Solid phase microextraction of volatile aromatic hydrocarbons from soil

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A headspace solid phase microextraction technique for determination of volatile aromatic hydrocarbons in soil is suggested. A solid phase microextraction was performed with polydimethylsiloxane fiber film 100 mm thick. Optimal extraction conditions were: extraction was carried out for 30 min from headspace of dry humic soil at a temperature of 60 °C and desorbed for 1 min at 190 °C. Precision, linearity, detection limits for benzene, toluene, o-xylene and p-xylene were determined. It was demonstrated that the extraction efficiency strongly depended on the humidity of soil. Standard addition method enables to eliminate the influence of moisture on the results of the analysis.

Key words: solid phase microextraction, gas chromatography, volatile aromatic hydrocarbons, soil

INTRODUCTION

Volatile aromatic hydrocarbons are important constituents of petroleum and petrochemical derivatives, common industrial solvents. They show a higher water solubility than the other petroleum components and can contaminate groundwater. Because of their toxicity, ubiquitous occurrence in natural, drinking and waste waters, they are often used as target analytes in environmental studies, and there is an increasing demand for the development of efficient and reliable analytical techniques.

Soil is a complicated matrix, it contains many organic compounds, and they may interfere with the chemical analysis of volatile aromatic hydrocarbons. The most difficult task in the chemical analysis of volatile aromatic hydrocarbons is extraction of the analytes from the soil and their purification. Classical solvent extraction techniques are laborious and require large amounts of solvent, while environmental regulations place restrictions on solvent use in laboratories. Other techniques such as supercritical fluid extraction and accelerated solvent extraction require expensive extraction equipment. So there was a need for new more convenient analytical techniques.

A modern extraction and concentration technique, solid phase microextraction (SPME), introduced by Pawliszyn et al. [1–3] helps to facilitate the extraction of volatile aromatic hydrocarbons from soil and to avoid severe background interference. It requires no solvents, is experimentally simpler than the other extraction techniques. This technique uses a fused fiber coated with a thin layer of a selective coating such as polyacrylate, polydimethylsiloxane, carbowax-divinylbenzene, polydimethylsiloxane-divinylbenzene, carboxen-polydimethylsiloxane to extract organic compounds from air, water or soil samples. Analytes are adsorbed onto the fiber. The fiber is transferred to the injection port of the gas chromatograph, where thermal desorption and transfer of the analytes onto the GC column take place.

Several applications of SPME for the analysis of volatile aromatic hydrocarbons in water have been reported [4–6].

The main objective of the present work was to examine the applicability of SPME for a simple and efficient determination of volatile aromatic hydrocarbons in soil.

EXPERIMENTAL

Chemicals and Samples

The reagents used (benzene, toluene, o-xylene, p-xylene and ethanol) were obtained from Merck (Darmstadt, Germany). All chemicals were of analytical-reagent grade and were used without further purification.

Stock standard solution of aromatic hydrocarbons in ethanol contained 28.0, 28.7, 28.2 and 27.4 g l^{-1} of benzene, toluene, o-xylene and p-xylene in ethanol, respectively. Standard solutions were prepared by diluting the stock standard solution in ethanol to desirable concentrations.

Humic soil "Veenbaas" (Holland) was used for the experiment. The content of organic materials in the soil is not less than 30%. Soil was previously dried at 105 °C for 8 hours. The chromatograms obtained after exposure of the polydimethylsiloxane fiber to the headspace of the soil for 30 min at 60 °C and after a consequent desorption in the injector at 220 °C for 2 min did non contain peaks of aromatic hydrocarbons.

Instrumentation

In [7], it was shown that the thickness of the coating determines the sensitivity and the relative error of extraction. In order to achieve better sensitivity and smaller relative standard deviations, in our work SPME was performed with a biggest commercially available polydimetylsiloxane fiber film 100 μm thick housed in its manual holder (Supelco Bellefonte, PA, USA). New fibers were conditioned under a nitrogen stream at a temperature of 250 °C for one hour.

Gas chromatography was carried out in a Chrom 5 (Czech) gas chromatograph equipped with a flame ionisation detector coupled with integrator. A glass column 2.5 m long and 3 mm i.d. packed with Separon SDA (150 μm) was employed. The following gas chromatographic conditions were used: flow rate of nitrogen 45 ml min^{-1}, hydrogen 30 ml min^{-1}, air 300 ml min^{-1}. The temperature of the injector was 190 °C, of the detector and of the column 180 °C.

RESULTS AND DISCUSSION

Effect of desorption temperature

To determine the optimal desorption temperature, the injector temperature was from 180 to 220 °C. No lower temperatures were examined, because the injector temperature should not be lower than the column temperature which in our case was 180 °C. In this and in the following experiments (if not specified differently), 10 g of humic soil spiked with 200 μl of standard solution containing 280, 287, 282 and 274 mg l^{-1} of benzene, toluene, o-xylene and p-xylene respectively was used. Humic soil was chosen, since we expected that because of the presence of a big quantity of organic matter the retention of aromatic hydrocarbons on it would be stronger that on sandy soil and it would take more time to reach an equilibrium between the soil and headspace. The fiber was exposed to the headspace of humic soil spiked with a standard solution of aromatic hydrocarbons for 15 min at room temperature and then thermally desorbed for 2 min. As can be seen in Fig. 1, until 190 °C the desorption increased and then became stable. So for the further work the lowest (190 °C) temperature from the optimal temperature range was chosen. It enabled to achieve an optimal desorption and on the other hand to minimize the thermal bleed of the polydimethylsiloxane film.

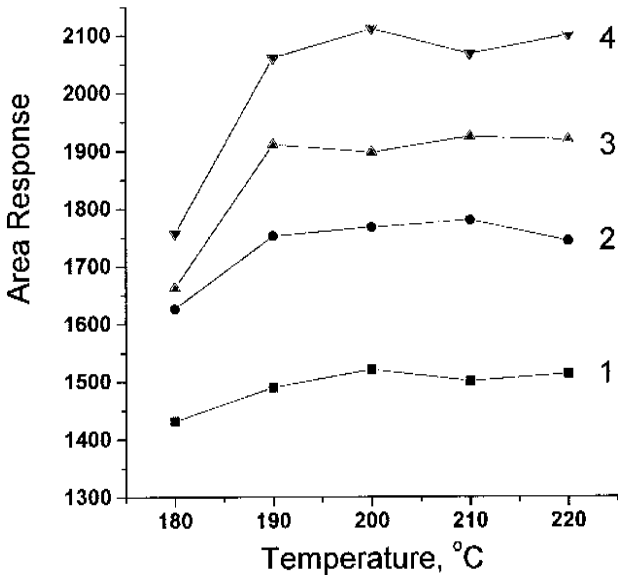

Fig. 1. Effect of desorption temperature on the peak area of *1* – benzene (5.607 μg g^{-1}), *2* – toluene(5.750 μg g^{-1}), *3* – p-xylene (5.487 μg g^{-1}), *4* – o-xylene (5.642 μg g^{-1}). The fiber was exposed for 15 min to headspace at room temperature and desorbed for 2 min

Effect of desorption time

At a temperature of 190 °C the effect of desorption time on desorption efficiency was studied. Desorption times from 1 s to 5 min were investigated. The results showed (Fig. 2) that benzene as an analyte with the lowest boiling point was desorbed most quickly and for xylenes the desorption time was longer, but 1 min of desorption time was quite sufficient for all the analytes studied.

Effect of sorption temperature

The effect of sorption temperature was studied by exposing SPME fiber for 15 min in the headspace of a soil sample at a temperature of 20–80 °C. Extraction curves showed that the amount of the analytes adsorbed increased with a temperature up to 60 °C for benzene and toluene and up to 70 °C for o-xylene and p-xylene (Fig. 3). This can be explained by the fact that at a higher temperature the vapour preasure of the analytes and hence their concentrations in the headspace increase. Above the temperatures mentioned the amount of the analytes extracted decreased, probably because desorption of the analytes from the SPME fiber coating increased

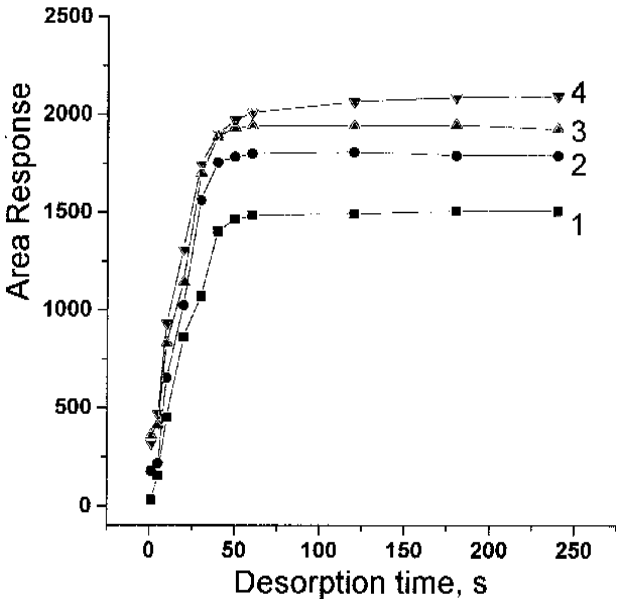

Fig. 2. Effect of desorption time on the peak area of *1* – benzene (5.607 μg g^{-1}), *2* – toluene(5.750 μg g^{-1}), *3* – p-xylene (5.487 μg g^{-1}), *4* – o-xylene (5.642 μg g^{-1}). The fiber was exposed for 15 min to headspace at room temperature and desorbed at 190 °C

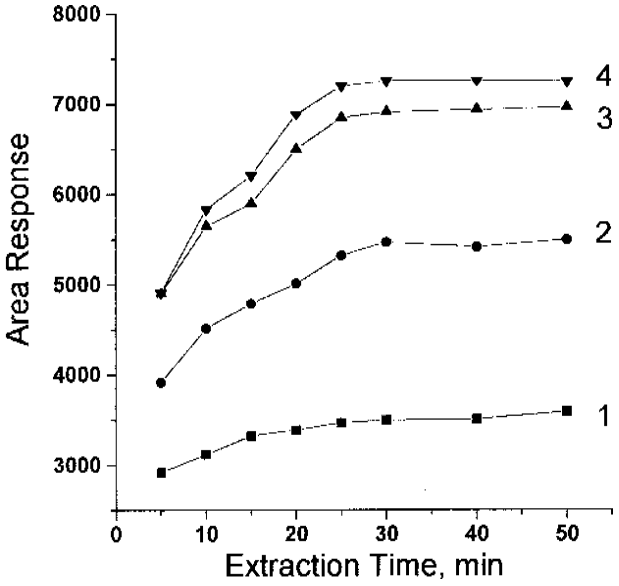

Fig. 4. Effect of extraction time on the peak area *1* – benzene (5.607 μg g^{-1}), *2* – toluene(5.750 μg g^{-1}), *3* – p-xylene (5.487 μg g^{-1}), *4* – o-xylene (5.642 μg g^{-1}). The fiber was exposed to headspace at 60 °C and desorbed at 190 °C for 1 min

more rapidly than the concentration of the analytes in the headspace. So the optimum extraction temperature was determined to be 60 °C.

Effect of sorption time

For optimum repeatability of the analysis, it is necessary to chose a time in which an equilibrium between the fiber and the headspace and between the headspace and soil is reached.

The equilibrium time was examined by exposing the fiber to the headspace for different periods of time at 60 °C. As can be seen in Fig. 4, the peak areas didn't increase any more after 30 min of exposure. As in [8], it was shown that the equilibrium distribution of the aromatic hydrocarbons between the gas phase and the polymeric fiber is achieved in a few minutes, though 30 minutes are neccesary to reach the equilibrium between the soil and the headspace.

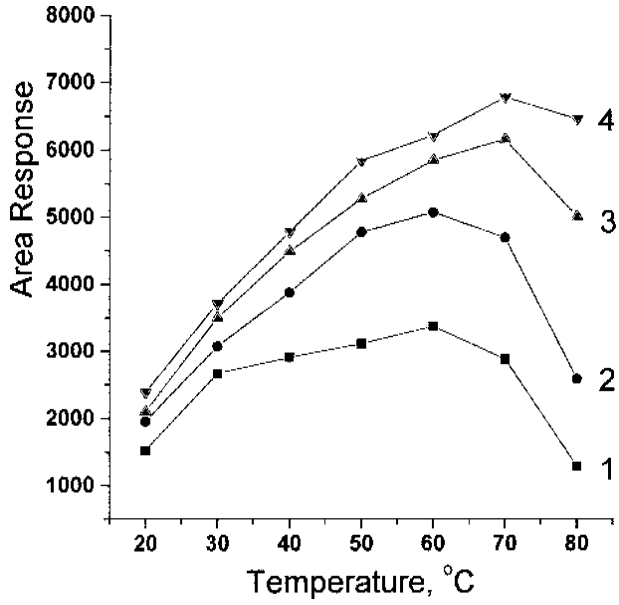

Fig. 3. Effect of extraction temperature on the peak area of *1* – benzene (5.607 μg g^{-1}), *2* – toluene (5.750 μg g^{-1}), *3* – p-xylene (5.487 μg g^{-1}), *4* – o-xylene (5.642 μg g^{-1}). The fiber was exposed to headspace for 15 min and desorbed at 190 °C for 1 min

Effect of headspace volume

For high sensitivity headspace extraction the volume of the gaseous phase should be minimized [9, 10]. We studied the effect of the headspace volume, using 15, 40, and 80 ml vials. The headspace volume after addition of 10 g of humic soil was 8, 33 and 73 ml, respectively. Using a 15 ml vial, an increase in the peak area 1.7 (for o-xylene) to 2.7 (for benzene) times in respect to a 40 ml vial and from 2.6 (for o-xylene) to 6.8 (for benzene) in respect to a 80 ml vial was obtained. For further work a 15 ml vial was chosen.

Precision, linearity and detection limits

The linear response range was examined on 10 g of soil spiked with 200 μl of standard solutions with different concentrations of aromatic hydrocarbons.

Headspace calibration for the volatile aromatic hydrocarbons studied for humic soil was linear in the concentration range up to 50 μg g^{-1}. The detection limits defined as the concentration of the analyte that produces a peak three times higher that the baseline noise were 53, 47, 106 and 86 ng g^{-1} for benzene, toluene, o-xylene and p-xylene, respectively. The correlation coefficients of the linear calibration graphs were 0.995–0.998 (n = 8).

In repeatability tests, five concurrent extractions and consequent GC measurements were made. Before analysis, the soil samples 10 g each were spiked with 200 μl of standard solution with two different concentrations of aromatic hydrocarbons and left for 24 h to adsorb. Then the analysis was carried out as described above. The bigger relative error (Table 1) was obtained for benzene and was probably caused by the fact that during the transport of the fiber trom the extraction vial to the injector of GC the most volatile benzene suffers bigger loss than the other analytes studied.

Table 1. **Repeatabilities for aromatic hydrocarbons in soil (n = 5, P = 0.95)**

Compound	Concentration, μg g^{-1}	RSD, %
Benzene	1.4	13
	5.6	10
Toluene	1.4	10
	5.7	9.3
o-Xylene	1.4	7.2
	5.6	6.0
p-Xylene	1.3	8.4
	5.5	6.2

Effect of addition of water

In most cases extraction is performed on dry matrices. However, volatile hydrocarbons can be lost when dried, especially if a soil sample is dried at a high temperature. In order to carry on an analysis of wet soil samples it was necessary to study the effect of the water content in soil on extraction efficiency. An extraction vial containing 10 g of soil was spiked with different amounts of water, then with a standard solution of aromatic hydrocarbons, and SPME was performed. We expected that water could compete with the analytes for adsorptive sites and hence facilitate the release of aromatic hydrocarbons to the headspace. However, as can be seen from Fig. 5 with addition of the water the extraction decreased. Probably this fact can be explained by partial water solubility of the aromatic hydrocarbons studied. The other reason can be that the fiber also extracts water,

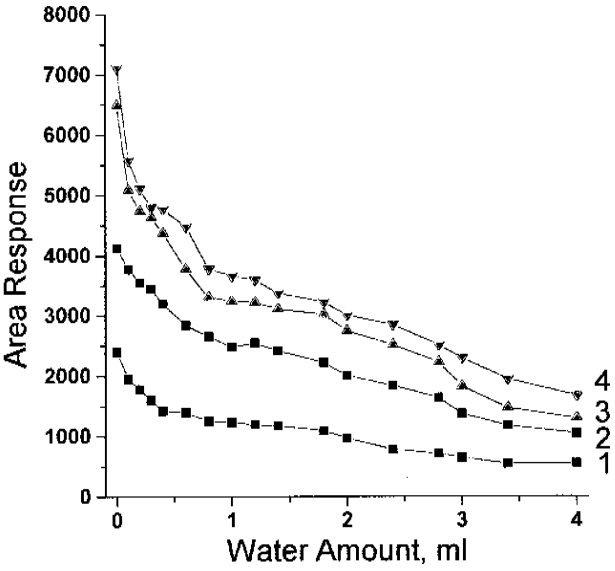

Fig. 5. Effect of water content in 10 g of soil on the peak area of *1* – benzene (5.607 μg g^{-1}), *2* – toluene(5.750 μg g^{-1}), *3* – p-xylene (5.487 μg g^{-1}), *4* – o-xylene (5.642 μg g^{-1}). The fiber was exposed for 30 min to headspace at 60 °C and desorbed for 1 min at 190 °C

even if it has a lower affinity to the fiber than do the analytes. Thus, water is able to compete for the active sites on the fiber surface [11]. So performing an analysis of natural soil, a correction of the extraction efficiency as a function of soil humidity should be done.

In order to overcome the moisture effect on the results of analysis, a standard addition method was examined. Two 10 g portions of soil were spiked with the same amount of aromatic hydrocarbons. Then one portion was analysed as described above. The other portion was spiked once again with 50 μl of a standard solution of aromatic hydrocarbons containing 280, 287, 282 and 274 mg l^{-1} of benzene, toluene, o-xylene and p-xylene respectively and also analysed. The results were calculated using a calibration curve made using dry soil and also according to the standard addition method. This procedure was performed with soil samples containing different amounts of water.

As can be seen from Table 2, for dry soil the results calculated using the calibration curve and the standard addition method are close. In the presence of water in the soil the calibration curve method gives reduced results, and the diminution of the results increases with the moisture. On the other hand, the results obtained using the standard addition method coincide well enough with those obtained for dry soil. So the standard addition method helps to eliminate the moisture influence on the results of the analysis.

Table 2. **The effect of water content in soil on the results of analysis (n = 3, P = 0.95)**

Compound	Concentration added, μg g^{-1}	Water content in 10 g of soil, ml	Concentration μg g^{-1} found by	
			calibration curve method	standard addition method
Benzene	1.4	0	1.5	1.5
		1	1.2	1.5
		2	1.0	1.5
	5.6	0	5.5	5.7
		1	3.5	5.6
		2	2.9	5.5
Toluene	1.4	0	1.5	1.5
		1	1.2	1.5
		2	0.94	1.5
	5.7	0	5.8	6.0
		1	3.4	5.7
		2	2.8	5.8
o-Xylene	1.4	0	1.4	1.5
		1	1.1	1.4
		2	0.92	1.5
	5.6	0	5.9	5.8
		1	3.0	5.9
		2	2.5	5.6
p-Xylene	1.3	0	1.4	1.4
		1	1.1	1.4
		2	0.93	1.4
	5.5	0	5.4	5.6
		1	2.5	5.6
		2	2.2	5.6

Application of optimised SPME to the analysis of real samples

The techniques were tested for analysis of natural soil samples. Chromatograms of the soil collected at one of the main road junctions in Vilnius near an old-fashioned gasoline station was obtained. The chromatogram of the soil is presented in Fig. 6. To the other aliquote of 10 g of the soil, 50 μl of standard solution of aromatic hydrocarbons was spiked and SPME accomplished once again. The moisture of the soil was determined using the third aliquote and was 18%. The results calculated using a standard addition method for dry soil were following: benzene – 72 ng g^{-1}, toluene – 150 ng g^{-1}, o-xylene 310 ng g^{-1}, p-xylene 330 ng g^{-1}. This example shows that headspace SPME can be succsessfuly applied for determination of volatile aromatic hydrocarbons in soil.

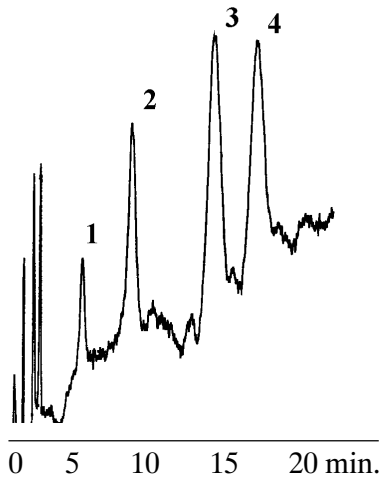

Fig. 6. A chromatogram obtained after headspace extraction of soil collected near one of the gasoline stations in Vilnius. *1* – benzene, *2* – toluene, *3* – p-xylene, *4* – o-xylene

Received
7 June 2000
Accepted
28 September 2000

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LAKIŲ AROMATINIŲ ANGLIAVANDENILIŲ KIETAFAZĖ MIKROEKSTRAKCIJA IŠ DIRVOS

S a n t r a u k a

Lakiems aromatiniams angliavandeniliams dirvoje nustatyti pasiūlytas kietafazės mikroekstrakcijos iš viršerdvės metodas. Kietafazė mikroekstrakcija atlikta kvarco strypeliu, padengtu 100 μm storio polidimetilsiloksano sluoksniu. Optimalios ekstrakcijos sąlygos tiriant sausą humusinę dirvą yra: ekstrakcijos trukmė 30 min., temperatūra 60 °C, desorbuojama 1 min. 190 °C temperatūroje. Nustatytos benzeno, tolueno, o-ksileno ir p-ksileno nustatymo ribos, įvertintas rezultatų tikslumas. Parodyta, kad ekstrakcijos išeiga labai priklauso nuo dirvos drėgmės ir, taikant kalibracinės kreivės metodą, gaunami mažesni analizės rezultatai. Siekiant eliminuoti drėgmės įtaką analizės rezultatams, pritaikytas standartinių priedų metodas.

И. Шядуйкене, В. Вичкачкайте, Р. Казлаускас

ТВЕРДОФАЗОВАЯ МИКРОЭКСТРАКЦИЯ ЛЕТУЧИХ АРОМАТИЧЕСКИХ УГЛЕВОДОРОДОВ ИЗ ПОЧВЫ

Р е з ю м е

Для определения летучих ароматических углеводородов в почве предложен метод твердофазовой микроэкстракции. Твердофазовая микроэкстракция выполнена кварцовым волокном, покрытым полидиметилсилоксановым слоем толщиной 100 мкм. Оптимальная температура экстракции 60 °С, а время экстракции – 30 мин. Десорбция проведена при температуре 190 °С в течение 1 мин. Для бензола, толуола, о-ксилола и п-ксилола определены пределы определения и точность результатов для сухой гумусовой почвы. Было показано, что на выход экстракции сильное влияние оказывает содержание воды в почве. При этом результаты анализа, полученные в результате применения метода калибровочной кривой, занижены. Влияние этого эффекта на результаты анализа удалось элиминировать методом стандартных добавок.