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Applicability of a SPME method for the Rapid Determination of VOCs

Alexandre Béné, Jean-Luc Luisier*, and Antoine Fornage

Abstract: A fast method for monitoring volatile organic compounds in water and air is described whereby the VOCs are adsorbed on a SPME and then desorbed directly in a flame ionization detector (FID) or a photoionization detector (PID). The signal obtained provides a global measure of the VOCs present in water or air. In most cases, such as accidental pollution by hydrocarbons, wastewater from industry or control of the absence of solvent in air, this information is very relevant. The analysis can be handled by a non-professional with a throughput of 10 samples/h. Low levels of about 10 μg organic volatile compounds per liter of water can be measured.

Keywords: Environmental pollution · Organic solvents · Screening · SPME · VOC

1. Introduction

In our previous publications [1][2] we have proposed a direct method for the measurement of volatile substances with solid phase micro extraction (SPME) and we have shown that this method could be applied with success to different food problems [3]. We describe here the application of our methodology in the determination of volatile organic compounds (VOC) in water and in air.

The determination of VOCs is an important task for governmental and industrial laboratories. Among other methods, SPME followed by gas chromatography was proposed for environmental applications [4][5]. Limits of determination in the low μg/l range have been reported in various publications [6][7], always after GC separation. The use of a global detection system, like UV absorption in conjunction with SPME, was also tested with success [8]. All these methods need trained personnel for the handling of the apparatus and for the interpretation of the data.

The SPME technology has mostly been used as a pre-concentration technique in conjunction with chromatographic separation of the adsorbed substances. But in many instances a separation is not necessary. This is the case for instance in the monitoring of an industrial process, in the monitoring of an environmental pollution where the pollutant is known, or more generally in quality control. The method proposed here avoids chromatographic separation and is well adapted for screening measurements of VOCs at low levels and, as the SPME adsorption method can be transferred without any adaptations to gas chromatography, it may be ideally complemented by the methods of the analytical laboratory.

With SPME two basically different absorption methods can be used for the determination of VOCs in water [9]: the immersion method and the headspace method. The latter is preferred because the fiber does not come in contact with the liquid, it can be used for a much longer time period and the matrix interference is minimized. These are the reasons why we have applied the headspace method.

2. Experimental Part

2.1. *Material and Reagents*

SPME fibers: 100 μm polydimethylsiloxane (PDMS), 75 μm carboxen/polydimethylsiloxane (CAR/PDMS) and 7 μm polydimethylsiloxane were obtained from Supelco, Switzerland. Vials '22 ml' (effective volume 25 ml) with screw caps and PTFE septa come from Supelco, Switzerland. Vials '20 ml' (effective volume 22 ml) with crimped caps and PTFE septa, used with the autosampler (Pal Combi V 2.0 from CTC Analytics AG, Switzerland) are from Brechbühler AG, Switzerland.

Benzene, ethylbenzene, toluene, cyclohexane, isooctane, dodecane, hexadecane, chloroform are from Fluka Chemie AG, Switzerland. Ethanol, acetone and dichloromethane come from Siegfried, Switzerland. The mixture of xylene isomers is from Merck, Germany. Acetonitrile is from Amman Technik AG, Switzerland. The water used for the preparation of the standard solutions is prepared with a Milli-Q filtration system from Millipore.

2.2. *Apparatus*

The experimental apparatus used can be seen as a simplified gas chromatograph without separating column and is des-cribed in [1]. It consists of a gas chromatography injector for wide bore columns, linked to the detector by a short capillary of 0.32 mm internal diameter and 30 cm length. The detectors are a FID (Carlo Erba EL 980). A flow of carrier gas (helium or nitrogen) drains the desorbed volatiles from the injector to the detector.

The experimental conditions are the following: injector temperature 225 °C, detector temperature: 250 °C. Helium flow rate 50 kPa 2 ml/min, hydrogen 60 kPa 750 ml/min, air from the laboratory filtered over active charcoal. The signal obtained is a simple peak with an apex at about 20 sec after injection and is interpreted using the

*Correspondence: Dr. J.-L. Luisier
University of Applied Sciences (HEVs)
Competence Group 'Process Engineering'
Route du Rawyl 64
CH-1950 Sion
Tel.: +41 27 606 86 55
Fax: +41 27 606 86 15
E-Mail: jluc.luisier@hevs.ch

integration program ChromCard (Fisons Instrument, ver. 1.21). The limit of determination (LOD) is calculated by using the equations proposed by Hädrich and Vogelsang [10].

The standard solutions were prepared by diluting the compound to be measured directly in water. The diluted standard solutions were used on the day of preparation. Two measurement procedures were developed. The *procedure 1* for determination with an autosampler is the following: pipette 8.0 ml of solution in a crimped cap vial, close the vial with the septum cap and place it on the autosampler. The first measurements are made after at least half an hour. The autosampler program is the following: pre-extraction time: 2 min; extraction temperature: 30 °C; agitation speed: 250 rpm; agitation on time: 5 s; agitation off time: 2 s; extraction time: 2 min; desorption time: 2 min. This allows for 10 measurements per hour.

The *procedure 2*, for manual operation is the following: pipette 8.0 ml of the water solution in the screw cap vial; close the vial with the septum cap, stir for at least 20 min in a water-bath at 30 °C (equilibration time), then extract with the SPME for 2 min and desorb immediately in the measuring device.

3. Results and Discussion

The ratio headspace/water plays an important role for the volatile concentration in the headspace as predicted by Henry's law. If the ratio headspace/water decreases, the concentration in the headspace increases and hence the signal height will be higher as it is proportional to the headspace concentration. Table 1 shows the area of the signal obtained by keeping the total volume constant (25 ml) while increasing the volume of a 60 µg/l aqueous solution of toluene in the vial. The good agreement between the measured and the calculated signal height*width shows that our system closely follows Henry's law.

The limit of detection (LOD) reported for different organic compounds using SPME lies in the low µg/l range or lower. These limits were measured with a FID and a gaschromatographic separation process. In our case, there is no separation and the LOD is due to the blank of the measurement, which comprises the noise of the signal, the signal from water used for the dilution and the effects of the SPME fiber. The noise of the FID signal lies at 0.003 mV*s and is negligible. However, the blank cannot be ignored and is mainly due to disturbances in the flow of the carrier gas and probably in the introduction of oxygen through the fiber. As no separation is made, this zero signal, which would be interpreted as a 'solvent peak' in gas chromatography is the real limiting factor for quantification. This signal lies at about 18 mV*s (values as height × width at half height).

Table 1. Effect of the volume ratio headspace/water on signal area

Headspace volume [ml]	Water volume [ml]	Ratio Headspace/water	Height * Width [H*W]	Calculated H*W
21	4	5.25	94	76
17	8	2.13	117	117
9	16	0.56	161	161

The choice of the type of fiber is especially important at the limit of determination. The selectivity of the SPME fiber is discussed in different papers (see [9], chap. 5) and can be quickly tested with our device. Different coatings were tested, each one having a specificity for a given analyte. Using optimized laboratory conditions may lower the determination limit by a factor ten or more for a particular analyte, but at the cost of throughput. For instance, with the CAR-PDMS fiber and an extraction time up to 30 min the LOD goes down to 1 ppb for benzene, toluene, and ethylbenzene, but these conditions would not fullfill the goals of a rapid method. Solvents with a high boiling point (*e.g.* hexadecane) need a higher injector temperature, 300 °C instead of 225 °C, to desorb from the fiber. Furthermore the desorption is slower and although there is no column, the time for the apex of the peak (retention time) is longer than for the lighter solvents.

One of the major interests in a rapid method for volatile compounds lies in the determination of petroleum products or aromatic hydrocarbons. The BTEX (benzene, toluene, ethylbenzene, and xylenes) components are frequently used as standard substances for this type of investigation. Hydrocarbons of the alkane type are also of great interest. The range of determination with our method goes from the µg/l range to over 500 mg/l for benzene and is very large. Fig. 1 shows a high concentration range for current lipophillic substances using a FID, measurement procedure 2 and the PDMS fiber. With this procedure, the LOD is between 10 and 30 µg/l for the different BTEX components.For lower concentrations, measurement procedure 1 has to be slightly modified by using a CAR-PDMS fiber and an extraction time of 30 min. Fig. 2 shows the calibration curve obtained under these conditions.

With hydrophilic solvents the determination limits are higher due to their higher solubility in water, their lower response on the FID and the low concentration of solvent in the headspace as indicated by their Henry's coefficient. The choice of the SPME fiber type is critical, as well as the choice of the measurement conditions. The extent of the concentration range towards

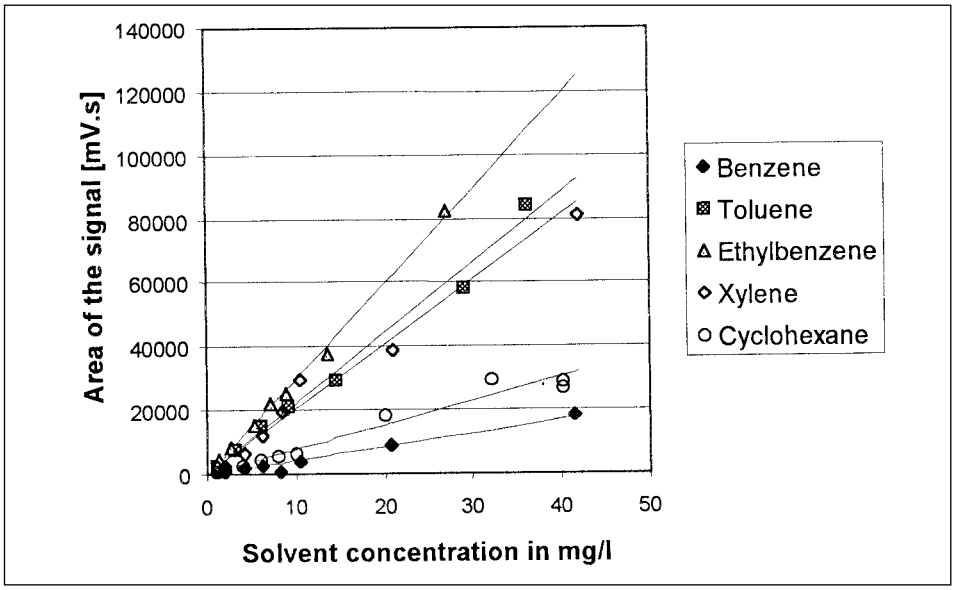

Fig. 1. Measurement range of concentration for lipophillic substances in water

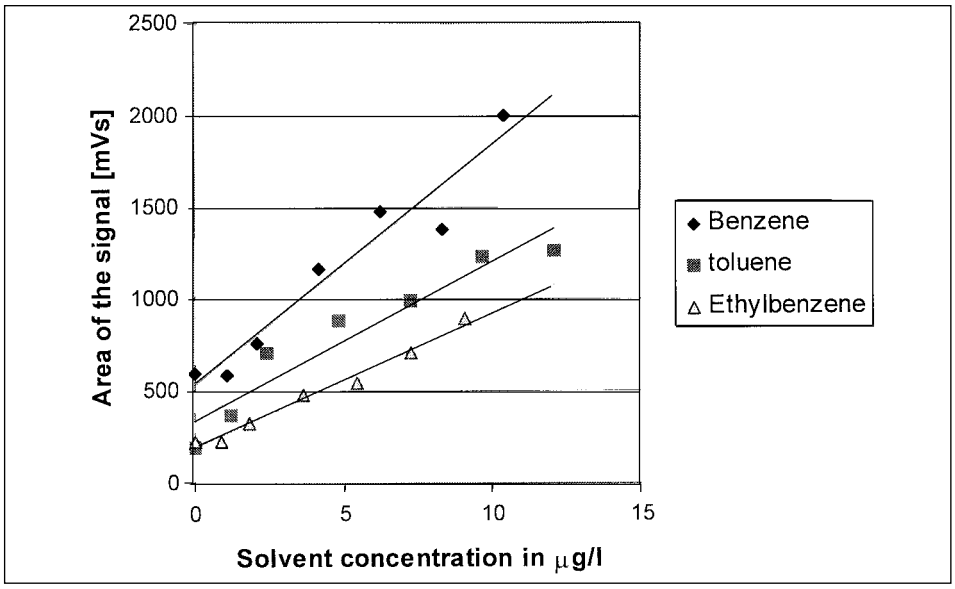

Fig. 2. Calibration at low concentrations for BTEX components

higher concentrations was not investigated, but for alcohols it is possible to make measurements in the percent range with good accuracy. For chlorinated solvents, the FID is not the best detector, the ECD may improve the response; nevertheless, we have tried with success the two most commonly used chlorinated solvents with a FID. At a low concentration range, using the standard conditions, the determination limit lies at 10 µg/l and the linearity of the determination is good over two orders of magnitude.

For the measured components, the domain of applicability of the fast method is reported in Table 2. Improvements of these determination limits can still be made by choosing a more appropriate type of fiber, modifying the extraction time, the volume of measurement, the addition of salts, the temperature of the sample, and the injector temperature, but a lower thoughtput.

Using a photoionization detector could further improve the limits of determination in some cases, in particular for ethanol, where the LOD is lowered by a factor of about 50. For dichloromethane and toluene, the LOD were of the same order of magnitude as with a FID.

Conclusion

The proposed method allows a rapid measurement of the organic solvents in water or in air at low levels and the response is mostly linear over several orders of magnitude. As we have focused on an easy and rapid method, improvements of the procedure would permit to reach lower levels but at the cost of lower throughput. It should be emphasized that the method does not allow for a differentiation of the compound responsible for the signal. This can be done by using the same sampling procedure and analyzing the sample in a traditional way with gas chromatography.

Table 2. Limits of determination in mg/l (ppm) in untreated water with the standard measurement procedure and a FID

Solvent	PDMS 100 µm	CAR/PDMS 75 µm
Benzene	0.015	>0.01
Toluene	0.010	>0.01
Ethylbenzene	0.015	>0.01
Xylenes	0.030	>0.01
Cyclohexane	0.065	>0.15
Isooctane	3	10
Dodecane	0.2*	>0.2
Hexadecane	0.08*	>0.7
Ethanol	>1	1
Acetone	1	0.2
Acetonitrile	>1	0.8
Chloroform	0.1	0.02
Dichloromethane	0.1	0.02

* PDMS 7 µm

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