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Analysis of chloro- and nitroanilines and -benzenes in soils by headspace solid-phase microextraction

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Abstract

Quantitative analysis by headspace solid-phase microextraction (HS-SPME) of twenty chloro- and nitrobenzenes and -anilines spiked into soil samples was possible when the calibration was performed with the same matrix. The SPME response increased with addition of water to the air dried soil samples, and by optimisation of extraction conditions such as temperature, extraction time and sample agitation. Distribution constants between the fibre coating materials and water were determined. They showed that polyacrylate, rather than polydimethylsiloxane, should be used in the analysis of polar compounds. Matrix effects, mainly depending on the organic carbon content of the soil, were so large that quantitative analyses of real soil samples would not be reliable with model matrix calibration. This problem would be overcome if a nearly exhaustive extraction could be achieved. Recovery studies showed that this was possible only in the case of extraction of the lightest non-polar analytes from a soil with a very low content of organic carbon. Instead quantification could be performed with calibration by standard addition. By this approach the non-linear calibration curves at concentrations near the detection limits would cause inaccurate results at trace level, whereas it could be applied successfully within the linear ranges. Hence, the potential of HS-SPME in soil analysis is primarily as a rapid screening technique.

Keywords: Headspace solid-phase microextraction; Soil; Sample preparation; Chloroanilines; Nitroanilines; Chlorobenzenes; Nitrobenzenes; Anilines; Benzenes

1. Introduction

Since the development of solid-phase microextraction (SPME) [1,2] the technique has been optimised for the quantitative analysis of phenols [3], polyaromatic hydrocarbons (PAHs) [4], polychlorinated biphenyls [4], pesticides [5,6] and volatile organic compounds found in drinking water [7]. The majority of the applications of SPME has been to aqueous samples. However, with headspace solid-phase microextraction (HS-SPME) [8] the possibility of analysing solid samples was introduced. This has led to some applications in the food industry [9,10] and in microbiological studies [11]. Furthermore, analysis of six volatile chlorinated organic compounds, the BTEX compounds (benzene, toluene, ethylbenzene and xylenes) and a few PAHs from a spiked sand matrix has been reported [12]. Recently, nearly quantitative extraction was obtained for the BTEX compounds from a spiked sand matrix and a spiked

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clay matrix using an internally cooled SPME device [13]. However, thus far, very little is known about the quantitative aspects of the matrix effects in soil analysis by HS-SPME, and for the more polar and less volatile compounds no data exist. The present paper examines the quantitative analysis of twenty chloro- and nitrobenzenes and -anilines in thirteen soils covering a broad variety of soil characteristics. Only 1,3-dichlorobenzene and 1,2,4-trichlorobenzene have been analysed earlier by SPME. The feasibility of soil analysis by HS-SPME is discussed.

2. Experimental

2.1. Analytes

The twenty chloro- and nitroanilines and -benzenes listed in Table 1 were analysed. They were all obtained as neat compounds of analytical quality from Aldrich (unless otherwise stated).

2.2. Soils

Two series of soils were used for the sample preparations, namely seven soils collected from a soil profile in Ispra, earlier characterised by Payá-Pérez and Pelusio [14] and six certified Euro soils [15]. The soils were air dried to constant weight at room temperature, hand pounded and passed through a 2 mm sieve. Their physico-chemical properties are given in Table 2.

2.3. Sample preparations

For the experiments where GC–electron-capture detection (ECD) analyses were performed a stock solution in methanol was prepared containing the analytes at differentiated concentrations (see Table 1) in order to avoid very different responses of the analytes due to differences in their ECD response factors. The same stock solution was used for the initial experiments with GC–MS analysis. A standard solution for direct injections was prepared by

Table 1
Analytes

Compound number	Compound (in order of elution, HT-8)	Concentration in the stock solution (mg/l methanol)	Boiling point (°C)[a]
1	1,3-Dichlorobenzene[b]	246	173.5
2	Nitrobenzene[c]	408	210.8
3	1,2,4-Trichlorobenzene[b]	130	213.5
4	2,3-Dichloroaniline	438	252
5	3-Chloronitrobenzene	27.1	235
6	4-Chloronitrobenzene	24.5	242
7	2-Chloronitrobenzene	25.3	246
8	2,6-Dichloroaniline	365	–
9	2,5-Dichloronitrobenzene	25.3	267
10	3,5-Dichloroaniline	454	260
11	3,4-Dichloronitrobenzene	20.3	225
12	2-Nitroaniline	184	285
13	3,4-Dichloroaniline	854	272
14	3-Nitroaniline	1817	306
15	1,2-Dinitrobenzene	36.9	319
16	4-Chloro-2-nitroaniline	38.8	–
17	4-Nitroaniline	372	331.7
18	2-Chloro-4-nitroaniline	35.4	–
19	2,6-Dichloro-4-nitroaniline	18.5	–
20	Pentachloronitrobenzene	16.5	–

[a] According to Ref. [20].
[b] Purchased from Fluka.
[c] Purchased from Supelco.

Table 2
Soil characteristics[a]

Letter code	Soil name	% Clay	% Silt	% Sand	pH	% Organic carbon
A	Euro soil 1	75.0	21.9	3.3	5.9	1.30
B	Euro soil 2	22.6	64.1	13.4	8.0	3.70
C	Euro soil 3	17.0	36.8	46.4	5.8	3.45
D	Euro soil 4	20.3	75.7	4.1	7.0	1.55
E	Euro soil 5	6.0	12.6	81.6	4.6	9.25
F	Euro soil 6	16.0	82.4	1.7	8.3	0.25
G	Ispra soil A1	5.3	8.9	85.8	4.5	6.34
H	Ispra soil A2	1.8	6.4	91.8	4.9	1.87
I	Ispra soil A3	1.1	1.4	97.5	5.0	0.50
K	Ispra soil C1	0.3	0.3	99.4	5.1	0.17
L	Ispra soil C2	0.5	0.2	99.3	5.2	0.03
M	Ispra soil C3	3.7	3.0	93.3	5.0	0.12
N	Ispra soil C4	1.6	3.4	95.0	4.8	0.16

[a] Data according to Kuhnt and Muntau [15] for the Euro soils and Payá-Pérez and Pelusio [14] for the Ispra soils.

diluting 10 μl of the stock solution in 1.8 ml of hexane.

For the preliminary experiments and the experiments concerning quantitative analysis the soil samples were prepared in 10 ml crimp cap vials with PTFE-coated silicone septa (Supelco) by weighing 5 g of soil directly into the vial, adding the desired amount of water and spiking 50 μl of the stock solution into the soil. For the calibration experiments samples were prepared in duplicate containing 0.5, 1, 10, 50 and 100 μl of the stock solution in order to cover extended concentration ranges. The preparation of the soil samples was concluded by repeated ultrasonic treatment and shaking of the vials, whereupon they were left to equilibrate. To examine the effect of the equilibration time, i.e. the time between spiking of the soil and analysis, a number of SPME analyses were performed at different times between 30 min and 480 h after the sample preparation. The effect of the water content in the soil was investigated with samples containing up to 33.3% (w/w).

Another stock solution in methanol containing 1 g/l of each of fifteen of the analytes (some isomers were excluded) was prepared for the recovery studies and the determination of distribution constants where the analyses were performed by GC–MS. Diluted solutions in methanol, 0.1, 1, 2.5, 10, 25, 50, 250 ng/μl, were used for spiking of the samples and for external calibration by direct injections. The water and soil samples were prepared in 4 ml screw cap vials with PTFE-coated silicone septa. Determination of distribution constants were performed with 50 ppb water samples. For the recovery studies 10, 100 and 1000 ppb soil samples were prepared. For the experiments without agitation water was added to a soil/water ratio 1:10. For the experiments with mechanical mixing water was added to a ratio 1:1. Soil E and soil F were chosen for these studies as they represent the extremes as regards organic carbon content with 9.25 and 0.25%, respectively.

2.4. Solid-phase microextraction procedure

The SPME fibres (Supelco) used in the present study were 100 mm fused silica rods coated with 1 cm long layers of 100 μm polydimethylsiloxane (PDMS) or 85 μm polyacrylate (PA). They were mounted in SPME devices (Supelco) for manual sampling.

The extractions were performed by piercing the septum of the sample vial with the SPME needle, pushing out the SPME fibre and exposing it to the headspace over the sample in the vial or, in the determination of distribution constants, directly to the aqueous phase. In the preliminary experiments and the experiments concerning quantitative analysis the vials were placed in a water bath at 80°C (±2°C) during the 30 min extraction. In the recovery studies and the determination of distribution constants the samples were heated to 50°C in an aluminium block

(±0.5°C) or, where sonication was performed, in a water bath (±2°C) during extraction times from 30 min to 18 h. After the extraction, the SPME fibre was retracted into the SPME needle and immediately transferred to the GC injection port for 5 min thermal desorption.

2.5. Analytical conditions

Initial experiments were carried out on an HP 5890A GC instrument coupled to a Carlo Erba QMD 1000 quadropole MS system for the establishment of the retention order of the compounds by direct injection of 1 μl of the standard solution in hexane. The split/splitless injector was operated at 200°C with the purge flow closed for 0.8 min. Helium was used as carrier gas. The GC separation was performed on a 50 m×0.22 mm I.D. HT-8 capillary column (SGE) with a film thickness of 0.25 μm. The GC oven was operated with the following temperature program: 60°C for 5 min, followed by 8°C/min to 280°C which was held for 5 min. The transfer line interfacing the GC with the MS was held at 200°C. The MS was operated under the Labbase software (VG) in the electron impact mode, scanning from m/z 35 to 500 in 1 s. Identification of the analytes was performed using the MassLib software (Chemical Concepts) searching in several mass spectral libraries.

In the preliminary experiments and the experiments concerning quantitative analysis an HP 5890 series II GC-ECD system was used for the analyses with the capillary column mentioned above. The injector temperature was 200°C when the fibre coated with polydimethylsiloxane was used, and 270°C when the polyacrylate fibre coating was used. The carrier gas was hydrogen at ~40 cm/s constant flow. The GC oven was operated with the temperature program given above. The ECD was operated at 300°C with argon with 10% methane as make-up gas. The acquisition and treatment of data was performed with the HP 3365 series II Chemstation software.

In the recovery studies and the determination of distribution constants a Shimadzu GC-17A QP-5000 MS system was used with a 30 m×0.25 mm SPB-5 capillary column (Supelco) with a film thickness of 0.25 μm. The split/splitless injector was operated at 250°C when the fibre coated with polydimethylsiloxane was used, and 280°C when the polyacrylate fibre coating was used, with the purge flow closed during the 5 min desorption. Helium was used as carrier gas. The column inlet pressure was constant 40 kPa (corresponding to 25–30 cm/s average linear velocity). The GC oven was programmed as follows: 40°C for 5 min, then 20°C/min to 120°C, and subsequently 8°C/min to 280°C which was held for 5 min. The MS was operated under the Class 5000 software (Shimadzu) in the electron impact mode, scanning from m/z 50 to 300 in 0.5 s after a 5 min solvent delay in the case of direct injection. The detector voltage was 1.50 kV and the characteristic masses listed in Table 3 were used for the quantitation.

3. Results and discussion

3.1. Preliminary experiments

Preliminary experiments were carried out with the 100 μm polydimethylsiloxane fibre and samples prepared with soils G and N (see Table 2). The elevated extraction temperature of 80°C was chosen, in spite of the loss of sensitivity of SPME with increasing temperature [7], to increase the diffusion velocity and to facilitate the liberation of the analytes from their sorption to the soil [16]. No statistically significant effect of the equilibration time before the extraction was observed on the response for any of the analytes in any of these soils at 95% significance level in a one-side variance analysis. Nonetheless, all samples were left for at least one week for equilibration before the analysis.

When comparing the chromatogram of direct injection with, in principle, no other discrimination of the analytes than their different ECD response factors Fig. 1 to the chromatograms of HS-SPME from the soils G and N Fig. 2 large differences in the relative intensities of the analytes are observed. The discrimination of some compounds can be ascribed partly to their lower affinities for the fibre coating material as discussed below. However, by comparison of the results for the two soils G and N (see Figs. 2,3) it clearly appears that the different degree of

Table 3
Quantitation masses and distribution constants between the fibre coating materials and water at 50°C

Compound number	Compound (in order of elution, SPB-5)	Quantitation mass	Log $K_{PA-water}$	Log $K_{PDMS-water}$
1	1,3-Dichlorobenzene	146	3.75	3.61
2	Nitrobenzene	123	2.43	1.79
3	1,2,4-Trichlorobenzene	180	4.32	3.99
5	3-Chloronitrobenzene	157	2.95	2.19
7	2-Chloronitrobenzene	157	2.93	2.06
9	2,5-Dichloronitrobenzene	191	3.40	2.49
10	3,5-Dichloroaniline	161	3.51	1.90
13	3,4-Dichloroaniline	161	3.31	1.71
15	1,2-Dinitrobenzene	168	2.32	0.71
14	3-Nitroaniline	138	2.08	0.26
16	4-Chloro-2-nitroaniline	172	2.96	0.90
17	4-Nitroaniline	138	2.16	0.38
18	2-Chloro-4-nitroaniline	172	2.73	0.45
19	2,6-Dichloro-4-nitroaniline	206	3.28	1.33
20	Pentachloronitrobenzene	295	5.10	4.07

sorption to the soil, depending on the compound and the soil characteristics, is of major importance. The peaks marked with an X in the chromatograms were caused by unknown impurities in the stock solution. The tailing of some of the peaks in the HS-SPME analyses should be ascribed to a relatively slow desorption from the fibre coating of the compounds having boiling points much above the desorption temperature of 200°C (see Table 1). This caused no difficulties in the integration of the peaks.

Although water vapour in the headspace during the extraction is expected to reduce the sensitivity of SPME slightly [17], a favourable effect of water addition to the soil samples is observed by comparison of the absolute responses in Figs. 2 and 3. The water helps to liberate the compounds from their sorption to the soil, thus favouring their extraction. The effect of the water addition was clearly positive

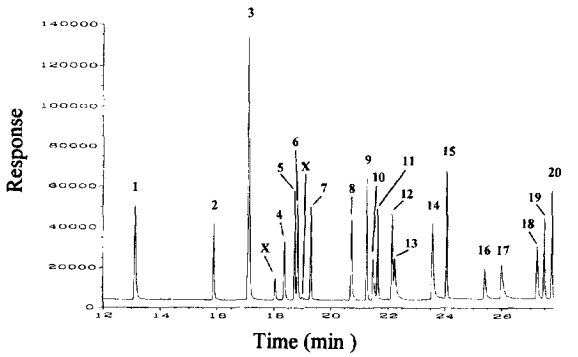

Fig. 1. Direct injection GC–ECD analysis of the standard solution; the compounds are numbered according to Table 1; X denotes unknown.

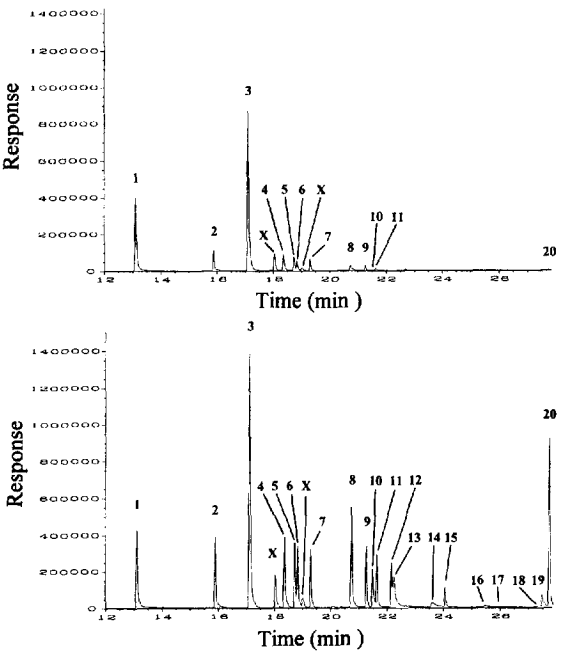

Fig. 2. HS-SPME–GC–ECD analysis of the spiked soils G (upper) and N (lower); the compounds are numbered according to Table 1; X denotes unknown.

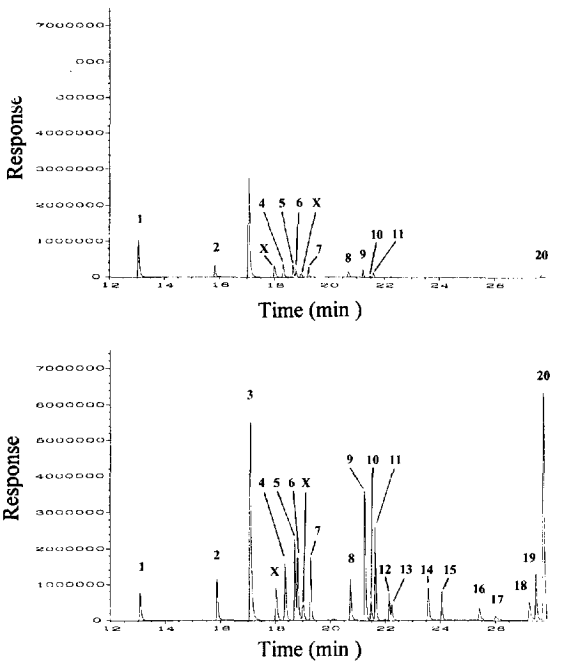

Fig. 3. HS-SPME–GC–ECD analysis of the spiked soils G (upper) and N (lower) after addition of 10% (w/w) water; the compounds are numbered according to Table 1; X denotes unknown.

for all of the analytes though not of equal importance. Fig. 4 illustrates for a representative compound, 2,3-dichloroaniline, that the effect of the water addition is most pronounced up to approximately 10% (w/w), after which the response stabilises or even decreases slightly at higher contents of water. The importance of water addition has been reported previously for the BTEX compounds [12,13]. It should be noticed that 0% water in Fig. 4 denotes soil dried to constant mass at 110°C, while the air dried soil having a low content of water is represented by the first data points. Fig. 4 also shows that the response is largely dependent on the soil characteristics.

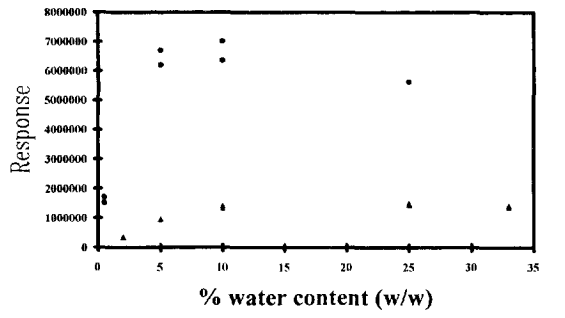

Fig. 4. Response versus water content for HS-SPME–GC–ECD analysis of 2,3-dichloroaniline from the soils G (triangle) and N (circle).

3.2. Choice of SPME fibre coating

The carry over of analytes from one analysis to the subsequent analysis was examined by alternate blank analyses. Generally, less than 0.5% or 0.7% of each analyte remained on the fibre coated with polyacrylate or polydimethylsiloxane, respectively. The slightly higher carry over on the fibre coated with polydimethylsiloxane has been observed earlier for chloro- and nitrophenols [3] and should be ascribed to the lower desorption temperature (200°C) with this fibre coating. During this work the manufacturers recommended maximum temperature of polydimethylsiloxane was raised and desorption could be performed at 250°C. At this temperature even smaller carry overs were observed. The relative carry over was dependent on the concentration, i.e. a higher relative carry over was observed when only a small amount of the analyte was adsorbed onto the fibre coating than when a high amount was adsorbed. The carry over was not equal for all of the compounds, and for some of the nitroanilines and 1,2-dinitrobenzene the relative carry over might be higher than stated above although they were not detected in the alternate blank analyses. Nonetheless, it can be concluded that for none of the analytes the carry over posed a practical problem unless a very low concentration sample was analysed immediately after a high concentration sample. In that case, an intermediate desorption of the fibre should be performed. Previously, it has been reported that the desorption temperature has to be just slightly higher than the boiling point of a given compound to ensure its complete desorption from the fibre coating [18]. In a later study, no complications were observed desorbing at 15–20°C below the boiling point [7]. In this study, acceptable carry overs were observed even when desorbing at temperatures far below the boiling points of the high-boiling compounds (see Table 1).

Distribution constants were determined as the ratio between the amount of the analyte in the fibre coating (determined by external calibration) and in

the water (determined as the spiked amount minus the amount in the fibre coating) at equilibrium corrected for the different volumes, 4 ml water sample versus $4.94 \cdot 10^{-4}$ ml polyacrylate or $6.28 \cdot 10^{-4}$ ml polydimethylsiloxane fibre coating. Variation of the extraction time showed that the equilibrium between the mechanically stirred water sample and the fibre coating had been reached for all of the analytes within 1 h both for polyacrylate and polydimethylsiloxane. The results of the comparison of polyacrylate and polydimethylsiloxane as fibre coating material are listed in Table 3. For the benzenes the distribution constants were favourable with both fibre coating materials. For the more polar anilines lower responses were observed and the nitroanilines were strongly discriminated by the polydimethylsiloxane fibre coating. This discrimination of polar compounds has been reported previously for other analytes [3,11]. The combined effect of sorption to the soil and strong discrimination by the fibre coating complicated the detection of nitroanilines at trace levels by HS-SPME of soil samples.

Generally, a higher number of chlorines increased the response; this higher affinity of the analyte for the coating has previously been reported for phenols [3]. Nitro groups, on the contrary, decreased the response especially with the polydimethylsiloxane fibre coating.

Considering the advantages of the fibre coated with polyacrylate, especially as regards the polar compounds, this fibre was selected for the further experiments.

3.3. Quantitative analysis

The calibration curves for the various analytes extracted from the air dried soil G typically exhibited r^2 factors down to 0.85 with standard deviations up to 50% or even higher for a few of the polar compounds. For the volatile, non-polar compounds 1,3-dichlorobenzene and 1,2,4-trichlorobenzene r^2 factors were above 0.95. On addition of 10% (w/w) water to the samples before the analysis, r^2 factors between 0.95 and 0.99 were obtained for most of the compounds. The standard deviations were in the range 8–20%, which is still higher than typical values in water analysis [3,7]. Similar or slightly lower r^2 factors could be obtained extracting from the air dried, sandy soil N without addition of water. The calibration curves exhibited a slow rise at low concentrations. At higher concentrations the rise was steeper and more linear. The r^2 factors given above refer to the approximately linear ranges. The linearity of ECD was tested in the given concentration ranges and r^2 factors above 0.99 were found for all of the compounds. Hence, the non-linearity of the calibration curves observed at concentrations near the detection limits, especially for the more polar compounds and when extracting from the dry soil G, must be ascribed to sorption of the analytes to active sites on the soil.

The detection limits were found to be in the lower ppb range. However, considering the non-linearity of the calibration curves at concentrations near the detection limits, it would not be appropriate to calculate exact detection limits using the concentration/signal-to-noise method.

At this point, it can be concluded that reliable quantitative results were obtainable even for polar analytes after optimisation of the analytical procedures when working with spiked samples. However, the real complications do not occur until we consider the importance of the soil characteristics and other factors possibly influencing the equilibration process which is fundamental for HS-SPME.

In a set of experiments including all of the twenty analytes in each of the thirteen soils three different extraction approaches were examined: (i) extraction from air dried soil in a vial in an upright position, (ii) extraction from air dried soil in a vial turned over approximately 45° and (iii) extraction from air dried soil after addition of 10% (w/w) water in a vial in an upright position. The results are presented in Figs. 5 and 6 for the two representative compounds 2,3-dichloroaniline and 1,2,4-trichlorobenzene, respectively.

Comparing the left black columns to the right black columns the positive impact on the extraction of the water addition was clearly confirmed for all of the compounds in all of the soils covering a wide variety in soil characteristics (see Table 2).

It is very interesting to notice the large matrix dependency of the measured responses. For example, the response was almost a hundred times higher when extracting 2,3-dichloroaniline from soil F than when extracting it from soil E. Hence, a logarithmic

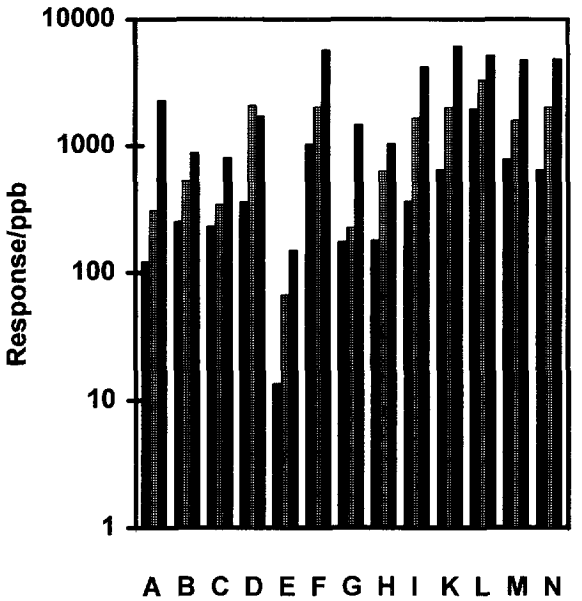

Fig. 5. Response/ppb of 2,3-dichloroaniline as a function of the soil type (represented by the letters given in Table 2) and the extraction approach: Air dried soil in an upright vial (left black column), air dried soil in a vial turned over approximately 45° (middle grey column) and air dried soil with 10% (w/w) water added in an upright vial (right black column). Please note the logarithmic scale.

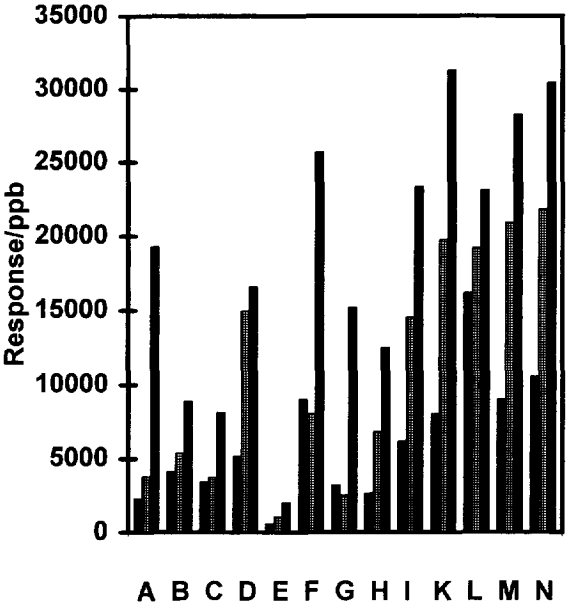

Fig. 6. Response/ppb of 1,2,4-trichlorobenzene as a function of the soil type (represented by the letters given in Table 2) and the extraction approach: Air dried soil in an upright vial (left black column), air dried soil in a vial turned over approximately 45° (middle grey column) and air dried soil with 10% (w/w) water added in an upright vial (right black column).

scale was needed for the graphical presentation in Fig. 5. For the more volatile, non-polar analyte 1,2,4-trichlorobenzene the matrix effect was less pronounced, yet still highly important. Comparison of the responses in Figs. 5 and 6 with the data given in Table 2 shows, not surprisingly, an extensive dependency on the organic carbon content of the soil. This is illustrated graphically in Fig. 7.

Another possibility of improving the response was to increase the soil/headspace surface area. This is shown in Figs. 5 and 6 by comparison of the results of the extractions from the air dried soils in vials in their upright position and in vials turned over which approximately triples the surface area. This reveals that the extraction is limited to a surface layer of the soil sample, i.e. the equilibrium has not been achieved, and is very far from being exhaustive. Actually, experiments with the two representative soils G and N showed that, in most cases, less than 1% of the amount of the analytes spiked into the soil was recovered by HS-SPME under the given conditions. This number could be increased by sonication or mechanical mixing of the soil during the extraction, a smaller sample amount and a longer extraction time as shown below.

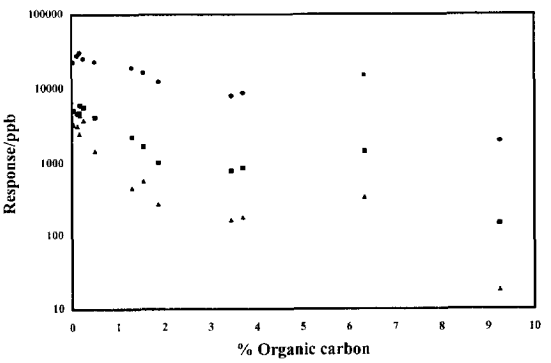

Fig. 7. HS-SPME–GC–ECD response versus organic carbon content of the soil for 1,2,4-trichlorobenzene (circle), 2,3-dichloroaniline (square) and 3,5-dichloroaniline (triangle). Please note the logarithmic scale.

3.4. Recovery studies

The basic principle of SPME is equilibration [2]. Hence, the goal is not necessarily to achieve 100% recovery as in the classical extraction techniques. However, influencing the equilibrium in order to extract a larger amount of the analytes causes a higher sensitivity of the method. Furthermore, in specific cases, like soil analysis with strong matrix effects, approaching exhaustive extraction will help to overcome the inaccuracies caused by unknown interferences of the equilibrium (e.g. an unknown organic carbon content).

It has been reported earlier that the SPME adsorption process is exothermic [7], thus a lower extraction temperature leads to a higher sensitivity and consequently a higher recovery. On the other hand, an elevated extraction temperature favours the equilibration by higher diffusion rates and by facilitating the liberation of the analytes from the sample matrix. A reasonable compromise for this study was thought to be 50°C.

As the amount extracted by SPME is proportional to the sample concentration [2], the recovery could also be increased by using smaller samples. Comparison of the results in Table 4 illustrates this. However, the precision was lower with the smaller samples.

Finally, the recovery could be improved by approaching equilibrium. Especially, for the highest boiling compounds large increases in the recoveries were observed when extracting for 120 min instead of 30 min. However, without mechanical mixing of the soil, the equilibration was very slow. The combination of SPME and mechanical mixing of the soil in small vials was not easy considering the delicate SPME fibre. Suspending the soil in water and stirring of the sample was a solution resulting in complete equilibrium after 30 min to 10 h depending on analyte and soil characteristics. The results in Table 4 shows that the recoveries were much improved by this approach. Ultrasonic treatment of identical samples was less efficient due to the missing mixing of the soil. It is important to notice the very determining matrix effects by comparison of the different recoveries from soil E and soil F. For this reason the calculations were based on the 1 ppm samples for soil E and the 100 ppb samples for soil F in order to be within the range of the external calibration. The soil samples of the two concentrations remaining were used merely to control the approximate linearity from 10–1000 ppb. Only for the lighter, non-polar analytes extracted from the soil poor in organic carbon nearly exhaustive extraction was achieved.

3.5. Discussion of the applicability of HS-SPME for quantitative soil analysis

Since the amount extracted is influenced strongly by the matrix, quantitative analysis of real samples on the basis of calibration in a model soil will not be feasible. Thus, only if a nearly exhaustive extraction can be realised accurate quantitative results of the analysis of real samples can be expected. Previously, an internally cooled SPME device possibly providing a solution for the BTEX compounds has been presented [13]. The results of the present work showed that ordinary HS-SPME was less suited for accurate quantitative measurements of more polar and less volatile compounds in soil. Also with calibration by standard addition the results would be less accurate at trace level due to the missing linearity of the calibration curves at concentrations near the detection limits and the fact, discussed by Zhang et al. [19], that an analyte spiked into the soil matrix might not behave as those present beforehand in their release from the soil. The same considerations would be valid for the use of internal standards. Furthermore, usually the value of internal standards in SPME is limited by the different behaviour of the compounds in the extraction process, unless the expensive isotope-labelled analogues are used. At concentrations somewhat above the detection limits, that is well within the linear range, HS-SPME with the calibration performed by standard addition will be very applicable for rapid screening analysis.

4. Conclusions

Quantitative analysis with HS-SPME of polar and less volatile compounds in soil is possible when working with spiked samples. The sensitivity can be improved much by manipulation of the matrix, e.g. water addition, and by optimisation of the extraction conditions, e.g. temperature, fibre coating material,

Table 4
Recoveries in percent

Sample	4 ml water		2.5 g soil				0.5 g soil					
Water content	Pure		1:10 (w/w)						1:1 (w/w)			
Type of agitation	Stirring		No agitation						Stirring		Ultrasound	
Equilibration time	Equilibrium		30 min		120 min		30 min		Equilibrium		120 min	
Compound (in order of elution, SPB-5)	PA fibre	PDMS fibre	Soil E	Soil F	Soil E	Soil F	Soil E	Soil F	Soil E	Soil F	Soil E	Soil F
1,3-Dichlorobenzene	41	39	1.4	20	1.6	30	10	35	7.8	81	5.6	40
Nitrobenzene	3.2	1.0	0.3	17	0.4	23	2.5	48	2.1	26	1.2	12
1,2,4-Trichlorobenzene	72	60	1.1	19	1.4	27	8.6	60	7.6	103	4.8	80
3-Chloronitrobenzene	9.9	2.4	0.3	30	0.4	44	1.9	76	2.4	68	1.2	22
2-Chloronitrobenzene	9.6	1.8	0.4	30	0.6	48	2.2	79	3.4	65	1.9	23
2,5-Dichloronitrobenzene	24	4.7	0.2	36	0.6	73	1.3	84	3.3	92	1.8	[illegible]
3,5-Dichloroaniline	28	1.2	0.04	7.9	0.07	19	0.1	30	0.5	84	0.6	
3,4-Dichloroaniline	20	0.8	0.03	3.6	0.02	13	0.03	14	0.2	55	0.3	[illegible]
1,2-Dinitrobenzene	2.5	0.08	0.01	1.3	0.08	7.0	0.06	4.3	0.9	26	0.3	1.6
3-Nitroaniline	1.5	0.03	$4\cdot10^{-4}$	0.2	$2\cdot10^{-3}$	1.9	$4\cdot10^{-3}$	0.7	0.02	10	0.01	1.0
4-Chloro-2-nitroaniline	10	0.1	$4\cdot10^{-4}$	0.3	0.01	2.7	$2\cdot10^{-3}$	1.3	0.1	15	0.03	1.7
4-Nitroaniline	1.8	0.04	$7\cdot10^{-4}$	0.06	$2\cdot10^{-3}$	0.4	0.01	0.2	0.07	4.1	0.04	0.5
2-Chloro-4-nitroaniline	6.2	0.04	$4\cdot10^{-4}$	0.05	$4\cdot10^{-4}$	0.8	–	0.3	0.02	10	0.01	0.7
2,6-Dichloro-4-nitroaniline	19	0.3	$6\cdot10^{-4}$	0.2	$4\cdot10^{-3}$	2.1	–	1.0	0.06	18	0.03	3.1
Pentachloronitrobenzene	94	65	0.05	10	0.3	38	0.3	39	3.1	96	1.44	51

mixing, extraction time. However, matrix effects determined by the soil characteristics, especially the organic carbon content, are so large that the quantitative analysis of real soil samples is not possible with calibration using a model matrix. Only for the lighter, non-polar analytes extracted from a soil with a low organic carbon content a nearly exhaustive extraction was achievable, so generally the inaccuracies caused by matrix effects in the analysis of real soil samples by HS-SPME cannot be avoided by improving the recoveries. Alternatively, a reliable calibration can be performed by standard addition within the linear range, whereas accurate quantification at trace level would be complicated by the non-linearity of the calibration curves at concentrations near the detection limits. HS-SPME should therefore mostly be regarded as a rapid and very valuable screening technique in soil analysis.

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