

MICRO-SOLID-PHASE EXTRACTION AND GC ANALYSIS OF VOLATILE AROMATIC HYDROCARBONS FROM WATER

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ABSTRACT. Four major volatile aromatic hydrocarbons: benzene, toluene, xylene, ethyl-benzene, were extracted from water using Micro-Solid-Phase Extraction and analysed by gas chromatography. The extraction and separation of these compounds were good and this method can be successfully applied in environmental samples analysis.

Keywords: Micro-Solid-Phase Extraction, gas chromatography, volatile aromatic hydrocarbons, benzene, toluene, xylene, ethyl-benzene

INTRODUCTION

Benzene, Toluene, Ethyl benzene and Xylene are some of the most important and frequent water contaminants. The mixture of the above compounds is also known as BTEX (Benzene-Toluene-Ethyl-benzene-Xylene). They appear in water due to various causes but especially from industrial waste waters. These compounds are used in large amounts as precursors in the chemical industry and as solvents. They are also present in fuels.

The volatile aromatic hydrocarbons are considered highly toxic, carcinogenic and dangerous for the environment.

The toxicity of volatile aromatic hydrocarbons is caused mainly by the degradation products which form free radicals with high reactivity. These radicals can react with protein and DNA (Williams et al., 2001).

Benzene affects mainly the hepatic functions and inhibits the activity of dehydrogenase and phosphatase (Williams et al., 2001).

Benzene toxicology differs from that of other solvents because it is a myelotoxin which affects the blood forming organs (e.g. marrow). The hematological effects caused by chronic exposure to benzene depend mainly upon the sensibility of the exposed person but in general the red cell number is significantly decreased (in some cases 50% from the normal value), decreased hemoglobin level and altered leukocyte counts.

The substituted volatile aromatic hydrocarbons are considered less toxic than benzene. Toluene however

affects the central nervous system causing dizziness, headaches and fatigue even at small concentration (e.g. 200 ppm for 8 hours) (Williams et al., 2001).

The main toxicological effects of substituted volatile aromatic hydrocarbons are presented below in table 1.

The small quantity of these compounds, often in traces, however makes their analysis from environmental matrixes very difficult and often losses occur during sample preparation.

The Micro-Solid-Phase Extraction is a very efficient method for the analysis of these compounds. This method can be used in a wide area of applications like environmental analysis, toxicology, analysis of pharmaceuticals, food, flavors and odors, volatile organic compounds a.s.o. (Wu et al., 2000, Pawliszyn 2000)

Although there are commercially available fibers and coatings, several fibers, coatings and methods were developed in the last decade.

The only manufacturer of commercial fibers is Supelco (Belafonte, P.A., USA).

The main types of commercially available coatings are presented in table 2.

Beside the commercially available coatings there were developed new coatings, for a wide range of applications; these coatings are presented in Table 3.

The details about the Solid Phase Micro-extraction are presented in the next section.

Table 1

Toxicological effects of substituted volatile aromatic hydrocarbons					
No.	Organism	Compound	Concentration	Effect	Reference
1.	Rat	Toluene	1000 ppm (16 h/day, 10 days)	Loss of auditive sensitivity	[Johnsson 1992]
2.	Mice	Toluene	1000 ppm (12 h/day, 7 days)	Locomotor Hyperactivity	[Bushnell et al., 1985]
3.	Rat	Toluene	795 ppm (8 h/day, 7 days)	Increase of liver volume	[Ungvary et al., 1982]
4.	Human	Ethyl – Benzene	100 ppm (8 h/day)	Fatigue	[Bordej et al., 1970]
5.	Guinea pig	Xylenes	2000 mg/kg	Liver disease	[DiVicenzo et al., 1974]

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Table 2

Commercially available coatings and their application			
No.	Name	Coating	Application
1.	PDMS	Poly-dimethyl-siloxane (7µm, 30 µm, 100 µm)	General use, unpolar compounds
2.	PA	Polyacrylate (85 µm)	Polar compounds
3.	PDMS / DVB	Poly-dimethyl-siloxane / Divinyl-benzene (65 µm)	Polar compounds, semi volatiles
4.	CW/DVB	Carbowax / Divinyl-benzene	Polar compounds, semi volatiles
5.	CW/TPR	Carbowax / Templated resin	Polar, selective extractions
6.	DVB/CW/PDMS	Divinyl-benzene / Carbowax/ poly-dimethyl-siloxane	Semi volatile compounds
7.	PEG	Poly-ethylene-glycol	BTEX (Benzene, Toluene, Ethyl-benzene, Xylenes), phenols, pesticides, diesthers

Table 3

New coatings and application						
No.	Coating	Application	Detection Limit	Relative Standard Deviation	Remarks	Reference
1.	Polymeric fullerene	BTEX, phthalic acid, naphthenes	ng/L – µg/L	12% n=6		[Xiao et al., 2000]
2.	Polythiophene (obtained by cyclic voltametry)	Organo – chlorine pesticides from water	0.5-1 ng/L	12-18% n=5		[Li et al., 2008]
3.	Activated carbon	C ₆ H ₅ CH ₂ Cl, C ₆ H ₅ CHCl ₂ and other halocarbons	ng/L	14.1-15.5% n=5		[Sun et al., 2005]
4.	Diglycidyl-oxo –calix [Ungvary et al., 1992]-arene and amide bridged calyx [Ungvary et al., 1992]-arene	Organo – chlorine pesticides from soil, aromatic amines from water	<1 ng/g soil, 1.2-40 ng/L water	8% n=6 (soil) 1.4-6.3% n=6 (water)	High sensitivity and selectivity	[Li et al., 2006] [Wang et al., 2005]
5.	Crown ethers	Aliphatic amines	0.1-1000 µg/L	<6% n=6	High temperature resistance	[Cai et al., 2003]
6.	PEG deposited on a fiber obtained by electro deposition of ZrO ₂ on NiTi alloy	Halo-phenols, phthalates from water	1.2-9.8 ng/L for phenols, 0.3-0.7 ng/L for phthalates	<12% n=6	Excellent mechanical resistance	[Budziak et al., 2007]
7.	Al ₂ O ₃ (Sol-gel technique)	Volatile organic compounds, BTEX, butyl-acetate, styrene	0.714 ng/L	4.1-7.2%		[Wei et al., 2004]
8.	Poly-pyrrole	Inorganic anions			Low stability of coating, limited applications	[Wu et al., 2004]

MATERIALS AND METHODS

Materials

We used a Supelco PDMS (poly-dimethyl-siloxane) coated fiber for the extractions.

All the tests were done on an Ultra Trace Gas Chromatograph with the following parameters:

- Injection temperature 220°C
- Oven temperature 60°C isothermal
- Detector temperature 250°C
- Hydrogen, 35 mL/min
- Air 250 mL/min
- Carrier: Nitrogen, 1.5 mL/min

- Column: DB-5 (poly-dimethyl-siloxane with 5% phenyl), length 30 m, internal diameter 0.25 mm, stationary phase (film thickness) 0.25 µm.

The sample was prepared using benzene (2 drops, approximately 0.04 mL), toluene (2 drops, approximately 0.04 mL) and a mixture of xylenes with 25% ethyl-benzene (also 2 drops- approximately 0.04 mL) in 1000 mL water.

The sample was agitated for 10 minutes. The extraction time was 5 minutes.

Methods

The Micro-Solid-Phase Extraction is an innovative, solvent free technique that is relatively easy to apply which uses a fiber coated with sorbent [Pawliszyn, 1997, Ouyang et al., 2006, Ciucanu et al., 2004, Abedin et al., 2003].

The fiber coating removes the compounds from the sample by adsorption and then the fiber is inserted directly into the Gas Chromatograph where the desorption takes place and also the separation and analysis of the compounds.

The schematic diagram and the MSPE device is presented below (Fig.1) [Ciucanu et al., 2004].

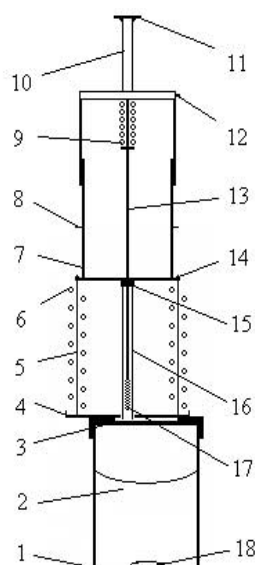


Fig. 1 Schematic diagram of MSPE device: (1) vial; (2) sample solution; (3) septum; (4) guide plate; (5) guide rod; (6) guide rod spring; (7) barrel; (8) limitation nut; (9) plunger spring; (10) plunger; (11) handle; (12) plunger stopper; (13) elongation arm; (14) adjustable nut; (15) sealing material; (16) protection tube; (17) fiber with polymeric coating; (18) magnetic stirring bar.

The whole procedure is presented below. For the extraction, the following steps have to be made (Fig. 2) [Ciucanu et al., 2004].

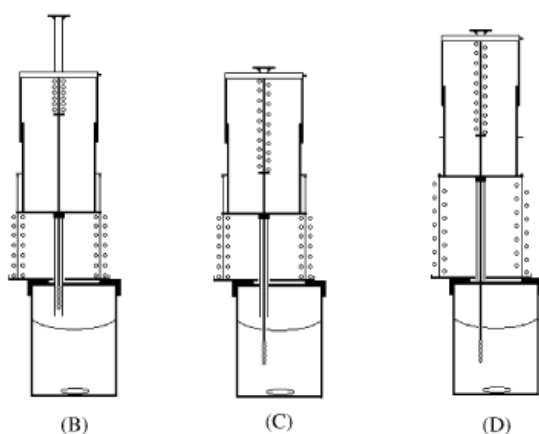


Fig. 2 The steps for MSPE

1. The needle is inserted in the sample vial (the needle is for the protection of the coated fiber)
2. The plunger is extended in order to "expose" the fiber
3. The fiber is retracted inside the needle and the device is removed from the sample vial.

After the extraction, the coated fiber is inserted directly into the Gas Chromatograph. The desorption is made in three steps (Fig. 3).

Desorption Procedure

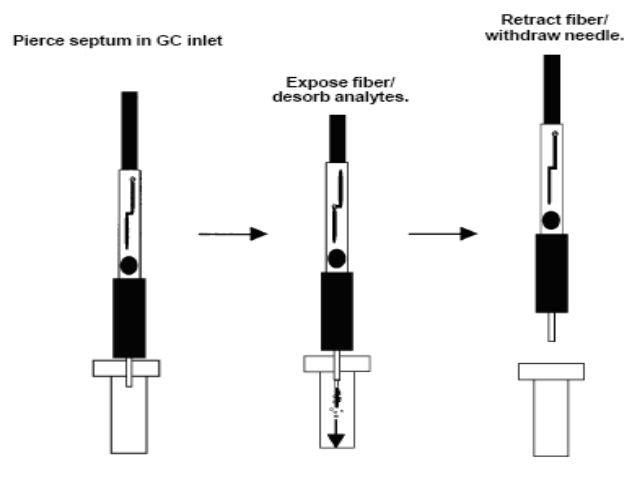


Fig. 3 The desorption of MSPE

1. The needle is inserted directly into the GC inlet
2. The fiber is "exposed" in order to desorb the extracted sample
3. The fiber is retracted and the device is removed from the GC inlet.

The quantity of the extracted analytes depends on the concentration of analytes from the sample, the coating, volume of coating and extraction time. Before the equilibrium is reached, the quantity of analytes extracted grows almost exponentially with the extraction time; after the equilibrium is reached the extracted quantity is maximal.

At the equilibrium the following formula can be applied [Pawliszyn, 1997]:

$$n = \frac{K_{fs} \cdot V_f \cdot V_s \cdot C_0}{K_{fs} \cdot V_f + V_s} \quad (1)$$

Where: n – extracted quantity of analyt

K_{fs} – distribution constant of analytes between sample and sorbent

V_f – volume of sorbent (coating)

V_s – volume of sample

C_0 – concentration of analyt in the sample

If the sample volume is very high compared with the coating volume, the equation (1) can be simplified

$$n = K_{fs} \cdot V_f \cdot C_0 \quad (2)$$

Before the equilibrium is reached the following relation can be applied [Ouyang et al., 2006]:

$$n = [1 - \exp(-a \cdot t)] \cdot \frac{K_{fs} \cdot V_f \cdot V_s \cdot C_0}{K_{fs} \cdot V_f + V_s} \quad (3)$$

Where: n – extracted quantity of analyt

a – constant depending on sorbent, mass transfer and distribution constant of analytes between sample and sorbent

t – extraction time

K_{fs} – distribution constant of analytes between sample and sorbent

V_f – volume of sorbent (coating)

V_s – volume of sample

C_0 – concentration of analyt in the sample

The direct relation between extracted quantity of analytes and concentration in sample is very important for the calibration.

RESULTS AND DISCUSSIONS

The gas chromatographic separation of aromatic compounds is presented in Figure 5.

The identification of the peaks was done using standard substances.

Table 4 shows the retention times of each identified compound.

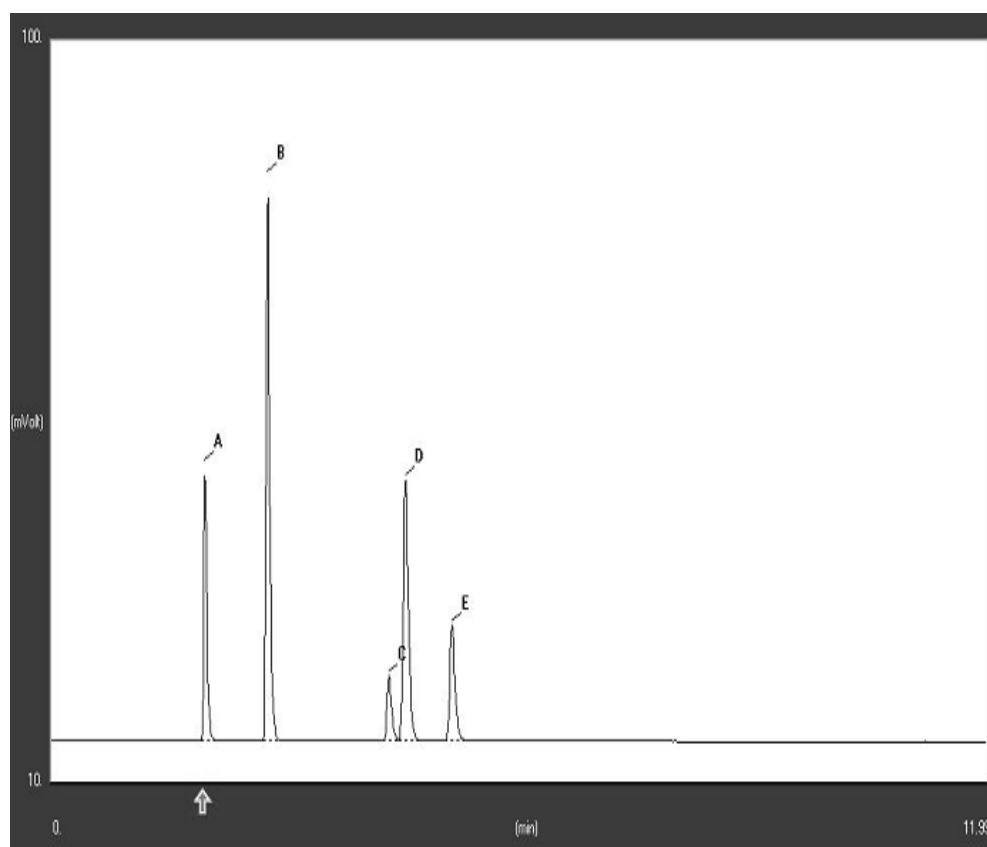


Fig. 4 Gas chromatographic separation of the aromatic compounds: (A)-benzene, (B)-toluene, (C)-Ethyl-benzene, (D)-m,p-xylene, (E)-o-xylene

Table 4

Retention times and peak areas of the aromatic compounds			
Retention Time (min)	Compound	Area (%)	Area
1.93	Benzene	22.1217	89501
2.74	Toluene	37.0529	149910
4.30	Ethyl-benzene	5.3846	21785
4.51	m , p-xylene	25.3624	102612
5.11	o-xylene	10.0785	40776

The gas chromatographic separation was good, all the peaks were symmetrical, narrow and without tailing. The extraction is very efficient, even at small concentration and short extraction time (5 minutes compared with a “classical” solvent extraction which takes at least 30 minutes, with several extractions, vaporization of solvents a.s.o.)

CONCLUSIONS

The results of the GC analysis prove that the separation is good, with symmetrical peaks, without tailing, and also the extraction is efficient due to the small concentration of the compounds.

This method is simple, fast, reproducible and can be easily applied to the analysis of more complex

environmental samples even if the contaminants are present in small amounts.

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REFERENCES

- Abedin M., Islam M., Mottaleb M., 2003, „Determination of Benzene, Toluene, Ethylbenzene and Xylene in River Water by Solid Phase Extraction and Gas Chromatography”, *Analytical Sciences*, Vol.19, p.1365-1369
- Bushnell P.J., Evans H.L., Palmes E.D., 1985, “Effects of toluene inhalation on carbon dioxide production and locomotor activity in mice”, *Fundam App Toxicol*, 5, p.971-977
- Bordej Z., Bardodejova E., 1970, “Biotransformation of Ethyl-benzene, styrene and alpha methylstyrene in man”, *Am Ind. Hyg. Assoc. J.*, Vol. 31 Issue 2, p.206-209.
- Budziak D., Martendal E., Carasek E., 2007, “New Poly-ethylene glycol solid phase microextraction fiber employing zirconium oxide electrochemically deposited onto NiTi alloy substrate for sol gel reactions”, *Journal of Chromatography A*, Vol. 1164, p. 18-24
- Cai L., Zhao Y., Dong L., Wu C., 2003, “Use of a Novel Sol Gel Dibenzo -18 – Crown 6 – Solid Phase Microextraction Fiber and a New Derivatizing Reagent for the Determination of Aliphatic Amines in Lake Water and Human Urine”, *Chromatographia*, Vol. 58, p.615-621
- Ciucanu I., Căpriță R., Swallow K., 2004, „Micro-Solid-Phase Extraction with Helical-Solid-Sorbent in the Presence of Organic Solvent for Gas Chromatography- Mass Spectroscopy Analysis of Per-O-Methylated Mono-and Disaccharides”, *Analytica Chimica Acta*, Vol. 519, Nr.1, p.93-101.
- Ciucanu I., 2002 „Helical Sorbent for Fast Sorption and Desorption in Solid-Phase Microextraction-Gas Chromatographic Analysis”, *Analytical Chemistry*, Vol.74, Nr.21, p.5501-5506.
- Ciucanu, I., 1990, „Cromatografia de gaze cu coloane capilare”, Editura Academiei Române, p. 59-93.
- DiVincenzo G.D., Krasavage W.J., 1974, “Serum ornithine carbamyl transferase as a liver response test for exposure to organic solvents”, *Am. Ind. Hyg. Assoc. J.*, Vol. 35, Issue 1, p.21-29
- Johnsson A.C., 1992, “Auditory sensitivity in rats exposed to toluene and/or acetyl-salicylic acid”, *Neuro Report*, Vol. 3, p.1141-1144
- Li X., Li C., Chen L., Li C., Sun C., 2008, “Polythiophene as a novel fiber coating for solid phase microextraction”, *Journal of Chromatography A*, Vol. 1198-1999, p.7-13
- Li X., Zeng Z., Xu Y., 2006, “A solid phase microextraction fiber coated with diglycidyl ether calix [Ungvary et al., 1992] arene yields very high extraction selectivity and sensitivity during analysis of chlorobenzenes from soil”, *Anal. Bioanal. Chem.*, Vol. 384, p.1428-1437
- Pawliszyn J., 1997, “Solid Phase Microextraction Theory and Practice”, Editura Wiley VCH.
- Ouyang G., Pawliszyn J., 2006, “MSPE in environmental analysis”, *Anal. Bioanal. Chem.*, Vol. 386, p.1059-1073
- Sun T.H., Cao L.K., Jia L.C., 2005, “Novel Activated Carbon Fiber Micro-Solid-Phase Extraction for Determination of Benzyl Chloride and Related Compounds in Water by Gas Chromatography – Mass Spectroscopy”, *Chromatographia*, Vol. 61, p.171-179.
- Ungvary G., Tartrai E., Szeberenyi S., 1982, “Effects of toluene exposure on the liver under different experimental conditions”, *Exp Mol Patol*, Vol. 36, p.347-360
- Wang W., Gong S., Cao Q., Chen Y., Li X., Zeng Z., 2005, “Solid Phase Microextraction of Aromatic Amines with an Amide Bridged Calix [Ungvary et al., 1992]-arene coated fiber”, *Chromatographia*, Vol.61, p.75-80
- Wei L., Ou Q., Li J., Liang B., 2004, “Preparation of Solid Phase Microextraction Fiber Coated with γ -Al₂O₃ and Determination of Volatile Organic Compounds in Indoor Air”, *Chromatographia*, Vol.59, p. 601-605.
- Williams P.L., James J.R., Roberts S.M., 2000, “Principles of toxicology: environmental and industrial application”, Editura John Wiley and Sons, p. 377-383
- Wu J., Yu X., Lord H., Pawliszyn J., 2000, “Solid Phase Microextraction of Inorganic Ions based on polypyrrole film”, *Analyst*, Vol.125, p.391-394.
- Xiao C.H., Liu Z.L., Wang Z.Y., Wu C.H., Han H.M., 2000, “Use of Polymeric Fullerene as a New Coating for Solid Phase Microextraction”, *Chromatographia*, Vol. 52, No.11-12, p. 803-809