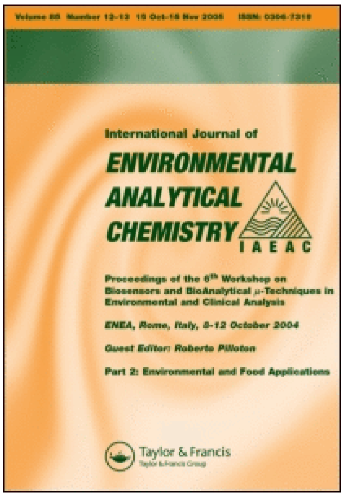

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ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN ENVIRONMENTAL WATER SAMPLES AND SOIL GAS BY SOLID-PHASE MICROEXTRACTION

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The basic principle of solid-phase microextraction (SPME) is equilibration. Therefore, all possible interferences on the extraction process should be taken into account in order to perform a reliable calibration for the quantitative analysis of environmental samples. Humic acids and suspended mineral oxides showed no effect on the SPME analysis of volatile organic compounds (VOCs), whereas salt had a positive effect on the extraction efficiency. The linearity was good in all cases, the precision of repeated analysis was around 5% average standard deviation, and detection limits were in the ng/l range. Thus, SPME can be applied for the quantitative analysis of VOCs in various environmental water samples, such as sea water, groundwater and heterogeneous samples like river and lake water containing suspended solids. SPME was established also as an alternative to liquid-liquid extraction in the study of TiO_2-catalysed photodegradation mechanisms. Finally, two new SPME sampling probes were designed and tested for rapid, on-site measurements of organic micropollutants in groundwater and soil gas. SPME is suited ideally to provide low-cost evaluation of groundwater properties in unconventional hydrogeologic settings, such as underground excavations, and to provide preliminary data on which to base the selection of boreholes for more extensive casing installation and instrumentation.

Keywords: Solid-phase microextraction; volatile organic compounds; water

INTRODUCTION

Well-established extraction techniques, like purge-and-trap, headspace, solid-phase extraction and liquid-liquid extraction, are available for the analysis of groundwater samples from groundwater wells. Unfortunately, those methods re-

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*Corresponding author. Fax No.: +39-332-785601; E-mail: torben.nilsson@jrc.it quire pumping of the groundwater to the surface, sampling into appropriate containers, and transport to the analytical laboratory. During all these steps serious sample losses and sample composition variations are possible. This is particularly true for the analysis of VOCs which are lost easily by evaporation during the pumping of the sample to the surface.

Consequently, a variety of downhole sampling devices have been developed in recent years.[1] However, each has limitations with respect to flexibility of sample type and sample size, maximum operating pressures and depth, portability, and adaptability to non-ideal field conditions. Only limited examples have been reported of *in situ* monitoring of specific groundwater contaminants.[2–3] These relay on optical sensor systems capable of measuring only a limited number of organic compounds in groundwater.

Performing on-site analysis in a mobile laboratory or using a portable gaschromatograph (GC) has a number of advantages, *e.g.* possibility to work in isolated areas, better representativity of samples containing VOCs, elimination of transport and storage of toxic and hazardous samples, rapid analytical response, and possibility of quick decisions in emergency situations. However, the analytical techniques have to fulfil special requirements as regards robustness and design in order to be applicable in the field. The relatively new, solventless extraction technique SPME[4–7] is ideal for field sampling. It is independent of sample volume and instrument configuration, the device is simple and portable, and it is impossible to plug the fibre with particulate matter. Moreover, SPME is a less expensive and faster alternative to traditional extraction techniques.

The extraction is based on equilibration of the analytes into an adsorbent material coated onto a fused silica fibre which is introduced directly into the sample[8] or exposed to the headspace over the sample.[9] Thus, all factors possibly having an impact on the equilibration should be examined in order to perform a reliable calibration for accurate quantitative analyses. Subsequently, the compounds are thermally desorbed directly into the GC injector without any clean-up or pre-concentration.

SPME has been applied successfully for the rapid analysis of various priority pollutants in aqueous samples already.[10–21] Previously, the effects of the extraction time,[10,13–16,18] the temperature,[11,18] different types of agitation of the sample,[12] the extraction approach[18,21] *i.e.* SPME directly from the aqueous phase[8] or headspace-SPME,[9] the methanol content[10,15,17] and NaCl addition[10,14–17,19–20] have been investigated thoroughly with spiked water samples. Furthermore, SPME was validated for the quantitative analysis of VOCs in drinking water in an inter-laboratory study.[21] SPME proved to be a reliable technique when the calibration and analyses were performed under controlled extraction conditions, and regarding accuracy, precision and detection limits SPME, purge-and-trap and headspace were equally valid.[21]

Hence, it is natural to wish to apply SPME for the analysis of groundwater and samples from rivers and lakes as well. Actually, the analysis of groundwater samples has been reported earlier.[13] However, the quantitative analysis of such samples might pose additional problems due to the higher content of humic substances and suspended solids. Previous results on the interactions between organic pollutants and humic substances[22] and adsorption of VOCs onto mineral oxides[23] prompted us to examine the possible influence of these factors on the SPME process. Furthermore, we describe here a device, invented and developed by us,[24] that allows for *in situ* extraction from groundwater.

EXPERIMENTAL

For the study of the effect of salt, humic acids and suspended mineral oxides on the SPME analysis spiked water samples containing 1,1,1-trichloroethane, trichloroethene and tetrachloroethene, being representative VOCs often encountered in environmental water samples, were prepared in 2 ml screw cap glass vials equipped with Teflon coated septa (Supelco). The neat compounds (Supelco) were used for the preparation of two spiking solutions in methanol containing 1 and 100 mg/l of each VOC, respectively. Appropriate volumes of these solutions were spiked into pure Milli-Q reagent water (Millipore), water containing 4% (w/w) NaCl, water containing 5 mg/l humic acids (Aldrich), water containing 1g/l TiO_2 and a 0.1 M solution of $NaClO_4$ (~ 1.2% (w/w)) containing 1g/l TiO_2 using a micro syringe in order to reach the concentrations 1, 10, 50, 200 and 1000 μg/l of each VOC, while keeping the methanol content of the sample below 1%.

The SPME procedure was 30 minutes extraction from unstirred samples at 20°C using fibres coated with 100 μm polydimethylsiloxane (Supelco). Immediately after, desorption was performed for 5 minutes at 250°C directly in the injection port of an HP 5890 series II GC with the split closed. 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 using hydrogen as carrier gas at 40 cm/s constant flow. The GC oven was operated with the following temperature program: 40°C for 5 minutes, followed by 8°C/minute to 150°C, then 50°C/minute to 250°C which was held for 3 minutes. The electron capture detector (ECD) was operated at 300°C with argon with 10% methane as make-up gas.

For the purpose of *in situ* extraction from groundwater a device in simple and rugged design was developed. Two prototypes are available of the device:[24] A

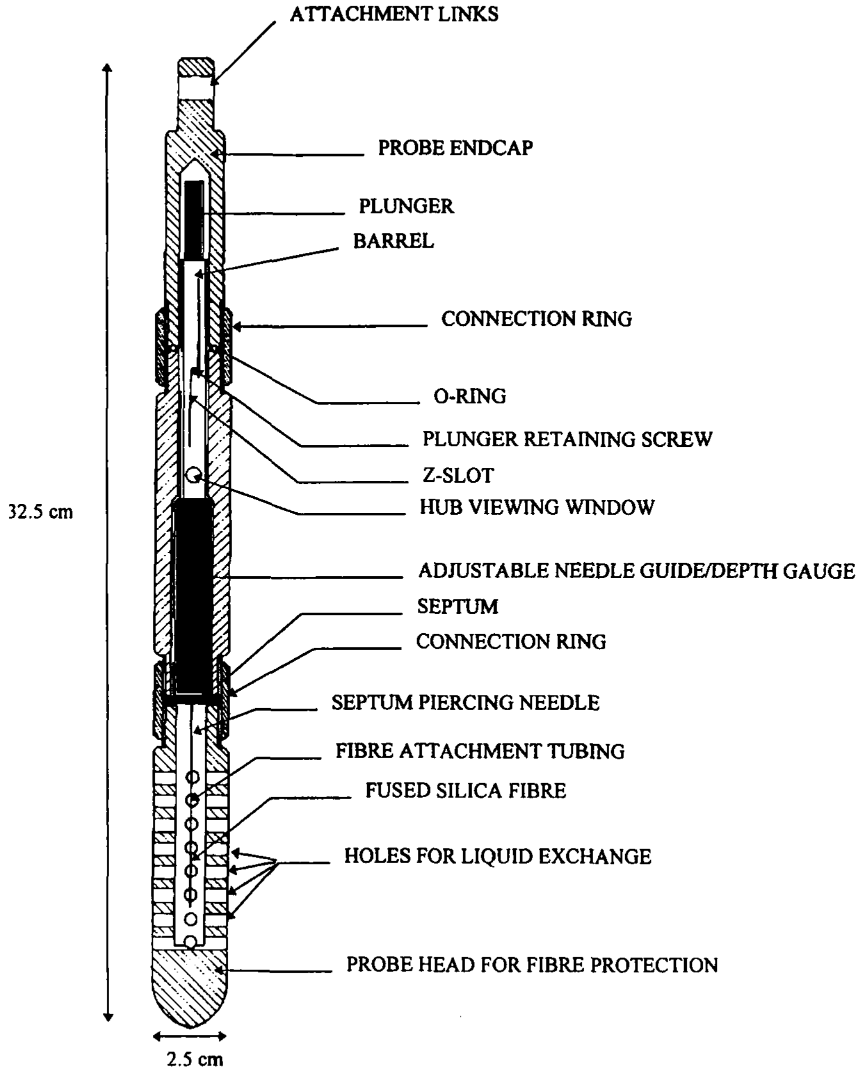

FIGURE 1 SPME device for *in situ* groundwater sampling from monitoring wells.

sampling probe for monitoring wells and a sampling probe for a drilling rod head. The first is a probe consisting in a hollow metal head with holes for the rapid exchange of the surrounding water with the inside volume, a SPME fibre mounted in a SPME holder assembly (Supelco) and an end-cap allowing for easy connection to a cord (see Figure 1). The following procedure is used for groundwater sampling: Firstly, the SPME fibre is extended out of the needle and blocked in this position by the plunger retaining screw. Then the device is introduced into the monitoring well and allowed to penetrate the groundwater surface. At this point the probe head fills up with water and the SPME process takes place. After an appropriate equilibration time, the probe is retracted to the surface and the fibre can be desorbed immediately in a portable GC or in a GC in a mobile laboratory. Analysis of soil gas close to the groundwater surface is also possible with the probe by equipping it with a sensor that registers the groundwater surface. The second prototype is similar to the first. However, it is designed to be adapted to the head of a cone penetrometer (see Figure 2). The extraction volume is consisting in a hollow probe with the end-cap open at the bottom for sample inlet. The SPME device can be actuated for sampling from the surface by compressed air. The sampling is level-determined which is a necessity in the investigation of groundwater contamination in heterogeneous geologic media.[25] The two prototypes have been tested during two measuring campaigns of the advanced mobile analytical laboratory (AMAL) developed in the frame of the EUREKA/EUROENVIRON project EU674. The preliminary testing took place during a measuring campaign at a former waste disposal site in Germany, while all the quantitative results reported here were obtained during a measuring campaign at a former industrial site in Italy. The SPME procedure for the quantitative analyses was 30 minutes extraction using a fibre coated with 100 μm polydimethylsiloxane (Supelco) directly in the groundwater wells or from unstirred samples collected in precleaned 40 ml screw cap vials equipped with Teflon coated septa (Supelco). The corresponding samples were taking from the same wells immediately before the *in situ* extraction and analysed shortly after (maximum 1–2 hours cool storage) at the same temperature, *i. e.* the natural temperature of the groundwater. The desorption was performed at 230°C directly in the injection port of a Varian 3400 GC mounted in the mobile laboratory. A 30 m × 0.25 mm (i.d.) Supelco SPB-5 capillary column with 0.25 μm film was used for the GC separation. The GC oven was operated with the following temperature program: 35°C for 5 minutes, followed by 8°C/minute to 220°C, then 30°C/minute to 270°C which was held for 3 minutes. Helium was used as carrier gas with a column head pressure of 20 psi (~ approximately 1 ml/minute). The GC was coupled to a Finnigan ITS-40 ion trap mass spectrometer (MS) (transfer-line 270°C) operated in the electron impact mode scanning from m/z 50 to m/z 350 in 1.5 second. The calibration curves were constructed by SPME analyses of spiked samples containing Supelco VOC mix 1–6 at concentrations from 500 ng/l to 500 μg/l performed under exactly the same conditions as the SPME analyses of groundwater. All quantifications were based on the area of one characteristic mass peak for each VOC.

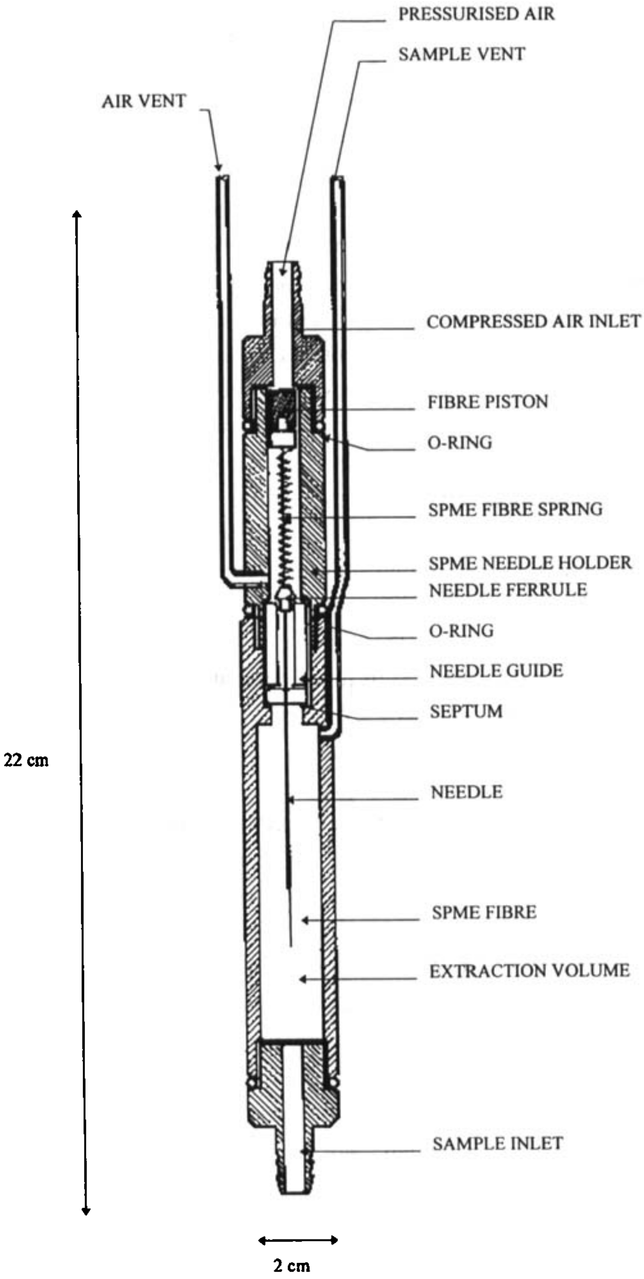

FIGURE 2 SPME device designed to be adapted to the head of a cone penetrometer for *in situ* groundwater sampling.

TABLE I Calibration curve data for spiked water samples containing humic acids, TiO_2 and salt.

SAMPLE COMPOSITION	*1,1,1-Trichloroethane*		*Trichloroethene*		*Tetrachloroethene*	
	Slope	r^2	*Slope*	r^2	*Slope*	r^2
Pure water	4025	0.995	1990	0.991	12784	0.998
5 mg/l humic acids	3901	0.994	2058	0.994	11786	0.994
1 g/l TiO_2	4292	0.996	2063	0.995	11628	0.987
1 g/l TiO_2 + 0.1 M $NaClO_4$	4712	1.000	2846	0.996	12110	0.963
4% NaCl	5573	0.995	2833	0.998	14774	0.995

RESULTS AND DISCUSSION

The results of the study of the influence of salt, humic acids and suspended mineral oxides on the SPME process are listed in Table I. It is seen that salt addition had a positive effect on the extraction efficiency as reported previously for other compounds.[10,14–17,19–20] This should be considered in the calibration for analysis of sea water samples. Furthermore, in general salt can be added for the purpose of improving the sensitivity of the method. The content of humic acids and TiO_2 showed no major effect (see Table I). The 5 mg/l humic acids is a typical concentration of dissolved organic carbon in surface water samples.[26] Its limited influence on the efficiency of SPME is in accordance with earlier results for triazines.[17] The standard deviation of repeated analysis was around 5% independently of the sample composition. The linearity was good in all cases (see Table I), and detection limits in the ng/l range could be estimated. Hence, SPME can be applied for the analysis of VOCs in a broad variety of environmental water samples, including heterogeneous samples, *e.g.* river and lake water containing suspended solids, groundwater and sea water. In the SPME analysis of soil samples[27] and more heavily contaminated water samples,[28] such as industrial waste water, stronger matrix effects have been reported.

TiO_2 was chosen as the model mineral oxide for its adsorbing properties with respect to chloroethenes.[23] Moreover, TiO_2 has a potential as a catalyst for the photocatalytic degradation of a number of volatile organic pollutants,[23,29–33] and thus it has been used in wastewater treatment.[32–33] Therefore, also samples containing 1 g/l TiO_2 in 0.1 M $NaClO_4$ like in photooxidation experiments were prepared. The successful analyses of these samples (see Table I) establish SPME as an alternative to the liquid-liquid extraction traditionally used in photodegradation studies. Besides being solventless and time-saving, SPME has the further advantage of requiring a much smaller sample volume than liquid-liquid extraction. This is of major importance when studying time-dependent reactions where

TABLE II Comparison of SPME performed *in situ* and in the mobile laboratory after traditional sampling from the same groundwater wells.

	Groundwater well S1, surface				*Groundwater well S2, surface*			
	Before pumping		*After pumping*		*Before pumping*		*After pumping*	
	In situ SPME [µg/l]	*SPME [µg/l]*	*In situ SPME [µg/l]*	*SPME [µg/l]*	*In situ SPME [µg/l]*	*SPME [µg/l]*	*In situ SPME [µg/l]*	*SPME [µg/l]*
Toluene	3.1	2.8	3.0	2.8	3.4	3.0	3.1	2.9
Tetrachloroethene	1.4	1.2	1.4	1.2	2.0	1.5	2.5	1.3
Ethylbenzene	trace	trace	trace	trace	trace	trace	trace	trace
m- + p-Xylene[1]	1.4	1.4	1.4	1.4	3.3	2.9	2.7	2.5
o-Xylene	1.5	1.4	1.6	1.6	1.7	1.6	1.6	1.4
tert-Butylbenzene	trace	trace	trace	trace	trace	trace	trace	trace
Naphthalene	0.6	0.6	0.8	0.7	1.4	1.4	1.3	1.3

Trace: No quantification was performed, because the compound was detected at a concentration lower than five times its detection limit. The average method detection limit was estimated to be around 200 ng/l.

[1] m- and p-xylene have similar mass spectra, and they co-eluted under the gas chromatographic conditions used in this study. Hence, the concentrations stated are the total amounts of m- and p-Xylene.

the volume preferably should be left approximately unchanged through-out the experiment. Hence, the first application of SPME in photodegradation studies will be published soon.[34]

The preliminary results obtained *in situ* with the SPME device shown in Figure 1 included detection and identification of a number of paraffins and toluene in groundwater. The results were confirmed by traditional sampling followed by headspace GC-FID analysis. Unless the SPME fibre is retracted into its steel housing (the needle) shortly after the sampling, a serious sample loss might occur by desorption of the more volatile compounds prior to analysis. This is especially true for the SPME device designed to be adapted to the head of a cone penetrometer which often cannot be retracted rapidly from the ground. Thus, this device has been equipped with a possibility to control the fibre retraction from the surface by compressed air (see Figure 2).

In Table II the results of SPME performed *in situ* and in the mobile laboratory after traditional sampling from the same groundwater wells are given. The results confirm the feasibility of the *in situ* sampling approach. Furthermore, the slightly lower results obtained in most cases after traditional sampling indicate that possibly it is advantageous to perform the extraction directly underground rather than pumping the sample to the surface prior to extraction as in the traditional methods. This tendency to obtain higher results with *in situ* SPME was clear, *i.e.* all of the results were higher or equal to those obtained by SPME after traditional sampling, although the differences were small and in most cases within the standard deviation of approximately 5%. Upon storage of the samples at ambient temperature prior to analysis some depletion was observed. This confirms earlier observations concerning sample loss during storage and transportation.[21]

The SPME device for *in situ* sampling was also tested for the screening analysis of soil gas during the measuring campaign in Italy. The findings of toluene and naphthalene were confirmed by collection of soil gas samples from the same sites on Tenax tubes.

CONCLUSION

Suspended mineral oxides and humic acids at levels typical for environmental water samples showed no effect on the SPME analysis of VOCs. Salt had a positive effect on the extraction efficiency. The linearity was good in all cases, and detection limits were in the ng/l range. Thus, it is concluded that SPME can be applied for the quantitative analysis of VOCs in a broad variety of environmental water samples, including river and lake water, groundwater and sea water. Furthermore, SPME fulfils the requirements for in-field measurements and the SPME device was designed for the extraction of VOCs from groundwater or soil gas directly underground has shown promising results.

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