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Calibration and Methodology of Commercial Solid-Phase Microextraction Preconcentration and Ultraviolet Absorption Spectroscopy for Determination of Aromatic Compounds in Water

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A new solid-phase microextraction (SPME) procedure extracts aromatic compounds in water at part-per-billion concenrations from aqueous samples using a small disk of poly (dimethyl siloxane) (PDMS) and ultraviolet absorption spectroscopy. The reversed-phase disk (PDMS) removes nonpolar aromatic compounds from contaminated water at equilibrium time measured using standards from each aromatic compound studied. It was found that equilibrium is established in the range of 40–60 min, with the exception of naphthalene and 1-methyl naphthalene, equilibrated within 90 and 100 min, respectively. After the equilibrium is established the concentration of aromatic hydrocarbon in the sorbent disk is determined quantitatively by UV absorption spectra at 260 nm. The detection limit of the procedure was ranging from 0.5 to 10 ppb. Relative standard deviation from the complete procedure was ranging from 3 to 12%.

INTRODUCTION

Aromatic compounds are an important group of chemicals that permeate our environment. Contamination of aromatic compounds are occasionally present in river water and they are also an important class of ground water contamination because of their wide use in fuels and as solvents. Numerous published methods exist for the separation and quantitation of aromatic compounds in water. The process first includes extraction methods such as liquid-liquid extraction, purge and trap, solid phase extraction, and supercritical fluid extraction[1–4]. Then the detection is achieved by using a detection method such as reversed-phase high-performance liquid chromatography (RP-HPLC), liquid chromatography with membrane introduction mass spectrometry (LC-MIMS), gas chromatography/flame ionization detector (GC/FID), gas chromatography/mass spectroscopy (GC/MS), laser-induced fluorescence (LIF), spontaneous Raman spectroscopy (SRS), and resonance Raman spectroscopy (RRS)[5–10]. All these techniques require complex instrumentation.

Solid-phase microextraction (SPME) is now a widely accepted method for separation and preconcentration of chemicals in aqueous matrices[11]. The renewed interest in SPME has been largely driven by more stringent regulations governing the use and disposal of solvents, as well as improvements in SPME technologies.

The purpose of the present study was to develop a simple and rapid analytical method for extraction and preconcentration of organic compounds from water into poly (dimethyl siloxane) (PDMS) disk, and detection of the aromatic compound pollutants using UV-spectroscopy. This method requires minimal level of sample preparation, and the instrumentation of UV-spectroscopy is less complex and has lower cost than RP-HPLC, LC-MIMS, GC-FID, GC-MS, LIF, SRS and RRS. Moreover, UV-spectroscopy is nondestructive to the sample, thus providing the ability to perform further analysis on the sample.

EXPERIMENTAL

Instrumentation: All the UV spectra were performed in the range from 190 to 350 nm using scanning double beam UV-Vis spectroscopy (Perkin-Elmer, Lambda 20). The instrument was allowed to warm for 30 min prior to use. All spectra were acquired at 2 nm resolution, the scan speed was fixed at 60 nm/min. The spectrophotometer cell was a standard 10 mm cuvette, of UV-grade silica; it had a total volume of 4.5 mL. A mask of black electrical tabe (which is opaque to UV radiation) was placed on one face of both the sample and reference cells. A razor blade was then used to cut a window measuring 3 mm × 4 mm out of each mask. This was done to prevent the UV radiation from diverting around the extraction medium.

Chemicals: Benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, ethyl benzene, 1,3,5-trimethyl benzene (mesitylene), naphthalene, 1-methyl naphthalene, acetonitrile were purchased from Sigma Aldrich.

Preparation of analyte solutions: Standards of the aromatic compounds were prepared by spiking the appropriate amount of the compound into 1 mL HPLC grade acetonitrile and then quantitatively transferring this solution to distilled water. The resulting spiked water solutions were containing 0.1% acetonitrile.

Sorbent disk geometry: The poly (dimethyl siloxane) (PDMS) used in this study is purchased as viscous gel. It was cut into rectangular shapes (10 × 3 × 5 mm) with the use of a razor blade. The optical length was 10 mm which is easily fit into the standard quartz cuvette.

Procedure: The sorbent disks were shaken with a wrist action shaker (1 agitation/s) in 50 mL aliquots of aromatic solution samples in 50 mL round-bottom flasks (fitted with round glass stoppers). After equilibrium was reached, the sorbent disks were removed from the extraction flasks and individually fitted into the cuvette such that the sorbent disk was directly in the centre of the mask's window, and parallel to the sides of the cell. The cell was filled with 3 mL of distilled water added to prevent evaporation of the analyte from the sorbent disk. Then, the cell was placed in the spectrophotometer. Following the spectroscopic analysis the sorbent disks were cleaned from the analytes by heating at 130°C for 30 min (there was no UV signal after these conditions).

Calibration graphs: Calibration graphs were constructed by performing triplicate extractions from 50 mL solution at five concentrations 50, 100, 250, 500 and 1000 ppb and plotting the average absorbance signal versus concentration.

Detection limit: The detection limits were calculated using signal-to-noise ratio of 2 (the ratio between the maximum absorption peak intensity and the noise). To calculate these values, water solutions were spiked with the aromatic compounds (in acetoniltrile) such that the concentrations of the aromatic compounds varied from 0.1 to 20 ppb.

RESULTS AND DISCUSSION

Background correction: An important consideration of the method for detection of the aromatic compounds is the transparency of the poly (dimethyl siloxane) (OV-1). Fig. 1 shows the UV spectra of OV-1 with an air reference and with an OV-1 reference. OV-1 is expected to be transparent in the UV region. It is assumed that the absorption of the UV-radiation by the OV-1 with an air reference is caused by the presence of contamination or due to light scattering.

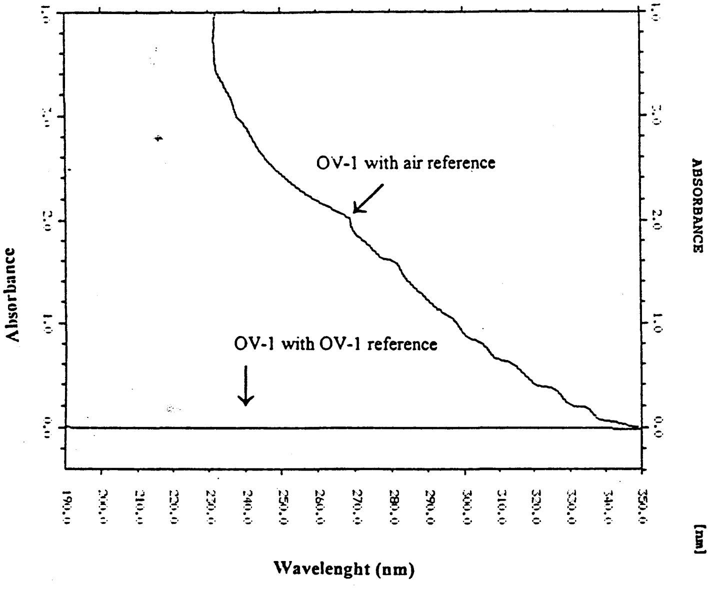

Fig. 1. UV spectra of OV-1 with an air reference and with an OV-1 reference.

Absorbance spectra: The UV absorption spectrum of the aromatic compounds accumulated into OV-1 disk was studied in the wavelength region of 190–350 nm utilizing OV-1 in the reference cell of the spectrometer. Figures 2, 3 and 4 show typical aromatic compound spectra obtained in OV-1 sorbent disks, using OV-1 disk as a reference background. UV spectra of these compounds do not differ markedly from each other. These spectra have all been found to be well defined, specially for benzene, clearly characteristic for each absorbing species, and well suited for quantitative purposes. Within the wavelength region studied,

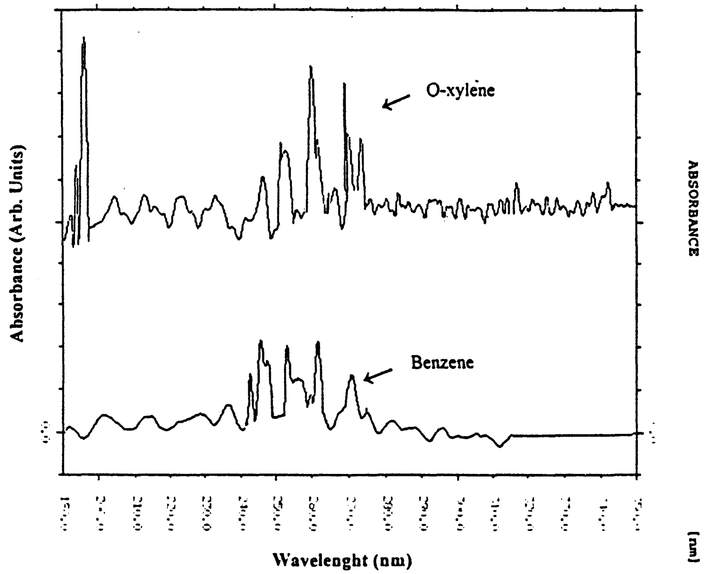

Fig. 2. Typical spectra of xylene and benzene in the poly (dimethylsiloxane) sorbent chips using poly (dimethylsiloxane) as the reference background.

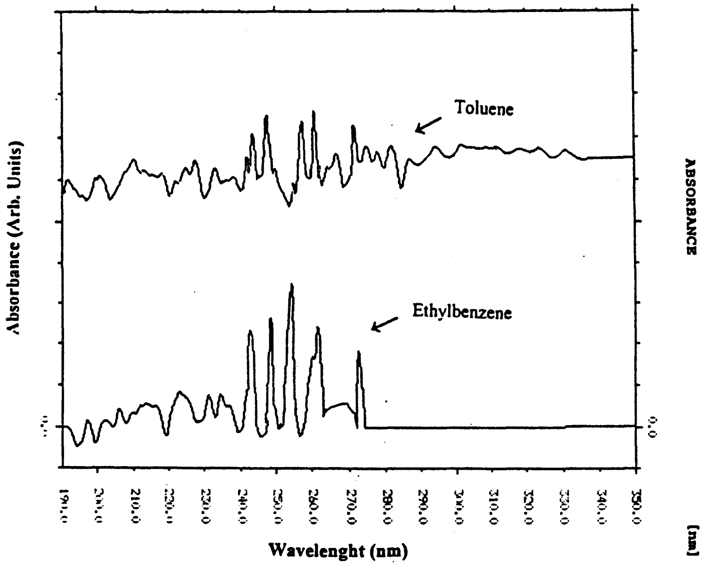

Fig. 3. Typical spectra of toluene and ethylbenzene in the poly (dimethylsiloxane) sorbent chips using poly (dimethylsiloxane) as the reference background.

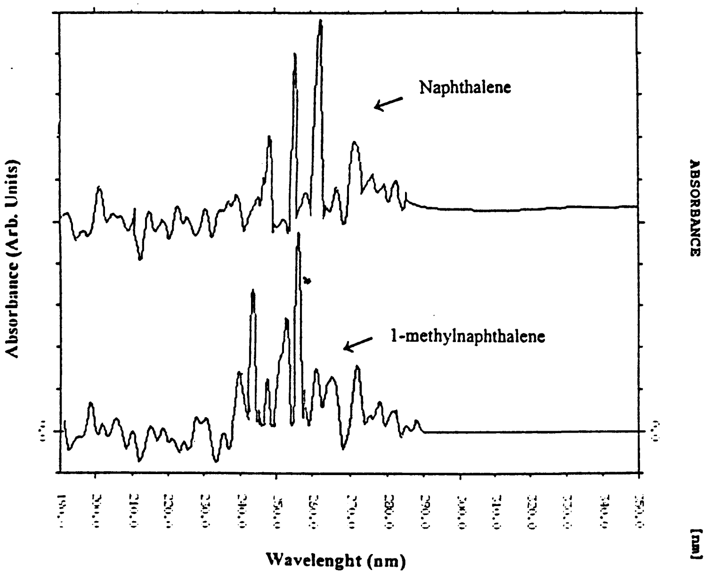

Fig. 4. Typical spectra of naphthalene and 1-methyl naphthalene in the poly (dimethylsiloxane) sorbent chips using poly (dimethylsiloxane) as the reference background.

there were five major UV absorption maxima (243, 247, 254, 260 and 273 nm), which is the characteristic of the electronic absorption spectrum of benzene ring. It is interesting to note that when a methyl group is linked to the ring it causes bathochromic shifts of the five bands because electrons on the substituent interact with the π electrons of the benzene ring. However, as the substituents become more complex, the spectrum loses more of its benzene ideal structure.

TABLE-1
EQUILIBRIUM TIMES AND PARTITION CONSTANTS FOR THE TESTED AROMATIC COMPOUNDS CALCULATED USING SPME PRECONCENTRATION AND UV ABSORPTION SPECTROSCOPY

Analyte	A Eq (min) (% RSD)	B K_D (% RSD)
Benzene	40 (3.1)	209 (11)
Toluene	42 (2.3)	312 (8)
Ethylbenzene	45 (5.0)	253 (3)
o-Xylene	48 (3.1)	332 (5)
m-Xylene	45 (2.4)	570 (6)
p-Xylene	44 (6.0)	418 (4)
1,3,5-Trimethyl benzene	50 (2.4)	2180 (5)
Naphthalene	90 (3.5)	3760 (3)
1-Methyl naphthalene	100 (4.6)	3095 (4)

TABLE-2
CALIBRATION DATA OF THE AROMATIC COMPOUNDS OBTAINED WITH THE USE OF SPME PRECONCENTRATION AND UV ABSORPTION SPECTROSCOPY

Compound	Slope	R^2	Linear range {ppb (w/w)}
Benzene	1.0×10^{-4}	0.993	250–15200
Toluene	0.8×10^{-4}	0.991	70–4500
Ethyl benzene	6.9×10^{-4}	0.999	50–1800
o-Xylene	3.2×10^{-3}	0.992	30–1900
m-Xylene	3.6×10^{-4}	0.995	30–1800
p-Xylene	4.3×10^{-3}	0.995	40–1900
1,3,5-Trimethyl benzene	4.3×10^{-3}	0.996	40–900
Naphthalene	1.9×10^{-3}	0.995	40–700
1-Metyl naphthalene	2.1×10^{-3}	0.999	30–500

Absorption/time profiles for PDMS: Absorption/time profiles were carried out to determine equilibrium time for each one of the analytes. Fig. 5 shows a construction plot of the UV absorbance (at 260 nm) versus extraction time. Equilibrium time is reached when the PDMS disk absorbance reaches a plateau. Table-1-A summarizes the equilibrium times. It is clear from Table-1-A that the equilibrium time range from 40 to 50 min with exception of naphthalene and 1-methyl naphthalene, equilibrated within 90 and 100 min, respectively. These two compounds require longer time to reach equilibrium compared to the other analytes studied. It should be remembered that, at equilibrium, the concentration of the analyte in the PDMS can be expressed by the classical extraction theory as

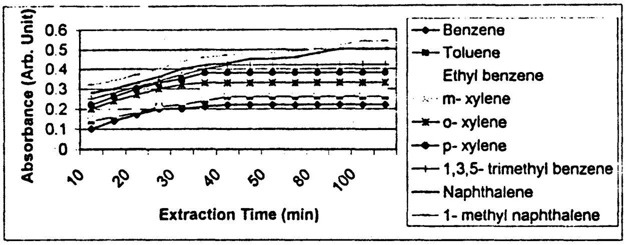

Fig. 5. Representative absorption/time profiles for benzene, toluene, ethyl benzene, *o*-xylene, *m*-xylene, *p*-xylene, 1,3,5-trimethyl benzene, naphthalene and 1-methyl naphthalene. All measurements were recorded in water solution concentrations of 500 ppb, and the absorbance was measured at 260 nm.

$$K_D = C_S/C_W$$

where K_D is the partition constant of the analyte in PDMS/water system, C_S is the concentration of the analyte in the solid phase and C_W is the concentration of the analyte in the aqueous phase. As shown in Table-1-B the K_D values for the tested analytes are relatively large. It is interesting to note that there is similarity in the trend between the K_D values determined in our work optically with those determined previously by Langenfel and co-workers using gas chromatography[12].

Calibration data: Calibration graphs were constructed for each of the analytes. The linearity of the system was studied at five points, both with and without the use of SPME. Tables 2 and 3 show the calibration data with and without the use of SPME. The correlation coefficients of the slopes were between 0.991 and 0.999. Tables 2 and 3 also show the linear range of calibrations. It should be noted that the concentrations of the aromatic compounds for equilibrium time and enrichment enhancement measurements were 250 ppb which is within the linear range of the calibrations.

TABLE-3
CALIBRATION DATA OF THE AROMATIC COMPOUNDS OBTAINED WITHOUT THE USE OF SPME

Compound	Slope	R^2	Linear range {ppb (w/w)}
Benzene	2.9×10^{-6}	0.991	500–800000
Toluene	3.1×10^{-6}	0.995	300–750000
o-xylene	4.4×10^{-6}	0.992	400–700000
m-xylene	4.9×10^{-6}	0.998	900–800000
p-xylene	5.1×10^{-6}	0.995	1000–55000
1.3,5-trimethyl benzene	3.2×10^{-6}	0.994	350–65000
Naphthalene	3.8×10^{-5}	0.998	500–5000
1-methyl naphthalene	4.5×10^{-5}	0.999	500–5000

TABLE-4
CALCULATION OF THE ENHANCEMENT FACTOR AND DETECTION LIMIT OF THE AROMATIC COMPOUNDS WITH AND WITHOUT THE USE OF SPME PRECONCENTRATION

Compound	A E_f	B LOD {ppb (w/w)}	
		with SPME (% RSD)	without SPME (% RSD)
Benzene	52	90 (9)	1000 (8)
Toluene	123	10 (7)	900 (6)
Ethyl benzene	147	5.8 (5)	1000 (7)
o-xylene	180	3.2 (6)	900 (5)
m-xylene	133	5.4 (5)	1000 (9)
p-xylene	132	4.3 (6)	900 (8)
1,3,5-trimethyl benzene	157	6.4 (3)	200 (12)
Naphthalene	802	0.5 (2)	75 (7)
1-methyl naphthalene	907	0.5 (3)	80 (6)

Enrichemnt enhancement: Table-4-A shows the enhancement factor, E_f, which is determined from the ratio of the calibration slopes with and without SPME preconcentration. The values of E_f are ranging from 123 to 157. Except for benzene E_f value was the lowest, equal to 52. However, naphthalene and 1-methyl-naphthalene have the highest E_f values 802 and 907, respectively. It should be noted that the value of E_f indicates the sensitivity improvement achieved with the use of SPME preconcentration.

Detection limits: The limit of detections (LOD) shown in Table-4-B were calculated using a signal to noise ratio of 2 (the ratio between the maximum absorbance intensity and the noise). The limits of detection were calculated with and without SPME preconcentration. The results shows that there is a great detection limit improvement achieved with the use of SPME, ranging from 0.5 to 10 ppb (w/w). Benzene possesses the poorest detection limit enhancement (11×) whereas naphthalene and 1-methyl naphthalene possess the greatest enhancement (150× and 160×, respectively).

It is noteworthy to know that the two factors affects the detection limit are the partition coefficient (K_D) and the molar absorptivity (ε). The greater the K_D and ε values the higher will be the analyte absorbance signal. Thus, from the compounds being studied benzene has both the lowest K_D and the poorest detection limit, but has the highest degree of spectroscopic fine structure. Conversely, naphthalene and 1-methyl naphthalene have the highest K_D and the highest detection limit, but both have lower degree of fine structure compared to benzene. It is entirely feasible that the value of E_f is related to the value of detection limit enhancement with the use of SPME preconcentration. On the other hand, the RSDs for the LOD are quite good. Therefore, SPME preconcentration would provide significantly good detection limit for the determination of aromatic compounds in water.

Conclusion: Our investigation shows that the use of SPME preconcentration and UV absorption spectroscopy appears to be extremely promising for simple, rapid and accurate method for determination of aromatic compounds in water. Procedures that employ this technique offer considerable saving in both labour and volume of the hazardous waste organic solvents produced by other methods. Most interesting among the results is the quite good detection limit obtained for the examined species.

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