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Evaluation of Total Fuel Aromatics in Natural Water by the Use of Solid Phase Microextraction Preconcentration and Ultraviolet Absorption Spectroscopy

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An apparently simple and novel technique was developed to aid detection of the total fuel aromatics in natural water. The method depends upon preconcentration of the aromatic compound into poly (dimethyl siloxane) disk and the use of ultraviolet absorption spectroscopy. The equilibrium times for the fuels studied, unleaded gasoline, kerosene, and no. 1 diesel fuel are 120, 220 and 250 min respectively. The limit of detection for unleaded gasoline kerosene and no. 1 diesel fuel at their equilibrium time are 4.5, 14 and 8.9 ppb, respectively for ground water, and 9.6, 16 and 10 ppb, respectively for pond water. The total recoveries of the fuel aromatics from unleaded gasoline, kerosene, and no. 1 diesel fuel from natural water matrices are in the range of 92–96% with RSDs in the range of 2.0–12%.

INTRODUCTION

Chemical group parameters such as dissolved organic carbon (DOC), adsorbed organo halogen (AOX) and chemical oxygen demand (COD) determination are routinely used for water quality monitoring[1]. It is increasingly recognized, however, that many chemical group parameters fail to give accurate information about the total aromatic compounds in contaminated water[2–5]. Examples of such methods are purge and trap or static headspace coupled with gas chromatography[6, 7]. Lord and Pawliszyn have mentioned that purge and trap, and static headspace suffer from a number of disadvantages[8].

We have recently demonstrated the calibration and methodology of the use of solid phase microextraction (SPME) coupled with ultraviolet absorption spectroscopy for determination of aromatic compounds in water[9]. Since its introduction, SPME has proved to be a simple, solvent free, reliable and flexible tool for the sampling of a variety of aromatic compounds.

This paper reports our application of determination of the total fuel aromatics in water by using a simple device consist of rectangular solid of poly (dimethyl siloxane) (PDMS) coupled with UV absorption spectroscopy The fuels which were used in this study are unleaded gasoline, kerosene and diesel fuel (no. 1).

EXPERIMENTAL

Instrumentation: UV/Vis spectroscopy (Perkin-Elmer, Lambda 20) was used for the UV spectra measurements. The 10 mm path length and 10 × 45 mm cross-section cuvette of UV-grade silica was used. Both the sample cell and the reference cell were masked with black electrical tape. A razor blade was then used to cut a window measuring 3 mm × 4 mm out of each mask. This was done to avoid UV radiation from diverting around the extraction medium.

Chemicals and reagents: The poly (dimethyl siloxane) (PDMS) used in this study is purchased as viscous gel. It was cut into rectangular shapes (10 × 2 × 5 mm) with the use of a razor blade. The optical length was 10 mm which is easily fit into the standard quartz cuvette. The unleaded gasoline, kerosene and no. 1 diesel fuel were purchased from local sources in the Gaza Strip. The fuels were stored in glass containers with teflon-lined screw-top caps. 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 fuels were prepared by spiking the appropriate amount of the fuel into 1 mL HPLC grade acetonitrile and then quantitatively transferring this solution to distilled, ground, or pond water. The resulting spiked water solutions were containing 0.1% acetonitrile.

Procedure: The sorbent disks were shaken with a wrist action shaker (1 agitation/s) in 50 mL aliquots of fuel solutions in 50 mL-round-bottom flasks (fitted with round glass stoppers). After equilibrium was reached, the sorbent disks were removed from the extraction flaks 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 for each of the three fuels by spiking appropriate amount of each in the water sample such that the final concentrations were 50, 100, 250, 500 and 1000 ppb and plotting the 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, appropriate amount of each of the fuels was spiked into the water sample according to the required concentration.

RESULTS AND DISCUSSION

Absorbance spectra: The UV absorption spectra of the three fuel aromatics extracted into PDMS disk was studied at five absorption maxima (243, 247, 254, 260 and 273 nm) utilizing PDMS disk in the reference cell of the spectrometer. We used all these absorption peaks to make calibration in order to determine the wavelength which gives the best response. The wavelength which will give the best response will be used for further analysis.

Absorption/time profiles for the fuels in PDMS disks: Absorption time/ profiles is determined for each fuel in order to determine the equilibrium time. The equilibrium time is reached when the absorbance no longer increases with the time allowed for extraction. Figure 1 shows the influence of extraction time on the absorbance at 260 nm for the three fuels. The extraction time is about 5 times longer than that observed for any one of the aromatic compounds studied in part 1. It should be remembered that the fuels are composed of numerous compounds including aromatic hydrocarbons (30–39%)[10], and the time of extraction of each species in the fuel is effected by the presence of the others.

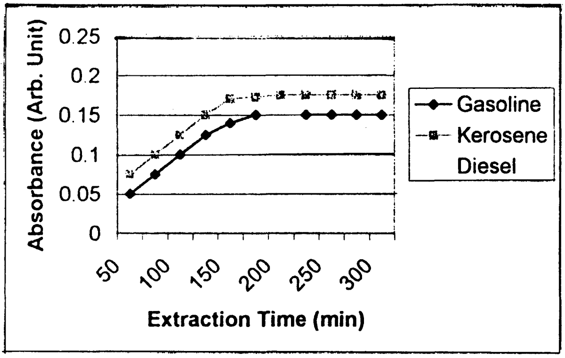

Fig. 1. Representative absorption/time profiles for unleaded gasoline, kerosene and diesel fuel (no. 1). All measurements were recorded in water solution concentrations of 1000 ppb, and the absorbance was measured at 260 nm.

Calibration graphs: Calibration data of the three fuels, at the five absorption maxima (243, 247, 254, 260 and 274 nm), and at their equilibrium time is shown in Table-1. It is interesting to note that there is similarity in response for unleaded gasoline, kerosene and diesel fuel specially at the absorption maxima 260 nm. The results indicate that the quantitative determination of the total fuel aromatics in contaminated water is better to be determined at 260 nm absorbance. It is important to remember that PDMS is nonpolar phase and will extract non- to low-polar analyte from contaminated water. The absorption maxima in UV region is exerted only by the aromatic compounds and not the numerous aliphatic compounds which do not have absorption in the UV region.

TABLE-1

CALIBRATION DATA OF THE THREE FUELS STUDIED WITH THE USE OF SPME PRECONCENTRATION AND UV ABSORPTION SPECTROSCOPY[a]

Fuel	Wavelength[b]				
	243	247	254	260	274
Unleaded gasoline	2.8×10^{-3}	3.2×10^{-3}	4.7×10^{-3}	1.9×10^{-3}	3.5×10^{-3}
Kerosene	3.8×10^{-4}	3.5×10^{-3}	3.2×10^{-3}	2.0×10^{-3}	3.7×10^{-3}
Diesel fuel	3.2×10^{-4}	2.7×10^{-3}	3.2×10^{-3}	2.1×10^{-3}	4.1×10^{-3}

[a] The values are recorded at 100% equilibrium time for each fuel,

[b] R^2 for all fuels are ranging from 0.993–0.999.

Response factor: The response factor of pure aromatic compounds and fuels were studied at the five absorption maxima (243, 247, 245, 260 and 273) inorder to select appropriate aromatic compound standard and wavelength that can be used to make general calibration graph for determining the concentration of the total fuel aromatics in contaminated water sample. The selected standard aromatic compound should give response that is similar to the fuel response (both have the same slope). Table-2 shows that naphthalene and 1-methyl naphthalene have very close match to the fuels at the five wavelengths studied. At 260 nm both have very close response factor to the three fuels studied. Therefore, naphthalene or 1-methyl naphthalene can be used as a general calibration standard for the determination of the concentration of the total aromatics in contaminated water. The efficiencies of both these standards were checked by spiking 1000 ppb unleaded gasoline (390 ppb aromatic compounds, because the unleaded gasoline is known to contain 39 wt% aromatic compounds) in water. Calibration plots for naphthalene and 1-methyl naphthalene were constructed, using the absorbance of 260 nm. From the calibration graphs of naphthalene and 1-methyl naphthalene the resulting concentrations of the total fuel aromatics were 380 and 395, respectively. It is interesting to note that these two values are very close to the spiked concentration.

Recoveries from natural water: The real water samples used in this study were collected from ground water and a local stagnant pond water (Wadi Gaza pond). Both water samples were extracted with the PDMS disks in triplicates before spiking them with the fuels to ensure that there are no extractable aromatics originally present in the water samples. The results have shown that there is no

TABLE-2
AROMATIC COMPOUNDS-RESPONSE FACTOR AT THE FIVE STUDIED WAVELENGTHS

Compound	Response factor, at the folloiwng wavelengths, nm				
	243	247	254	260	273
Benzene	8.5×10^{-5}	6.1×10^{-5}	9.5×10^{-5}	1.2×10^{-4}	5.9×10^{-5}
Toluene	3.6×10^{-4}	2.8×10^{-4}	5.3×10^{-4}	3.9×10^{-4}	4.2×10^{-4}
Ethyl benzene	4.7×10^{-4}	3.5×10^{-4}	7.0×10^{-4}	5.8×10^{-4}	5.0×10^{-4}
o-Xylene	3.7×10^{-4}	4.2×10^{-4}	3.6×10^{-4}	3.1×10^{-4}	3.5×10^{-4}
m-Xylene	2.8×19^{-4}	3.0×10^{-4}	3.6×10^{-4}	1.9×10^{-3}	4.8×10^{-4}
p-Xylene	2.7×10^{-4}	3.2×10^{-4}	1.4×10^{-3}	3.1×10^{-4}	2.5×10^{-4}
1,3,5-Trimethyl benzene	3.8×10^{-4}	3.5×10^{-4}	1.5×10^{-3}	2.6×10^{-4}	2.7×10^{-4}
Naphthalene	3.6×10^{-3}	3.3×10^{-3}	3.4×10^{-3}	2.1×10^{-3}	3.8×10^{-3}
1-Methyl naphthalene	3.3×10^{-3}	3.5×10^{-3}	3.6×10^{-3}	2.0×10^{-3}	3.1×10^{-3}

TABLE-3
RECOVERIES OF THE THREE FUELS FROM POND WATER AFTER THREE EXTRACTION PROCEDURES

(The values repoted are the mean of 4 measurements).

Analyte	% Recovery, for extraction no.			Total % recovery
	1	2	3	
Unleaded gasoline	79	12	6.0	97
Kerosene	75	10	7.0	92
Diesel fuel	78	11	5.0	94

UV absorption band. Thus, there is no aromatic compound originally present in the ground or pond water samples collected. Unleaded gasoline, kerosene and diesel fuel were spiked individually into the two "real" water samples at the concentration of 1000 ppb and extracted into the PDMS disk. The absorbance values at 260 nm for each of the fuels in natural water were compared to that of the distilled water absorbance. The recovery data observed at 260 nm are summarized in Fig. 2. The recoveries of the fuels determined from distilled and ground water are very close ranging from 93–96%, with RSD ranging from 5 to 9%. However, lower recoveries were generally obtained for the three fuels from pond water, ranging from 73 to 78% (mean 76%), with RSD ranging from 2 to 12% (n = 4). To check for completeness of extraction from pond water, the pond water was subjected to additional extraction with PDMS disk. Surprisingly, up to 12% more analytes were recovered from second extraction, and up to 7% more analytes were recovered from the third extraction. Consequently, we can reasonably attribute this to the presence of humic and fulvic acids, which result from the breakdown of dead organic matter in pond water. It is conceivable that the fuel aromatic compounds bound large molecular weight humic and fulvic acids. Alternatively, the humic and fulvic acids may physico-chemically prevent aromatic compounds from penetration to the PDMS disk.

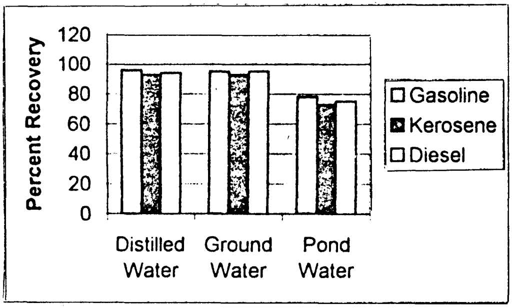

Fig. 2. Comparison of the recoveries data of the three fuels in different types of water. The fuels concentrations were 1000 ppb, the absorbance was measured at 260 nm and the results reported are from the first extraction procedure.

TABLE-4
DETECTION LIMITS OF THE FUELS WITH THE USE OF SPME PRECONCENTRATION FOR THREE TYPES OF WATER SAMPLES

Analyte	Detection limit, {ppb (w/w)} (% RSD)[a]		
	Distilled water	Ground water	Pond water
Unldeaded gasoline	4 (3.5)	4.5 (6.2)	9.6 (4.2)
Kerosene	12 (2.5)	14 (5.3)	16 (6.8)
Diesel fuel	10 (4.8)	8.9 (4.6)	10 (3.5)

[a] Average and relative standard deviation from five measurements.

Detection limits: Tables 4 and 5 illustrate the detection limits of the fuels in three different types of water, with and without the use of PDMS preconcentration, respectively. The detection limit for the fuels in natural water with the use of SPME is lower than without the use of SPME. The results have shown that the detection limits in distilled and ground water are lower than in pond water, which may be caused from UV absorption of the naturally occurring humic and fulvic acids in pond water. Fulvic and humic acids may also cause light scattering, which is most prominently observed at shorter wavelength and result in a sloping baseline which was difficult to be corrected sometimes.

TABLE-5
DETECTION LIMITS OF THE FUELS WITHOUT THE USE OF SPME PRECONCENTRATION

Analyte	Detection limit {ppb (w/w)} (% RSD)[a]		
	Distilled water	Ground water	Pond water
Unleaded gasoline	3500 (6.7)	3900 (8.6)	7600 (7.8)
Kerosene	3600 (11)	4500 (5.8)	8000(12)
Diesel fuel	3600 (12)	4000 (10)	7900 (6.7)

[a] Average and relative standard deviation from five measurements.

Conclusion

We demonstrated the use of solid phase microextraction preconcentration using poly (dimethyl siloxane) coupled with UV absorption spectroscopy to determine the total fuel aromatic compounds in natural water. The results have shown that preconcentration afforded by poly (dimethyl siloxane) disk allows the detection of the total aromatic compounds in water samples contaminated with unleaded gasoline, kerosene and diesel fuel (no. 1) in low-ppb range. For the determination of the total fuel aromatics in pond water it is recommended to make three extractions, because of the possibility of the presence of fulvic and humic acids. It is also recommended to use either naphthalene or 1-methyl naphthalene as a reference calibration standard because they have similar response factor to that of the three fuels studied.

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