

# Refrigerated Sorptive Extraction: Determination of BTEX in Water Samples

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## Abstract

Benzene, toluene, ethyl benzene, *o*-xylene, *m*-xylene, and *p*-xylene (BTEX) enrichment from aqueous samples is performed using refrigerated sorptive extraction (RSE). RSE implies the sorption of volatile compounds into polydimethylsiloxane (~ 0.39 mg) coated on an open stainless steel tube internally refrigerated by cold water. A metal tube is inserted into a 30-mL headspace vial through a hole at both sides of the vial. The sample inside the vial is equilibrated with stirring for 60 min at 40°C. After the extraction, the analytes are desorbed with 280 µL of methanol under ultrasonic bath. BTEXs are analyzed by high resolution gas chromatography–flame ionization detection. Optimization of temperature and extraction time were carried out, as well validation in terms of linearity, precision, recuperation, limits of detection and quantification. Linearity is the range 0.999–0.998, linear range between 50 and 1000 µg/L, precision is 6.1% to 14.7% in the 0.1 µg/mL level and 3.5% to 5.6% in the 1 µg/mL level. Recovery ranged from 30% to 50%, detection limits from 1.7 to 19.6 µg/L, and quantification limits from 6.7 to 64.6 µg/L. The optimized method was applied to the analysis of water samples collected near a gas station, which was suspected of contamination by gas oil leaking from storage tanks.

## Introduction

There are several applications of polydimethylsiloxane (PDMS) as an extraction medium for the enrichment of volatile and semi-volatile compounds from gaseous (headspace) and aqueous samples. Solid-phase microextraction techniques (SPME) (1) and, more recently, stir-bar sorptive extraction (SBSE) (2–4) have been widely accepted for the analysis of different water pollutants.

In the SPME technique developed by Arthur and Pawliszyn (5), the analytes are sampled directly by immersion of a fused-silica fiber coated with a liquid polymeric phase in an aqueous phase (6) or by headspace in the gaseous phase (7). SPME is an interesting technique but presents low extraction efficiencies, requiring the use of very sensitive detectors (8).

Baltussen et al. (8) described the SBSE technique using stir bars of 10 and 40 mm length, coated with PDMS. This technique, coupled with thermo desorption and gas chromatography–mass spectrometry (GC–MS) allowed detection limits in the ng/L range and much higher recoveries than the SPME technique for volatile and semi-volatiles compounds. Sandra et al. (9) described a headspace method for volatile and semi-volatile compounds in aqueous and solids samples using sorptive extraction at room temperature. The authors used a glass rod coated with PDMS (50 mg), fixed in a closed vial. After 60 min equilibration time, the rods are desorbed in a thermal desorption unit and posterior cryofocussing prior to injection and detection by GC–MS.

In an attempt to obtain better sensitivity and recoveries with the SPME method, Zhang and Pawliszyn (10) developed a new approach for headspace SPME sampling by heating the sample matrix while simultaneously cooling the fiber coating. With this procedure, the partition coefficients of analytes are significantly increased, achieving quantitative extraction for BTEX.

Sorptive extraction, like SPME and SBSE, has proven to be an interesting and environmentally friendly alternative to liquid extraction. These techniques have been optimized to reach better extraction recoveries and better limits of quantification. SBSE was born with this purpose, using more PDMS phase than SPME to promote better recoveries during the extraction process. SPME has been optimized by heating the sample matrix while simultaneously cooling the fiber coating (10). Considering these developments to enhance the extraction, cooling the PDMS phase in a SBSE system could reach adequate limits of quantification to analyze important volatile environmental pollutants like benzene, toluene, ethyl benzene, *o*-xylene, *m*-xylene, and *p*-xylene (BTEX).

In this paper, a simple and low cost method for BTEX determination in water using refrigerated sorptive extraction (RSE) is presented. A stainless steel tube, 1.5 cm length, 1 mm i.d., coated with PDMS (~ 41 µL) is placed in a closed vial with the sample, and cooled internally with iced water, while simultaneously heating the sample matrix to 40°C, obtaining a lower temperature in the PDMS coating than the sample, increasing the partition

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coefficients of analytes and improving the extraction process.

The optimization of the procedure is described for temperature and extraction time, as well as the validation for linear range, precision, recuperation, and limits of detection and quantification, allowing the determination of all the analytes in water samples at the ng/mL levels.

The method developed was applied to the sample analysis of water contaminated with BTEX. Detection and quantification is performed by capillary GC–flame ionization detection (FID).

## Experimental

### Chemicals

The reagents included: benzene from Merck (Darmsdat, Germany), toluene from Malinckrodt (Phillipsbourg, NJ), *o*-xylene, *m*-xylene, *p*-xylene from Merck (Darmsdat, Germany), ethyl benzene from Supelco (Bellefonte, PA) and methanol (nanograde) from Malinckrodt (Phillipsbourg, NJ). HPLC-grade water was used obtained in a Milli-Q system (Millipore, Milford, MA). A Sylgard 184 polymeric kit from Dow Corning (Midland, TX) was employed to obtain the PDMS phase.

A 1000 mg/L stock solution of BTEX in methanol was used to prepare an intermediate solution of 100 mg/L and a working solution of 10 mg/L of these chemicals.

### Procedure

#### Sample preparation

A 15.5 mL Milli-Q purified water sample spiked with BETX was added into a 30-mL vial. Then, 4.5 g of NaCl was added (30%). The vials have a hole at both sides, and a stainless steel tube of 1 mm i.d. and 9 cm length, with a 1.5 cm PDMS coat is passed through the vial hole and fixed with a silicon septum. The top of the vial is sealed with a headspace cap fitted with a PTFE-faced septum (Figure 1) (11). Water from an iced water bath (0°C) is pumped with an aquarium pump through the inside of the metallic tube at 20 mL/min. The samples were stirred with a magnetic stirrer at 600 rpm to speed up phase equilibrium. The analytes were desorbed from the PDMS phase with 280  $\mu$ L methanol (volume necessary to cover the bar in an adequate vial



Figure 1. Sampling set up for refrigerated sorptive extraction (RSE).

to extract the analytes) in ultrasonic bath for 20 min at 30°C; 2  $\mu$ L of this solution was injected in a gas chromatograph.

### Optimization

Optimization was performed for both temperature and extraction time. Temperature optimization was carried out at: 25, 35, 40, 60, and 85°C in 60 min time equilibration. Extraction time of: 30, 60, 90, and 120 min at 40°C were used. Concentration of BTEX in samples was 1  $\mu$ g/mL.

### Validation

**Linearity.** Linearity was evaluated by using the external standardization method with spiked samples at six concentration levels (at each concentration level, triplicate analyses were performed) with linear range between 50 and 1000  $\mu$ g/L.

**Precision.** Precision was evaluated by analysis of five replicates with spiked samples at two concentrations (100 and 1000  $\mu$ g/L) and measured by the relative standard deviation.

**Recuperation.** Recovery was evaluated by analysis of three replicates with spiked samples at two concentrations (300 and 1000  $\mu$ g/L).

**Limit of detection (LOD) and limit of quantification (LOQ).** For LOD, a concentration giving a signal-to noise ratio of 3 was considered, and for LOQ a signal-to-noise ratio of 10 was considered.

### Preparation of the tube coated with PDMS phase

A 9 cm stainless steel tube, 1 mm d.i., was coated with PDMS phase, 1.5 cm length. The metallic tube was placed in a Teflon mold (Figure 2) and covered with PDMS polymer that contains a cure agent in the proportion 10:1 (w/w) (12). The Teflon mold that contains the tube is put into a metallic ring and placed in an oven at 60°C for 1 h; after that, the mold is cooled at room temperature. The coated tube without the mold is placed again in an oven at 40°C for 30 min and then adjusted to 250°C at 10°C/min for 2 h. This treatment promotes the cross-linking of the PDMS polymer and its usage for several runs. The PDMS coating obtained has 39.5 mg weight (~ 41  $\mu$ L).

### Chromatographic equipment and operating conditions

The determinations were performed with a Shimadzu GC model QP-5050 (Kyoto, Japan) equipped with an FID detector,

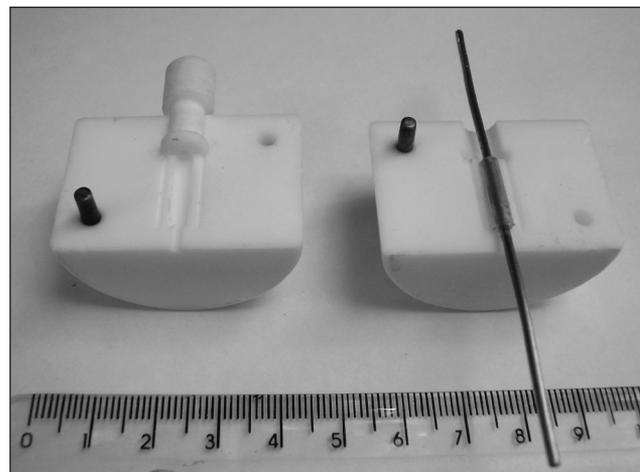


Figure 2. Teflon mold used in the PDMS cross-linking.

NST-5 column (50 m × 0.25 mm i.d. × 0.40 μm thickness), and split-splitless injector. Chromatographic conditions were: split, 10:1; carrier, hydrogen (1.5 mL/min); injector and detector temperatures, 250°C and 270°C, respectively. Column program: initial temperature, 40°C; held for 4 min, and then increased at 10°C/min to 115°C.

Confirmation values of LOD for the benzene were made in a Shimadzu GC-MS model 17-A.

## Results and Discussion

### Method optimization

To optimize extraction temperature, a 1000 μg/L BTEX solution with 30% NaCl was held at temperatures of 25, 35, 40, 60, and 85°C with 600 rpm stirring for 60 min equilibration time. From these values, the best temperature was 40°C (Figure 3). As a result, the extraction time optimization was performed at this temperature for several time values. In Figure 4 it is possible to appreciate that 60 min time is the optimum equilibration time. Addition of 30% NaCl to the water was chosen to enhance the response in RSE.

A study of the influence of the temperature in the extraction efficiency was performed by measurement of the temperature at the outlet of the tube coated with the PDMS phase. Temperature

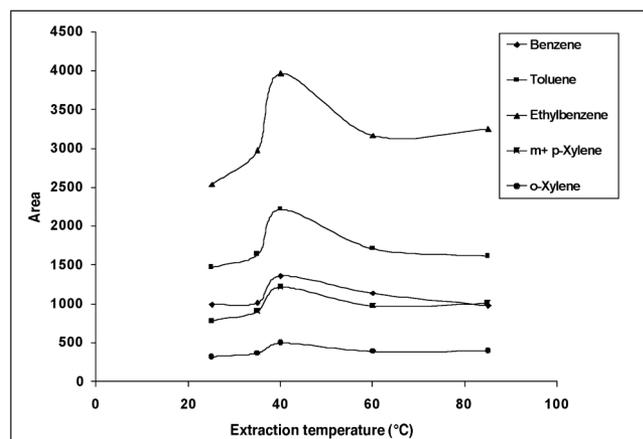


Figure 3. Extraction temperature profile of 1000 μg/L BTEX in aqueous solution (30% NaCl) at 60 min equilibration time.

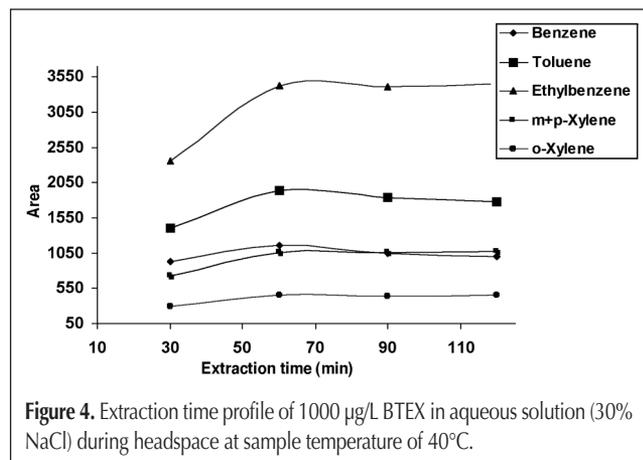


Figure 4. Extraction time profile of 1000 μg/L BTEX in aqueous solution (30% NaCl) during headspace at sample temperature of 40°C.

changes modify the flow rate of the water from the iced water bath passing through the tube in the sample vial. At different flow rates, outlet temperatures of 10, 11, 12, 15, 20, and 28°C were obtained (28°C with the water bath at room temperature), sample temperature was maintained at 40°C. Figure 5 illustrates the influence of outlets temperature in the response. Fiber/headspace partition coefficient of the analytes increases its value at lower temperatures (10). The lowest temperature reached with the experimental conditions of the method was 10°C, and that temperature was used for all the experiments.

### Method Validation

#### Linearity, precision, LOD, and LOQ of the method

To evaluate the linearity of the method, a calibration curve was performed with concentrations of 50, 130, 320, 550, 800, and 1000 μg/L for all analytes. Three replicate samples for each point were made. The regression coefficients for the analyzed compounds are in order of 0.999 (Figure 6).

The precision of the RSE method was evaluated at two concentration levels (100 and 1000 μg/L) to give relative standard deviation (RSD) between 6% to 15% for the low level and 4% to 6% for the high level (Table I). Five extraction replicates for each level were made.

Recovery for 300 μg/L levels goes from 25% to 46% and for 1000 μg/L level from 30% to 50% (Table II). Values were obtained

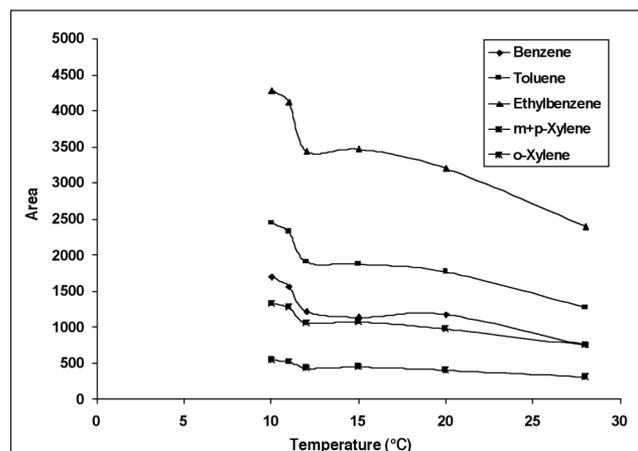


Figure 5. Effect of different water outlets temperatures in the headspace vial on the extraction response.

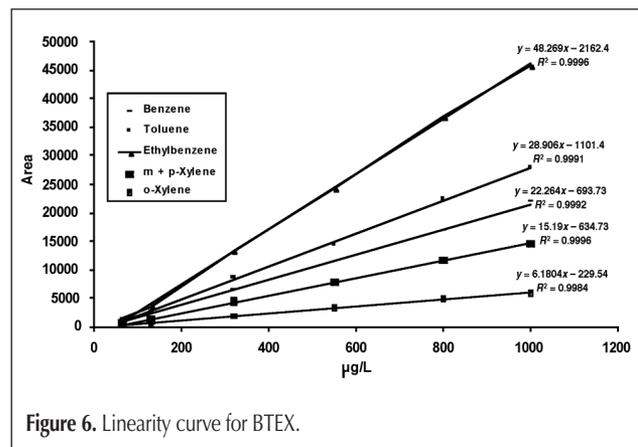


Figure 6. Linearity curve for BTEX.

in triplicate.

The detection and quantification limits were calculated as 3 and 10 times the average of the baseline noise, respectively (13). The LOD and LOQ for all the BTEX are in the  $\mu\text{g/L}$  level (Table III).

The detection limits for the same type of analytes depends on the PDMS coating temperature, on the matrix sample temperature, on the headspace volume, and on the injection system used.

The effect of PDMS and sample matrix temperature were studied by Zhang and Pawliszyn (10). Partition coefficients and the sensitivity increased when the temperature of the PDMS coating was low. This effect is more pronounced if the gap

**Table I. Precision of the RSE Method at Two Conc. Levels\***

BTEX	Precision (RSD %)	
	100 $\mu\text{g/L}$	1000 $\mu\text{g/L}$
Benzene	14.8	5.6
Toluene	18.8	4.2
Ethylbenzene	6.1	4.0
<i>m + p</i> -Xylene	9.0	4.6
<i>o</i> -Xylene	10.3	3.5

\* 5 replicates at each level.

**Table II. Recovery Values at Two Conc. Levels**

Compound	Recovery (%) level (300 $\mu\text{g/L}$ )	Recovery (%) level 1000 $\mu\text{g/L}$
Benzene	25	30
Toluene	39	42
Ethylbenzene	43	48
<i>m + p</i> -Xylene	44	49
<i>o</i> -Xylene	46	50

\* 3 replicates each level.

**Table III. Limits of Detection and Quantification**

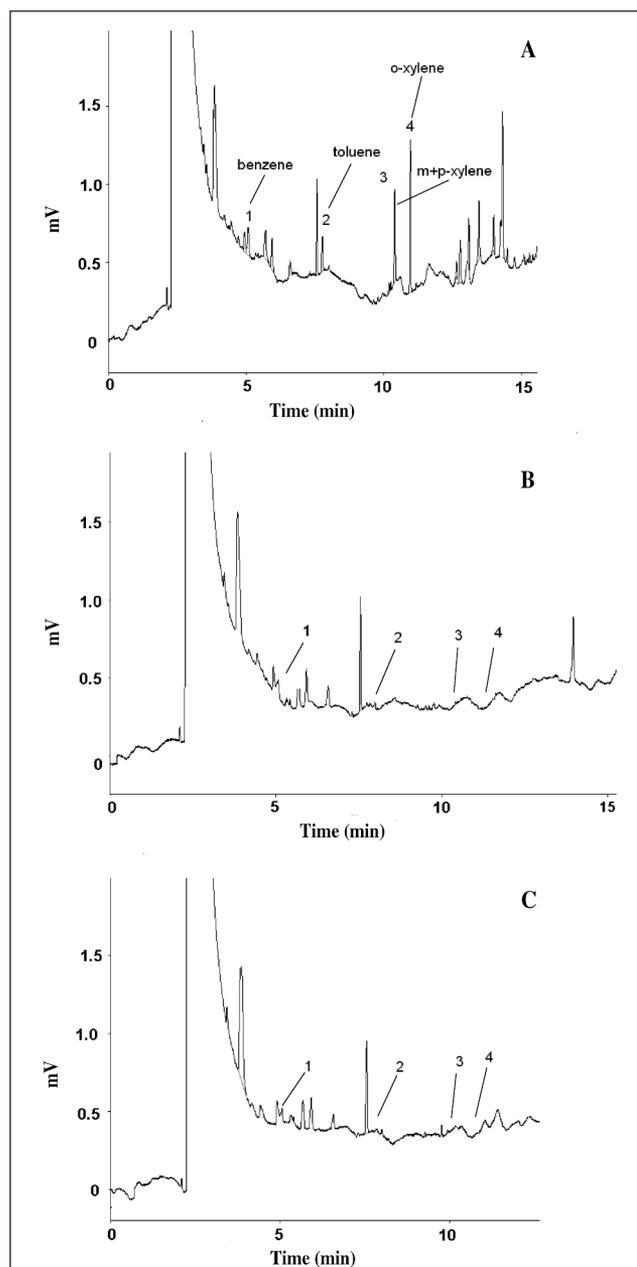
BTEX	LOD ( $\mu\text{g/L}$ )	LOQ ( $\mu\text{g/L}$ )
Benzene	3.2	10.7
Toluene	3.0	10.0
Ethylbenzene	1.7	6.7
<i>m + p</i> -xylene	7.7	24.7
<i>o</i> -Xylene	19.6	64.6

**Table IV. PDMS/headspace BTEX's Partition Coefficients**

Compound	$K^*$	$K^\dagger$
Benzene	559	493
Toluene	1557	1322
Ethylbenzene	1557	1322
<i>o</i> -Xylene	5293	4417

\* Sample temperature at 40°C, PDMS phase 10°C.  
 $\dagger$  Sample and PDMS phase at 25°C (10).

between the coating and the matrix increases. In Table IV, the values for PDMS/headspace partition coefficients of the BTEX, calculated according equation from the literature (10), are presented. The temperature of the coating could be lowered by getting a higher flow rate of the refrigerant water passing through the metallic tube. This is possible using a more powerful pump. Temperature of the sample matrix should not be higher than 40°C because an increase in this temperature decreases the partition coefficient between the PDMS and the headspace (Figure 4).



**Figure 7.** Water samples of industrial site suspected contaminate with gasoline. Water sample collected near a gas station and suspected to be contaminated with benzene (68  $\mu\text{g/L}$ ), toluene (70  $\mu\text{g/L}$ ), *m + p*-xylene (147  $\mu\text{g/L}$ ) and *o*-xylene (621  $\mu\text{g/L}$ ) (A). The arrows and numbers indicate the retention time and identity of the analytes expected to be present in the sample: 1. Benzene (5.037 min); 2. Toluene (7.731 min); 3. *m + p*-Xylene (10.363 min) and 4. *p*-Xylene (10.935 min). No BTEX found (B); Blank water (C).

Minimum headspace volume attained was 14.5 mL. The headspace volume is limited, in that case, for the size and the design of the vial. With a smaller headspace volume, a higher response could be obtained (1); this was proved in this work and in early experiments.

Sample injection was performed in the split mode 10:1, which gives better results in terms of efficiency than the splitless mode for volatile compounds, such as benzene and toluene. With the use of a thermo desorption unit coupled with the GC, the LOD could be improved several times. Also, the detection limits could be enhanced with the use of a large volume injector.

Recovery could be better by lowering the PDMS temperature and using a coating phase of a volume higher than 41  $\mu\text{L}$ , for instance 100  $\mu\text{L}$ .

Once in the retention time of benzene, a small peak of solvent impurity is seen. A confirmation of the LOD of the benzene was made in GC-MS.

Four BTEXs were detected in a real water sample contaminated by gas oil leak from storage tanks from a gas station. In other water samples also suspected of being contaminated by a gasoline leak, none of these compounds were detected (Figure 7).

## Conclusion

A novel approach has been developed for the headspace sorptive extraction method for volatiles compounds in water samples that allows the enhancement of PDMS/headspace partition coefficients. The method is quite simple, reliable, and low cost; it also uses no complicated equipment, and the detection is realized with an FID detector.

The method presents good linearity, repeatability, and good LODs and LOQs for its application in the analysis of BTEX in contaminated water samples.

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