absorption capacity of the fibre coating, an important decrease in sensitivity was observed between 30 and 100 μl. But no variation in the response was found with acetone volumes higher than 200 μl. Although maximum sensitivity was achieved at approximately 30 μl of acetone, there were wide variations in the responses between 10 and 50 μl (Fig. 2), so poor repeatability should be expected for headspace

Table 1
Absorption time profiles for chlorobenzenes in a soil using a 100 μm polydimethylsiloxane fibre at a sampling temperature of 30°C

Compound	Mean[a] (n=2) (relative responses to ethanol/g of soil)			
	Ethanol	Methanol	Dichloromethane	Acetone
1,2,3-Trichlorobenzene	100	230	611	385
1,2,3,4-Tetrachlorobenzene	100	275	371	453
Pentachlorobenzene	100	408	246	587

[a] Peak area/soil mass.

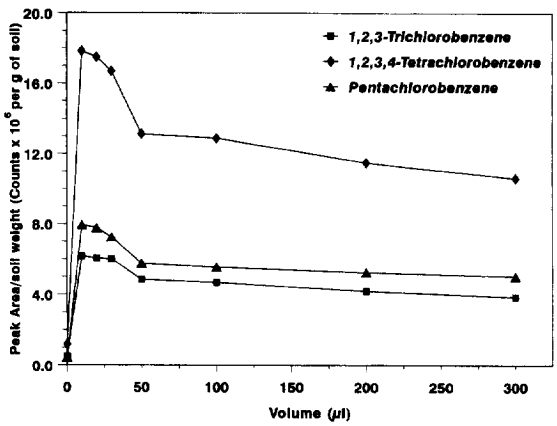

Fig. 3. Water effect on chlorobenzenes response by headspace SPME-GC–IT-MS. (0.1 g of CRM-529 soil; sampling temperature, 30°C; exposure time, 25 min).

SPME in these conditions. Fig. 2 shows that, when higher volumes of acetone were added (>100 µl), lower responses than for a dry soil were found for all the compounds. These results agreed with those for aqueous solutions of Horng and Huang [27], who observed that an increase in methanol decreased the sensitivity of SPME. The increase in the headspace SPME responses when 10 to 30 µl of acetone were added can be explained because the solvent molecules helps to liberate the analytes from the active sites on the soil and hence dragging them from the matrix into the gas phase. When the sample becomes a slurry (>100 µl of acetone added), an additional phase is present in the equilibrium, and the solvent may be functioning as a medium in which the analytes remain explaining the decrease on sensitivity. Nevertheless, acetone can be a good choice for the analysis of these compounds in soil samples when an enhancement of sensitivity is necessary. The addition of water to the soil was also studied. Although water vapour in the headspace during the extraction can reduce slightly the sensitivity of SPME [41], the addition of small amounts of water can facilitate the desorption and vaporization of analytes, as indicated by Zhang and Pawliszyn [34,36], due to the release of volatile organic compounds from their absorption sites in the soil by the polar water molecules. Responses obtained when different volumes of water were added to the soil using headspace SPME-GC–IT-MS procedure are given in Fig. 3, where an important increase in the responses for all the compounds can be observed with the addition of 10–30 µl of water. These results agreed with those obtained by Fromberg et al. [37], who concluded that the addition of water clearly improved the sensitivity of the SPME for the analysis of chloro- and nitrobenzenes and -anilines in spiked soils. A slight decrease in the responses (Fig. 3) was observed for volumes higher than 50 µl, although an improvement in sensitivity against the dry sample occurred. Adding relatively high volumes of water (>50 µl) to the soil, the responses seemed to be independent of the water amount, on the contrary for lower water volumes (10–30 µl) poor repeatability was observed. For these reasons, 200 µl of water were chosen as the optimal amount for quantitative analysis. In order to improve the response of the analytes, water seemed to be better than acetone; but acetone is a better solvent for chlorobenzenes and can be a good choice for samples with a high concentration of chlorobenzenes.

Table 2
Repeatability of the optimized headspace SPME-GC–IT-MS procedure using a 100 µm polydimethylsiloxane fibre (CRM-529 soil)

Compound	Repeatability (n=5)			
	Adding acetone		Adding water	
	Mean[a] (counts g^{-1} of soil)	R.S.D. (%)	Mean[a] (counts g^{-1} of soil)	R.S.D. (%)
1,2,3-Trichlorobenzene	$3.4 \cdot 10^5$	15	$4.8 \cdot 10^6$	5
1,2,3,4-Tetrachlorobenzene	$1.1 \cdot 10^6$	13	$1.3 \cdot 10^7$	6
Pentachlorobenzene	$7.8 \cdot 10^5$	12	$5.5 \cdot 10^6$	7

[a] Peak area/soil mass.

3.2. Quality parameters

Linear dynamic ranges of the GC–IT-MS system were established by plotting relative areas per amount of compound [(A_i/A_{is})/pg injected] versus relative mass injected (m_i/m_{is}), using standard mixtures of chlorobenzenes at different concentration levels in *n*-hexane and 1,3,5-tribromobenzene as internal standard. The linear ranges were from 20 to 50 000 pg injected for all the compounds.

The repeatability of the SPME-GC–IT-MS procedure was studied by analysing five replicates of the soil sample suspended in 200 μl of both solvents, acetone and water; the results obtained are given in Table 2. Higher sensitivity and lower relative standard deviations, between 5 and 7%, were obtained when water was added. Therefore, water was preferred for the determination of chlorobenzenes in the CRM-529 soil. The mass of soil to be extracted, the vial volume (headspace volume) used and the spiking levels were determined while taking into account the linear dynamic range for not overloading the response of the ion trap detector.

Detection limits defined as the concentration of the analytes in the sample which causes a peak with a signal-to-noise ratio (*S/N*) of 3, were also determined. In order to calculate their values, an agricultural soil without detectable quantities of chlorobenzenes was spiked with 200 μl of chlorobenzene standard solutions in water and the compounds were extracted with the established headspace SPME procedure. Under these conditions, detection limits of the method for these compounds were 0.03 ng g^{-1} for 1,2,3-trichlorobenzene, 0.04 ng g^{-1} for 1,2,3,4-tetrachlorobenzene and 0.10 ng g^{-1} for pentachlorobenzene.

3.3. Analysis of CRM-529 soil

Both the headspace SPME procedure and Soxhlet extraction were used to determine the three chlorobenzenes in the sandy soil, CRM-529. For headspace SPME, duplicate analyse of three samples of soil were carried out by standard addition, spiking the samples at three different concentration levels between 0.18 and 1.35 μg g^{-1}. For Soxhlet extraction, five replicates of soil were analysed on two different days. The recoveries were calculated from the slope of the addition standard curve obtained by spiking the samples between 0.15 and 2.25 μg g^{-1} and were higher than 93% for the compounds. The HRGC–ECD chromatogram obtained from the Soxhlet extract using the DB-17 column, the GC–IT-MS total-

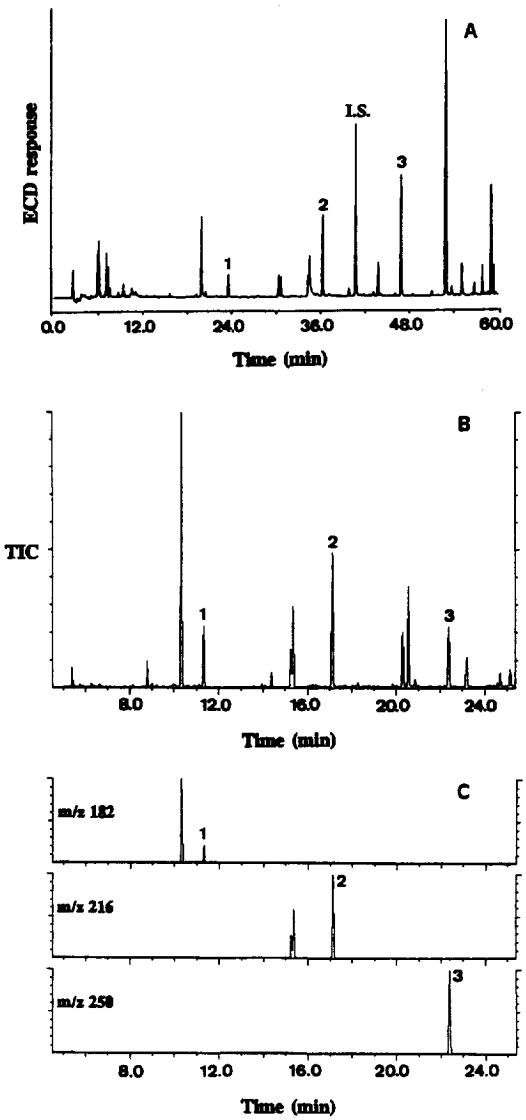

Fig. 4. (A) HRGC-ECD chromatogram (60 m DB-17 column), I.S.=1,3,5-tribromobenzene (as internal standard for Soxhlet extraction), (B) headspace SPME–GC–IT–MS total-ion chromatogram (30 m DB-5 MS column) and (C) single-ion chromatograms of chlorobenzenes from CRM-529 soil. Peaks: 1=1,2,3-trichlorobenzene; 2=1,2,3,4-tetrachlorobenzene; 3=pentachlorobenzene.

ion chromatogram obtained by headspace SPME extraction and the single-ion chromatograms selected for each chlorobenzene studied (m/z 182 for 1,2,3-trichlorobenzene, m/z 216 for 1,2,3,4-tetrachlorobenzene and m/z 250 for pentachlorobenzene) are given in Fig. 4. As can be seen, the headspace SPME-GC–IT-MS procedure using 100 μm polydimethylsiloxane fibre is a highly selective procedure for the analysis of chlorobenzenes in contaminated soils which show no interference from other compounds potentially present in the sample matrix (Fig. 4B). In fact, the chromatogram was cleaner than the one obtained after the Soxhlet extraction and a Florisil clean-up step (Fig. 4A).

The results obtained with headspace SPME-GC–IT-MS procedure are shown in Table 3, where the mean values obtained by our laboratory using Soxhlet extraction and the mean of all the European laboratories which participated in an intercomparison exercise organised under the aegis of the MAT (Measurement and Testing) programme are also given. The results obtained with headspace SPME-GC–IT-MS agreed with the mean values obtained by our laboratory using Soxhlet extraction. Comparable standard deviations were obtained for the two methods, being slightly lower for 1,2,3,4-tetrachlorobenzene using headspace SPME (only 3% versus 8% with the Soxhlet extraction). The values also agreed with the results obtained by several laboratories in the intercomparison exercise. These results showed that headspace SPME can be considered a quicker and cheaper alternative, with the additional advantage of being a solventless method for the determination of chlorobenzenes in contaminated soils.

4. Conclusions

Headspace SPME procedure is a fast, inexpensive and solvent-free method that has been proved accurate in the analysis of chlorobenzenes in soils. Headspace SPME-GC–IT-MS procedure has been optimized using a 100 μm polydimethylsiloxane fibre for the analysis of chlorobenzenes in CRM-529 soil. The addition of some solvents to the soil before extraction led to an increase in the sensitivity of headspace SPME, especially when very low amounts of solvent were added. Good repeatability and higher responses were obtained adding 200 μl of water (R.S.D. between 5 and 7%). The proposed headspace SPME-GC–IT-MS method was applied to the analysis of chlorobenzenes in CRM-529 soil, giving good reproducibility (R.S.D. between 3 and 5%) and adequate detection limits (0.03 to 0.1 ng g^{-1} of soil). The results with headspace SPME-GC–IT-MS agreed closely with those in a European intercomparison exercise. Optimized headspace SPME can be proposed as a fast and accurate method for analysing chlorobenzenes in soils and can be used instead of the Soxhlet technique which involves high volumes of solvents, clean-up procedures and time-consuming steps. Further investigations related with the applicability of the headspace SPME procedure to the analysis of chlorobenzenes in contaminated soils at different concentration levels are being developed.

Acknowledgments

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Table 3
Analysis of chlorobenzenes in the sandy CRM-529 soil

Compound	Concentration (μg g^{-1} of soil)						
	Headspace SPME-GC–IT-MS		Soxhlet extraction		Intercomparison exercise		
	Mean[a]	S.D.[a]	Mean[b]	S.D.[b]	No. of results	Mean	S.D.
1,2,3-Trichlorobenzene	0.591	0.032	0.639	0.052	9	0.623	0.064
1,2,3,4-Tetrachlorobenzene	1.557	0.055	1.703	0.135	10	1.517	0.251
Pentachlorobenzene	1.420	0.069	1.588	0.080	11	1.326	0.272

[a] $n=3$.
[b] $n=5$.

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