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Short communication

Optimisation of solid-phase microextraction of volatiles

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Abstract

The results of a systematic study on the precision and repeatability of measurements of the headspace solid phase micro-extraction (SPME) with open-cap vials in combination with capillary gas chromatography in comparison with septum-sealed vials are reported. Benzene, toluene, ethylbenzene, and xylene isomers (BTEX) were used as the target analytes in the investigation of spiked water samples at concentration levels of 42.5 μg l^{-1}. The dependence of a sample volume versus peak area showed maximum SPME recovery. The influence of sample volume on the precision and the time of taking the sample on the losses of volatile analytes was examined.

Keywords: Solid-phase microextraction; Open-cap vials; Septum-closed vials; Water analysis; Volatile compounds

1. Introduction

Solid phase micro-extraction (SPME) is an established method for sample preparation in the analysis of volatile and semi-volatile, polar and non-polar compounds in various matrices. Several review articles summarise the theory of the partitioning of analytes between the sample matrix or its headspace and the polymeric film on the SPME fibre, optimised methods of compound extraction and coupling to gas chromatography for their thermal desorption, separation and quantitation [1–7].

The most frequent sample matrix for SPME has been water [2,4,6,7]. In the analysis of volatile organic compounds (VOCs), in order to avoid contamination of the fibre with the sample matrix, much attention has been devoted to headspace sampling. Headspace SPME is preferred due to faster equilibrium times for VOCs compared to direct sampling [8–10] and due to the higher selectivity when dirty samples are analysed [1]. In addition, the GC column is protected against contamination from high-molecular mass non-volatile compounds.

Recently, the headspace SPME method using ''open-cap vials'' was developed by our group [11]. The caps made of teflon contain a narrow bore capillary in the centre. Concern about the potential losses of volatile analytes through the bore has been negated by our preliminary experiments showing that the loss of volatiles (benzene, toluene, ethylbenzene and xylene isomers; BTEX) as model compounds in the spiked water samples is negligible under the experimental conditions used. The linearity of the preconcentration and GC measurements was investigated: minimum detection limits were found to be very good for the determination of BTEX components in the concentration range 4.25–4250 μg l^{-1} in water.

Open-cap vial SPME allows for easier sample manipulation using the SPME device when com-

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pared to septa-closed vials. Cost savings for septa are also a welcome side-effect. The open-cap vials method applied to SPME has already been successful in the analysis of other groups of volatile oxygenated compounds of environmental and/or industrial interest in water matrix [12].

According to our preliminary experiments the general philosophy behind the technique is that it is better to have a constant and predictable loss of analyte than a variable unpredictable loss due to poor septum performance [11]. However, the technique introduces more parameters into the system, in particular the time of taking the sample. Therefore, currently this device is not recommended with a classical autosampler.

In the present paper we report the results of a systematic study on the precision and repeatability of measurements of headspace SPME with open-cap vials and septum-sealed vials in combination with capillary gas chromatography. BTEX were used as the target analytes in the investigation of water samples. The influence of a sample volume as well as the time of taking the sample was investigated.

2. Experimental

2.1. Materials and methods

A standard stock solution containing benzene (Be), toluene (To), ethyl benzene (EtBe), *p*-xylene (*p*-Xy), and *o*-xylene (*o*-Xy) (E. Merck, Darmstadt, Germany) was prepared by differential weighing of ~87 mg of each compound in 10 ml methanol (LiChrosolv, E. Merck, Darmstadt, Germany with a purity >99.5%). The stock solutions were stored in a refrigerator at −18 °C. Spiked water samples were prepared daily by adding a portion of the stock solution (10 μl) to 25 ml of deionised water and then adding 1.2 ml of this solution to 100 ml of deionised water yielding a final concentration of ~42.5 μg l^{-1}. An aliquot of 1.3–3.1 ml of the water sample was pipetted into a 4-ml glass vial (Chromacol, Herts, UK) either containing/or without a stirring bar, which was closed and stored at 4 °C before analysis using headspace SPME.

Headspace SPME was performed with stirring. The vials with screw caps were stoppered with open teflon caps manufactured in our workshop [11], or with teflon-lined septa (Chromacol, Herts, UK) and placed in a small thermostatted water bath (constant temperatures (25 °C) were achieved after 7 min of mixing). The fibres (100-μm polydimethylsiloxan, PMDS) were reproducibly placed in the headspace above the water samples in the centre of the vials 2 mm above the solution prior to mixing. During the mixing process, due to the formation of a vortex, the fibre distance from the solution increased. Headspace sampling was carried out over a period of 5 min. The fibre was withdrawn into the needle and inserted in the GC. The desorption time in the GC injector was 3 min with the valve closed for 1.5 min.

2.2. Instrumentation

Standards were weighed on Sartorius MC 1 analytical balances (Sartorius, Gottingen, Germany) with precision ±10 μg. A manual SPME device (Supelco, Bellefonte, PA, USA) with fibre coated with 100 μm PMDS (Supelco, Bellefonte, PA, USA) was utilised. New fibres were conditioned under a helium stream at the desorption temperature 250 °C (recommended by the manufacturer) for 60 min. The temperature of water samples was controlled by means of a thermostat (Julabo F 25, Julabo Labortechnik, Seelbach, Germany) with precision ±0.01 °C.

A gas chromatograph (HP 5890 Series, Hewlett-Packard, Avondale, PA, USA) fitted with a flame ionisation detector (FID), split/splitless injector system and capillary column (CP-Sil 13 CB, 25 m× 0.32 mm I.D., film thickness 1.2 μm, Chrompack, Middelburg, the Netherlands) combined with a deactivated empty precolumn (1 m×0.53 mm I.D.) was used. The fibres were desorbed in the GC injector in splitless mode at 180 °C. At the onset of fibre desorption, the column temperature was kept isothermal at 35 °C for 1.5 min, then increased at 35 °C/min to 88 °C, then at 2 °C/min to 95 °C, and at 40 °C/min to 150 °C. The detector temperature was 280 °C. The carrier gas was high purity helium (>99.996%) with linear velocity 29 cm/s measured under isothermal conditions at 100 °C.

3. Results and discussion

In the first step much attention was devoted to the repeatability of the spiked water sample preparation at the concentration level 42.5 μg l^{-1}. Potential losses of volatile compounds during sample preparation were tested. SPME–GC results showed that the vials with stock solution of BTEX, after thermostatting to laboratory temperature and after multiple openings (second, third) and withdrawing, showed significant losses (up to 14% of the peak areas). All further experiments were therefore conducted with a new vial of the stock solution.

3.1. Influence of the sample volume on preconcentration

The influence of the sample volume on SPME–GC response and precision of measurements was investigated for samples closed with teflon-lined septa and open-cap vials.

For sample volumes of 1.3, 1.9 and 2.5 ml in vials closed with teflon-lined septa, the measured peak areas were observed to linearly increase. However, for a sample volume of 3.1 ml, the peak areas slightly decreased (Fig. 1a). Each point in Fig. 1 represents the average peak area of five measurements. The repeatability of measurements expressed by the relative standard deviation was found to be sample volume dependent. The best repeatability was found to be for the lowest volumes 1.3 and 1.9 ml with RSD values in the range 1.5–2.5%. With higher volumes of 2.5 and 3.1 ml, RSD values increased to 3.9 and 4.2%, respectively.

With open-cap vials, similar results of the dependence of peak areas on the sample volume were obtained and are shown in Fig. 1b. A higher degree of repeatability was obtained with open-cap vials for all the tested volumes with the exception of 3.1-ml sample volume. RSD values for volumes 1.3–2.5 ml were not compound-dependent and were in the range 1–1.5%. For the sample volume of 3.1 ml, RSD values increased to 4.8%. They were observed to be dependent on the VOCs analysed, increasing from benzene up to *o*-xylene.

The precision of SPME is considered to be very high as it is a single-step method and therefore the random sources of error associated with transfer of

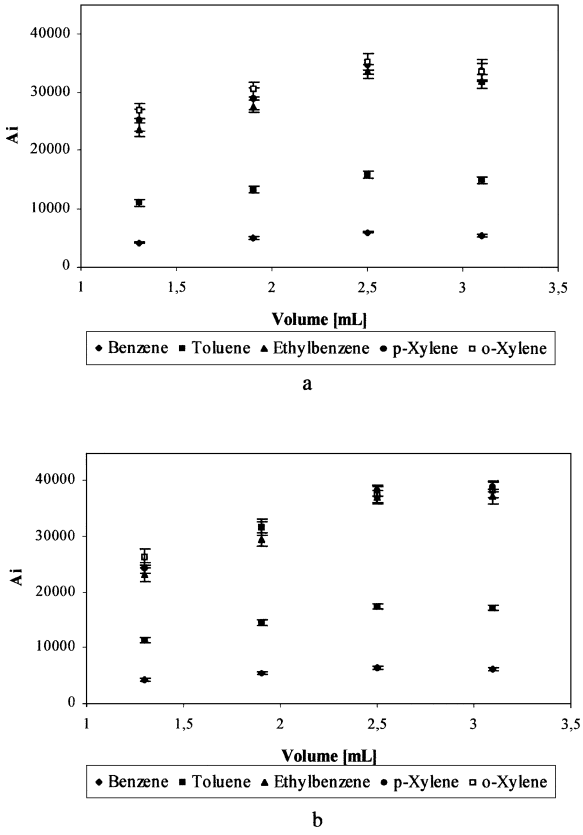


Fig. 1. The dependences of peak area of BTEX determined by head-space SPME–GC with PMDS fibre on the volume of the spiked water sample with concentration level 42 μg l^{-1} in 4-ml vials: (a) septum-closed vials; (b) open-cap vials.

analytes are minimised [3,13]. Precision is typically ~5% RSD for manual operation. With headspace SPME of volatile organic compounds the precision expressed by the relative standard deviation depends on the type of compounds analysed, the SPME conditions used, analytes concentration level, sample matrix and number of measurements [8,12,14,15].

The dependence of peak area on the sample volume in the range used, and the observation of a maximum for all the analytes under study (Fig. 1a,b), can be explained by the following assumption. If we consider, that the mass transfer takes place as the equilibrium process, then the dependence of the quantity of the analyte in the gas phase, n_g, as the function of volume of the liquid phase, V_l, should be a Langmuir-like curve. The results show that the

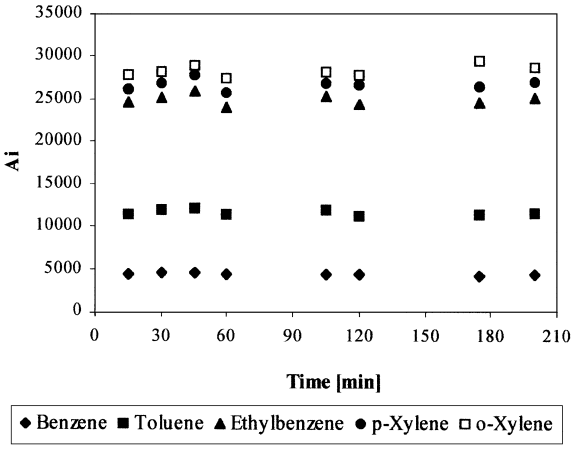
curves have maxima, which indicates that the kinetics of the mass transport from the liquid phase to the gas phase plays a certain role.

The dependences in Fig. 1 are relatively flat, up to the maximum (volume 2.5 ml) and could be considered as straight lines, as observed from the results of the linear regression (Table 1).

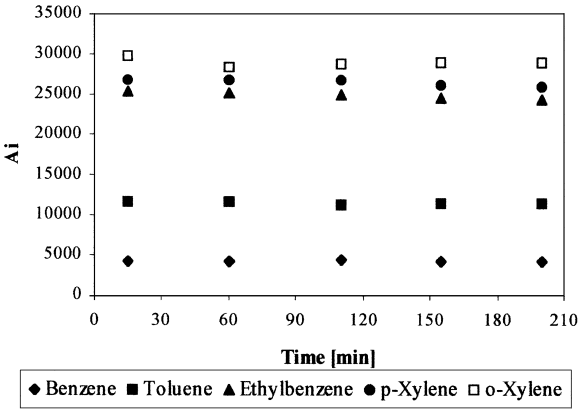
3.2. Influence of the time of taking the sample on losses of analytes

Septum-closed vials have been utilised in both manual and automatic modes of sampling for SPME [3]. For the open-cap vials the concentration of most volatiles decreases with time, so that this device is not recommended for use with a classical autosampler [11]. The present study was performed to determine the losses of analytes in spiked water samples stored at 4 °C and laboratory temperature (24 °C) in 4-ml vials closed with open-caps directly after filling with BTEX solution and the results were compared with the septum-closed vials. The sample volume 1.3 ml was chosen, as with both types of vials very good repeatability of SPME–GC was obtained. The dependence of BTEX peak areas on the time of sample storage at 4 °C is shown in Fig. 2. Up to 200 min the graphs do not show a decrease in the peaks areas. As in the previous case, better repeatability was obtained with the open-cap vials (RSD in the range 1.4–2.9%) compared to septum-closed vials (RSD in the range 2.4–3.6%).

The measurements at 24 °C showed good stability of peak areas with the septum-closed vials. For up to 165 min of storage peak areas were found to be within the repeatability of measurements. Further storage resulted in a measurable decrease of the peak areas. For example, at 200 min the reduction in peak area was up to 10%, while at 300 min it was up to 16%. With the open-cap vials, a decrease of peak area was also observed with increasing storage time at laboratory temperature. The percentages of the losses were compound dependent (Table 2). From the obtained results, it follows that with the septum-



a



b

Fig. 2. The dependences of peak area of BTEX determined by head-space SPME–GC with PMDS fibre on the time of sample storage at 4 °C (1.3 ml of the spiked water sample with concentration level 42 μg l^{-1} in 4-ml vials): (a) septum-closed vials; (b) open-cap vials.

Table 1
Correlation coefficients (*r*) of the linear dependence of BTEX peak areas versus spiked sample volume after headspace SPME–GC measurements using vials with teflon-lined septa and open-cap vials

Compound	Vials with septa, *r*	Open-cap vials, *r*
Benzene	0.9920	0.9997
Toluene	0.9955	1.0000
Ethylbenzene	0.9949	0.9985
p-Xylene	0.9913	0.9996
o-Xylene	0.9981	0.9994

Concentration ~42.5 μg l^{-1}.

Table 2
The dependence of values of BTEX percentages of peaks areas ($\%_{Ai}$) after headspace SPME–GC measurements on the storage time of spiked water samples in 4-ml open-cap vials at 24 °C

Time (min)	Compound				
	Benzene, $\%_{Ai}$	Toluene, $\%_{Ai}$	Ethylbenzene, $\%_{Ai}$	*p*-Xylene, $\%_{Ai}$	*o*-Xylene, $\%_{Ai}$
15	100.0	100.0	100.0	100.0	100.0
40	99.4	99.1	101.3	100.6	101.5
70	93.7	98.1	100.5	100.0	100.1
100	91.5	91.7	92.0	92.0	94.0
130	90.4	92.7	91.7	90.4	93.4

Concentration ~42.5 μg l^{-1}.

closed vials utilisation of autosampler is acceptable, but only within a limited period of storage in the autosampler. With open-cap vials utilisation of autosampler is more limited. Using a well chosen internal standard, quantitation of the concentration of analyte is more precise.

4. Conclusions

The results demonstrate the feasibility of headspace SPME with open-cap vials for the analysis of aqueous non-polar volatile compounds, such as low molecular mass alkylbenzenes–BTEX, utilising polydimethylsiloxane fibre as the sorbent of substrate. Precision of the SPME technique with the open-cap vials is very high and compares favourably with septum-closed vials. In both types of vials, the precision is dependent on the sample volume. The dependence of the peak areas for the BTEX samples on the volume of the spiked water samples at the concentration level 42.5 μg l^{-1} exhibits maxima for SPME recovery. Within a certain volume range the dependence could be considered as linear. Increasing the sample volume, however, reduces the precision of measurements.

With open-cap vials negligible losses of the volatile contaminants were observed using the SPME procedure. Effect of the time of taking the sample on SPME–GC results was examined open-cap vials and the results were compared to septum-closed vials at 4 °C and laboratory temperature. The results demonstrated that the losses of volatile analytes, as expected at laboratory temperature, increased with storage time and were greater for the open-cap vials. Sampling the vials using the autosampler is therefore more reliable for the septum-closed vials. Well chosen internal standard(s) would improve the reliability of analytical results in both types of vials.

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