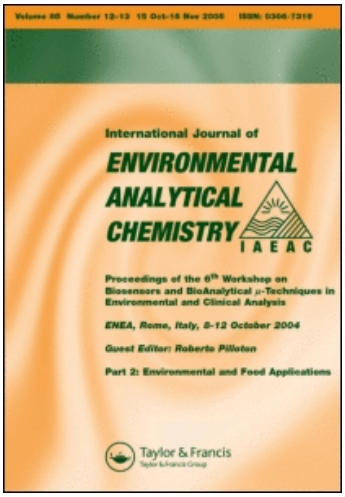

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Comparative study of direct immersion and headspace single drop microextraction techniques for BTEX determination in water samples using GC-FID

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Comparative study of direct immersion and headspace single drop microextraction techniques for BTEX determination in water samples using GC-FID

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In the present work the determination of benzene, toluene, ethylbenzene and o-xylene (BTEX) in environmental sample solutions using gas chromatography with flame ionisation detection (GC-FID) combined with three different sampling techniques, such as; direct single drop microextraction (DI-SDME), headspace single drop microextraction (HS-SDME) and ultrasonic assisted HS-SDME, were compared. In all of these techniques, for the determination of BTEX, the experimental parameters such as organic solvent effect, extraction time, agitation speed and salting effect were optimised. At their optimised conditions of operation the detection limits, times of extraction and precision for the three techniques are established. A detailed comparison of the analytical performance characteristics of these techniques for final GC-FID determination of BTEX in water samples was given. The technique provided a linear range of 50–20000 ng mL^{-1} for DI-SDME and 10–20000 ng mL^{-1} for HS-SDME methods, good repeatability (RSDs $<$4.72–7.74% for DI-SDME and 1.80–7.05% for HS-SDME ($n = 5$), good linearity ($r \geq 0.9978$) and limits of detection (LODs) in the range of 0.006–10 ng mL^{-1} for DI-SDME, 0.1–3 ng mL^{-1} for HS-SDME methods (S/N = 3). Then the optimised techniques were also applied to real samples (river and waste waters) containing BTEX and similar precision (RSD < 8.2, $n = 3$) was obtained.

Keywords: single drop microextraction (SDME); headspace single drop microextraction (HS-SDME); BTEX; water analysis; GC-FID

1. Introduction

The term BTEX defines the mixture of benzene, toluene, ethylbenzene and the three xylenes isomers (*ortho*, *meta* and *para*), all being harmful volatile organic compounds (VOCs). BTEX are emitted to the environment from an extensive variety of sources, including combustion products of wood and fuels, industrial paints, adhesives, degreasing agents and aerosols. These compounds are well known due to their contaminations in soil and groundwater. In order to reduce the human intake of these hazardous substances, a chemical control and consequently methods of analysis is desirable.

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Gas chromatography (GC) is the main alternative of choice for the determination of BTEX in environmental samples. Although the direct analysis of the samples has been traditionally employed for their determination, microextraction techniques such as liquid phase microextraction (LPME) are proposed as useful alternatives to the conventional approach [1–6].

Nowadays, LPME methods have been commonly used instead of the conventional LLE methods, due to some advantages, such as: speed, simplicity, using very little amount of organic solvent which is very good for a green environment, and high enrichment factor [7–12]. Also, the methods can be easily automated [13]. The LPME was classified into several operational modes, such as single drop microextraction (SDME) [14,15], membrane protected LPME [16,17], and all of these methods could be achieved in two and three phases [2,4]. A closer look at LPME applications indicates that the single drop microextraction (SDME) technique is the modality of choice for this type of application. In SDME the extraction phase is a drop of water-immiscible solvent suspended in the stirred aqueous solution. Because of its extreme simplicity, many successful applications of SDME have been reported in the literature [18,19].

In the present work, we tried to compare the two modes of these methods, namely direct immersion (DI-SDME) and headspace single drop microextraction (HS-SDME), and the methods combined with GC-FID for the determination of BTEX as one of the major contaminants in the environmental water samples.

The normalised quality limit for drinking water according to the EPA is for benzene 5, toluene 1000, and ethylbenzene 700 and for xylenes 10000 $\mu g\,L^{-1}$, respectively [20]. The analysis of BTEX in aqueous samples is usually achieved by purge-and-trap gas chromatography [21]. In order to determine BTEX at trace or ultra trace levels of concentration in water samples, the solid phase microextraction with headspace analysis has also been used [22]. Recently, the determination of BTEX in water samples using ionic liquid-based SDME followed by GC-MS determination has been reported [23]. In this work we used SDME to extract the analytes from the water samples and then used the gas chromatograph for analysis. In these methods, a microdrop of organic solvent as an acceptor phase was used in two different modes. In the first one, acceptor microdrop was directly immersed in the sample solution and in the second one, it was kept in the headspace above the sample solution until the equilibrium was reached. Afterwards, the microdrop was withdrawn back inside the syringe and injected into the GC-FID for the analysis.

Although some works have been reported on this issue [5,6], here we compared three different modes. Moreover, the addition of the surfactant into the acceptor phase has increased the extraction efficiency. Therefore, the comparison of these two modified methods with each other produces some novelties to the technique.

2. Experimental

2.1 *Reagents and standards*

Methanol, 2-octanone, heptanol and n-heptane were Suprasolv quality (for organic trace analysis) and were obtained from Merck (Darmstadt, Germany) and 1-octanol and 2-octanol were purchased from Fluka (Buchs, Switzerland). Triton X-100 was obtained from Merck. Analytical grade reagents; benzene, toluene, ethylbenzene and o-xylene also were purchased from Merck (Darmstadt, Germany). Stock solutions of BTEX

($2000\,\mu g\,mL^{-1}$) were prepared by dissolving calculated amounts of each ones in methanol. Fresh working solutions ($2\,\mu g\,mL^{-1}$) were prepared daily by diluting the stock solution in distilled water.

2.2 *SDME extraction apparatus*

A Hamilton 10 μL syringe (Hamilton Bonaduz AG, Bonaduz, Switzerland) was used to introduce the acceptor phase, hold the microdrop through extraction process and act as the injection syringe. In the processes, a tiny septum at the tip of the needle of a syringe is used to prevent falling microdrops and increase the stability and precision. A VELP SCIENTIFICA, ARE heating-magnetic stirrer (0–1200 rpm, Italy) was used to mix the sample solution, and decrease the time of microextraction procedure. After extraction for a prescribed period of time (typically 20 min), 1 μL of the organic solvent was withdrawn into the microsyringe and then injected into the GC-FID for analysis. In the HS-SDME with ultrasonic waves we used a BRANSON ultrasonic bath; model 1510 E-DTH, which radiates waves in 42 KHz ± 6% frequency. Cavitation occurs and the analytes put out from the solution through space over it during these waves production. Afterwards the vaporised compounds were extracted into the microdrop solvent. The sample vial must be firmly fixed during the extraction process.

2.3 *Instrumentation*

Chromatographic analyses were performed on Chrompack CP9001 (Middelburg, the Netherlands) gas chromatography equipped with a split/split-less injector used in split mode and flame ionisation detector (FID). Separations were conducted using a CP-Sil 24CB (50% phenyl, 50% dimethylsiloxane) capillary column, WCOT Fused silica, 30 m × 0.32 mm ID with 0.25 μm stationary film thickness (Chrompack, Middelburg, the Netherlands). The carrier gas was ultra pure helium (99.999%, Sabalan Co., Iran) at a flow rate of $1.11\,mL\,min^{-1}$ and split mode was 1 : 46.

The GC conditions were as follows: injector temperature 210°C; initial oven temperature 60°C for 1 min increased to 90°C at a rate of $5°C\,min^{-1}$ and a second ramp to 200°C at a rate of $30°C\,min^{-1}$. The total time for one GC run was 17 min. The FID temperature was maintained at 250°C. The flow rates of air and hydrogen (99.99%, Sabalan Co., Tehran, Iran) for FID were 250 and $30\,mL\,min^{-1}$, respectively.

3. Results and discussion

3.1 *Optimisation of DI-SDME*

Factors affecting the DI-SDME efficiency such as: kind of organic extraction solvent, the extraction time, microdrop volume, stirring rate, surfactant effect, etc., were optimised.

The first parameter to be optimised was organic solvent. The extraction solvent must have good affinity for target compounds and must be immiscible with water. The organic solvent should have excellent gas chromatographic behaviour. On the basis of these considerations and with reference to our previous work [24,25], 2-octanone, heptanol, n-octanol, 2-octanone and n-heptane were tested in preliminary experiments. Some solvents such as hexane have a good extraction performance but its peak has interference with the analytes peaks.

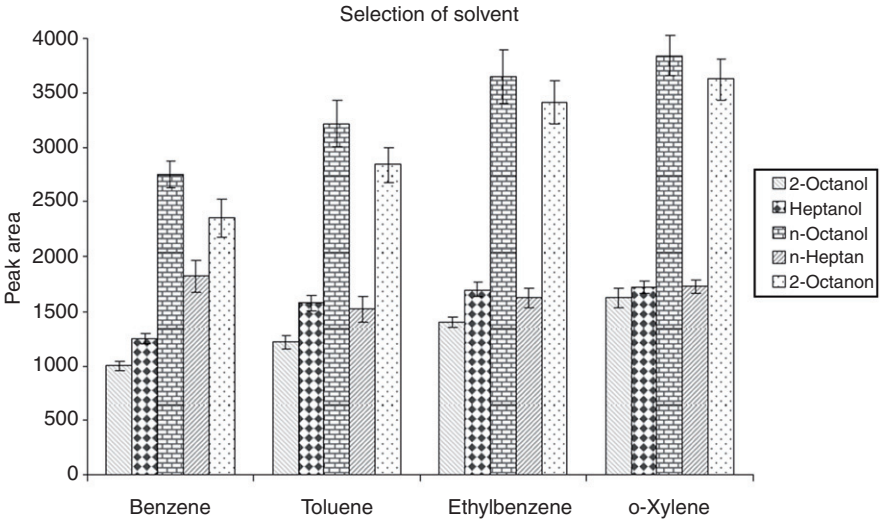

Figure 1. Effect of extraction solvent on DI-SDME extraction efficiency ($n = 3$). Other experimental conditions are as follows: analytes concentration level at $2\,\mu g\,mL^{-1}$, 600 rpm stirring speed, 25 min extraction time, 5 mL donor sample volume.

Thus, n-octanol showed the best extraction performance among the five extraction solvents in terms of analyte peak areas (Figure 1).

Moreover, n-octanol has shown a good selectivity for all analytes and has the least solvent loss due to the vaporisation. Consequently, n-octanol was used for the subsequent experiments.

Surfactants, or surface active agents, are amphiphilic molecules which are added to donor phase. The head of it is polar, or hydrophilic, and the tail of it is hydrophobic. The tail is generally a hydrocarbon chain with a different number of carbon atoms and may be linear or branched, and also contains aromatic rings. The surfactant molecules can be associated in aqueous solution to form molecular aggregates, called micelle. The minimum concentration of surfactant required for producing micelle is called critical micellar concentration (CMC). One of the most important properties of these compounds is their good capacity to solubilise solutes of different character and nature [20,26–30]. These solutes may interact electrostatically, hydrophobically or by a combination of both effects. This capacity of the surfactant to solubilise different compounds has been used for organic compounds and bio-analysis of different basic drugs as model compounds [12]. In this work, nonionic surfactants, Triton X-100, Brij54, and Brij58 were used. The nonionic surfactants could be a good choice for extracting of BTEX in our analysis. Surfactant concentration is an important parameter for effective extraction. The extraction efficiency of the relative non-polar organic compounds can be reached to about 100% even when very low surfactant concentrations are used [29].

The concentration of surfactants must be kept under the amount of it in the case of CMC, because around the optimal concentration of CMC, the efficiency of extraction will be decreased. In the same conditions Triton X-100 has shown better results than others and at an optimised concentration of 0.2 mM has the best efficiency for this analysis (Figures 2 and 3).

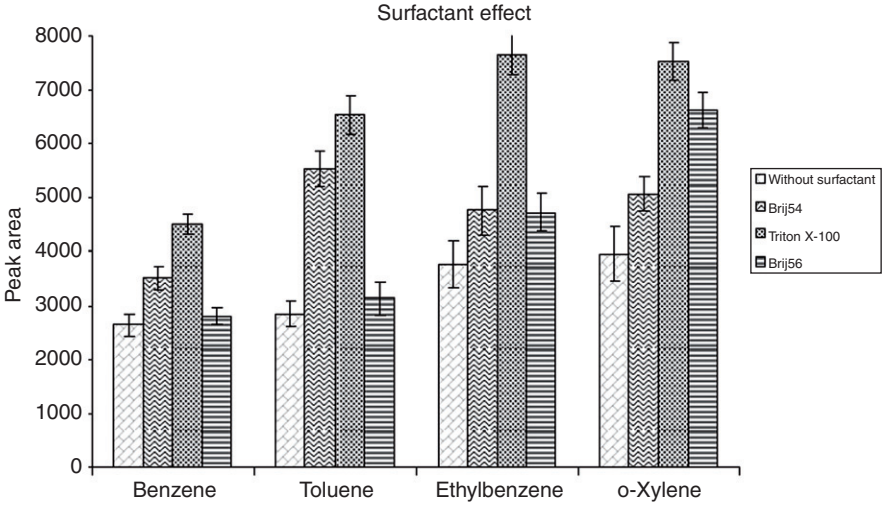

Figure 2. Effect of surfactant on DI-SDME extraction efficiency ($n = 3$). Other experimental conditions were fixed. Concentration of each surfactant is steady and less than CMC for same surfactant.

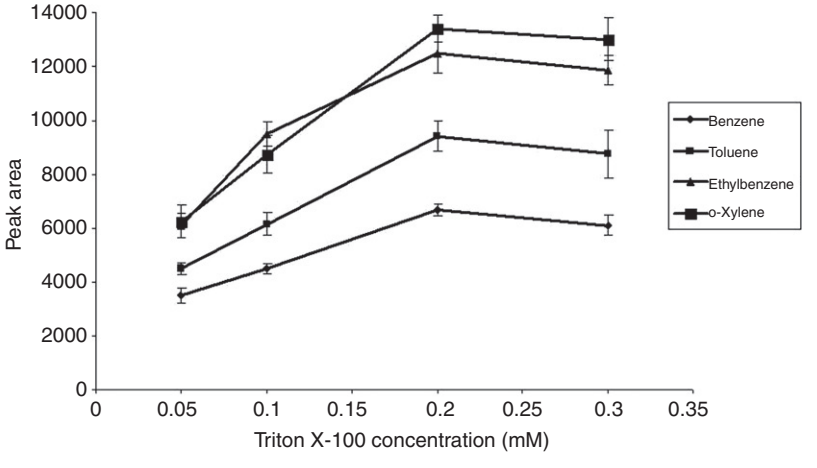

Figure 3. Effect of surfactant concentration on the DI-SDME extraction. Other experimental conditions are as follows: analytes concentration level at 2 μg mL^{-1}, 600 rpm stirring speed, 25 min extraction time, 5 mL donor sample volume, Triton X-100 as the optimal surfactant.

It is important to establish the extraction time profiles of target analytes so as to configure optimal extraction time. Extractions were performed in a period of 5, 10, 15, 20, 25, and 30 min, respectively, while the other parameters remained constant. The results demonstrated that all target compounds gave a similar trend. All the analytes studied yielded the largest peak areas in a period of 20 min and then the peak areas were decreased with the increase in the extraction time. So a period of 20 min was used for the subsequent experiments.

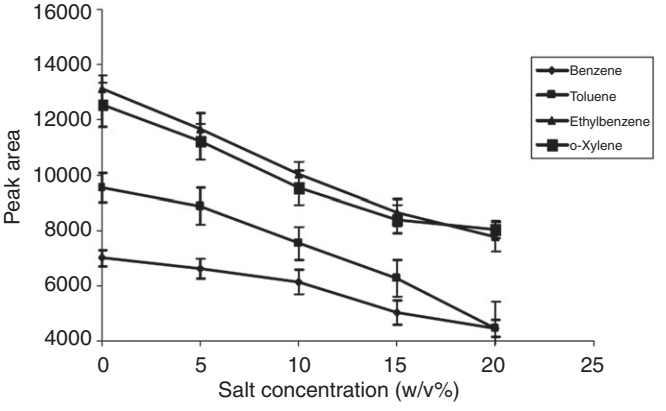

Figure 4. The effect of salt on the extraction efficiency of BTEX compounds when using n-octanol as the optimal solvent and Triton X-100 concentration at 0.2 mM. Other extraction conditions: analytes concentration 1 μg mL^{-1}, stirring rate 720 rpm, extraction time 20 min.

In the case of agitation effect on the extraction process, as we have explained in the previous research [24,25], the instrumental response was examined for several stirring rates ranging from 0 to 1200 rpm for a 20 min extraction of 5 mL aqueous samples 2 μg mL^{-1} of each target analyte. The results confirmed that agitation of the sample greatly enhances extraction efficiency. Therefore, a 720 rpm setting was selected as optimal stirring rate for the subsequent experiments.

The effect of the salt addition to the donor solution prior to the extraction has been widely investigated [31]. Depending on the target analytes, an increase in the ionic strength of aqueous solution may have various effects on the extraction: it may enhance [4,32], not influence [33,34], or limit the extraction efficiency [33,34]. To investigate the salt effect on the process, the extraction was performed with 5 mL sample solution containing various concentrations of NaCl (0, 5, 10, 15 and 20%). The peak area decreased with increasing salt concentration in the aqueous sample (Figure 4). We have found the same results for BTEX determination in our lab [24,25]. Therefore, no salt was added to the sample solution in further extractions.

Different volumes of water samples were examined while other conditions were kept constant; in 5 mL of water sample better extraction efficiency was obtained in 20 min. Different volumes of microdrop were selected (1, 1.5, 2, 2.5 and 3 μL). Although, the efficiency at 2 μL of the microdrop solvent is the best, for more safety of the capillary column, 1 μL of the solvent was injected into GC column.

3.2 *Method validation of DI-SDME*

Under the optimised processes, the following conditions were selected: 2μL n-octanol microdrop as organic solvent, Triton X-100 concentration as surfactant, 0.2 mM, 5 mL water samples, 720 rpm stirring rate, no NaCl addition and 20 min extraction time. All experiments were carried out at room temperature, $22 \pm 0.5^{\circ}$C.

The dynamic linear ranges, precisions and the limits of detection (LOD) have been evaluated in order to assess the performance of the microextraction method. Results are shown in Table 1. The calibration curves were linear in the ranges studied for

Table 1. Linearity, enrichment factors, precision (RSDs, $n = 5$) and LODs (S/N = 3) of DI-SDME.

Compound	Enrichment factor	RSD% ($n = 5$)	Linear range ($ng\,mL^{-1}$)	r	LOD ($ng\,mL^{-1}$, $n = 5$)
Benzene	43.8	4.72	50–20000	0.9997	10
Toluene	54.4	6.54	50–20000	0.9993	5
Ethylbenzene	57.3	8.09	50–20000	0.9978	5
o-Xylene	64.5	7.74	50–20000	0.9983	6

each compound, with correlation coefficients (r) between 0.9978 and 0.9997, so a direct proportional relationship between the extracted amount of compounds and the initial concentration of the sample was demonstrated. Limits of detection were calculated as the minimum concentration providing chromatographic signals which is 3 times higher than background noise. LODs were determined in the distilled water.

LODs were below $10\,ng\,mL^{-1}$ for all analytes which shows a good sensitivity of the method. Benzene with higher LOD is the compound with the lower response in the GC system and the lower sensitivity can be also attributed to lower enrichment factor which was achieved in the organic solvent than the other compounds. The RSD values obtained were satisfactory and ranged between 4.72 and 8.09% for all analytes.

3.3 *Optimisation of HS-SDME*

The HS-SDME method was used for BTEX determination employing the conventional mode which uses magnetic stirrer and heating. In addition, in this method, ultrasonic waves are radiated through the sample vial in an ultrasonic cleaner.

Different solvents, i.e. n-octanol, 2-octanol, 2-octanone and n-heptane, were examined at the same conditions ($2\,\mu g\,mL^{-1}$ analytes concentration, stirring rate 960 rpm, 15 min extraction time, 50°C water pool temperature and 5 mL donor sample volume). The n-octanol was selected as the best extraction solvent. This result was also applied for the HS-SDME by ultrasonic waves (Figure 5).

In the HS-SDME method, the temperature of the sample solution is the main factor that must be optimised, while keeping other conditions constant.

At 35°C the maximum extraction efficiency has been achieved and beyond 35°C it decreased. This effect is not so significant for benzene and toluene, but for o-xylene and ethylbenzene may be due to their higher boiling points and competitions in transformation to the gas phase, the effect is more pronounced. Therefore the optimal experimental conditions were: $2\,\mu g\,mL^{-1}$ analytes concentration, 960 rpm stirring rate, 5 mL sample volume, 1 μL drop volume and 15 min extraction time.

In this method because of un-sideway contact between aqueous sample and acceptor phase, perturbations of samples are not too efficient on extraction. We used a high and steady stirring rate for this method. Optimal stirring rate was 960 rpm.

Extraction time, in a period of 5, 10, 15, 20, and 25 min, was examined while the other parameters were kept constant. The optimum extraction time was found to be 20 min.

The salt effect on extraction efficiency was tested by adding salt to the donor solution prior to extraction, Therefore the extraction was accomplished with 5 mL sample solution

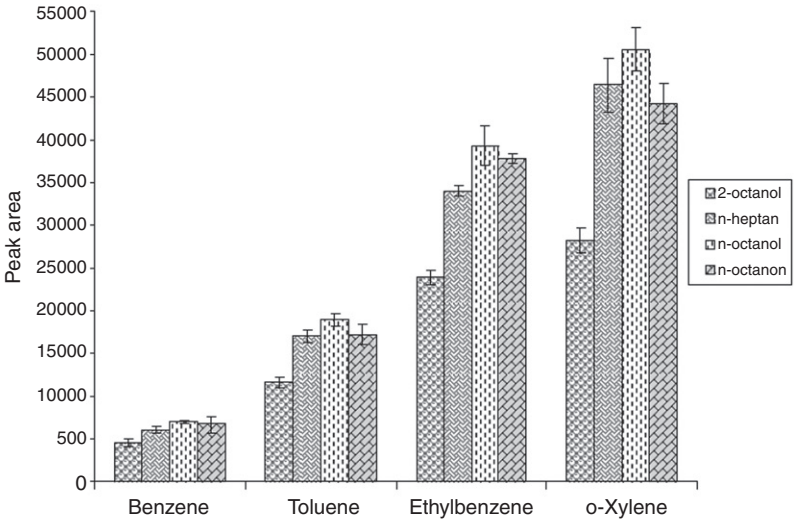

Figure 5. Effect of extraction solvent on HS-SDME extraction efficiency ($n = 3$). Other experimental conditions are as follows: concentration level at 2 μg mL^{-1}, 960 rpm stirring speed, 50 °C water pool temperature, 15 min extraction time, 5 mL donor sample volume and 1μL microdrop volume.

containing various concentrations of NaCl (0, 5, 10, 15 and 20%). The peak area was decreased with increasing the salt concentration in the aqueous sample. So, no salt was added to the sample solution in further extractions.

Using different volumes of water samples (3, 4, 5, 6 and 7 mL) and also microdrops (1, 1.5, 2, and 2.5 μL) were examined while keeping the other parameters constant. The volume of the water sample was changed and its effect was investigated on the extraction efficiency. Equilibrium between water sample and solvent microdrop in the headspace due to the reduction of free space over water and increasing analytes density in that space becomes so quick. Therefore, the optimal volume was 6 mL which was selected for further analysis. For microdrop volume, at 2 μL volume the maximum efficiency was obtained but 1 μL of it was injected into GC due to its limitation.

3.4 *Method validation of HS-SDME*

After optimising all experimental factors, the following conditions were selected: a 2μL n-octanol drop as organic solvent, 35°C extraction temperatures, 960 rpm stirring rate, without NaCl content, 20 min extraction time and 6 mL water samples. Linearity, precision and detection limits have been evaluated and the results are shown in Table 2. The calibration curves were linear in the range of study for each compound, with correlation coefficients, between 0.9986 and 0.9993. Limits of detection were calculated as already mentioned. LODs were below 1 ng mL^{-1} for the all analytes which confirm the good sensitivity of the method. The RSD values obtained for HS-SDME ranged between 1.80 and 6.63% for all analytes. This method has relatively better results than DI-SDME. Usually due to relative volatility of BTEX compounds, headspace methods can produce better results.

Table 2. Linearity, enrichment factors, precision (R.S.D.s, $n = 5$) and LODs (S/N = 3) of HS-SDME.

Compound	Enrichment factor	RSD% ($n = 5$)	Linear range ($ng\,mL^{-1}$)	r	LOD ($ng\,mL^{-1}$, $n = 5$)
Benzene	82.8	1.80	10–20000	0.9993	1
Toluene	206.6	4.31	10–20000	0.9993	0.1
Ethylbenzene	387.7	6.63	10–20000	0.9986	0.1
o-Xylene	418.3	5.83	10–20000	0.9987	0.1

Table 3. Linearity, enrichment factors, precision (R.S.D.s, $n = 5$) and LODs (S/N = 3) of HS-SDME with radiate ultrasonic waves on water sample.

Compound	Enrichment factor	RSD% ($n = 5$)	Linear range ($ng\,mL^{-1}$)	r	LOD ($ng\,mL^{-1}$, $n = 5$)
Benzene	72.6	2.32	10–20000	0.9940	3
Toluene	182.8	7.05	10–20000	0.9994	1
Ethylbenzene	378.7	4.90	10–20000	0.9982	0.1
o-Xylene	408.5	5.16	10–20000	0.9984	0.1

Finally, we used ultrasonic waves instead of the magnetic stirrer to examine a new modification of the HS-SDME method [36,37]. The ultrasonic wave that was used in this method radiated from an ultrasonic cleaner with 44 kHz ±6% frequency and has low intensity. Position of the sample vial in ultrasonic cleaner is important and must be fixed during the extraction; the vial containing analytes is placed in the sono-bath cleaner, under the ultrasonic waves applied to it. Due to the irradiation process in the bath while the extraction is happening, the water of the pool was being gently warmed. This effect will cause some errors in the extraction. Therefore we tried to keep the temperature of the water pool constant throughout the extraction process.

The parameters which were optimised in this method are nearly the same as those used for HS-SDME. These are organic solvent, extraction temperature, water sample and microdrop volume, the extraction time and salt effect which must be examined.

Extractions were performed for 5, 10, 15, 20, and 25 min, while the other parameters remained constant. The results showed that 20 min is the best extraction time. In this method the salt effect has the same effect as the last method, i.e. exceeding the percentage of salt in donor solution causes decrease in the extraction efficiency, so no salt addition was recommended for further experiments.

In the ultrasonic wave assisted method optimising factors are: 2 μL of n-octanol as organic solvent microdrop, 35°C extraction temperature, 20 min extraction time, no NaCl content, and 6 mL water samples. Linearity range, precision and the detection limits have been evaluated. Results are shown in Table 3. The calibration curves were linear in the range studied for each compound, with correlation coefficients, between 0.9982 and 0.9994. LODs were below 1 $ng\,mL^{-1}$ for all analytes which show the good sensitivity for method. The RSD values obtained for HS-SDME ranged between 2.32 and 7.05% for the analytes.

Table 4. The concentration (Conc.) of BTEX compounds ($n=3$) ($\mu g\,mL^{-1}$) found in wastewater sample and spiked river water sample at concentration level of $2\,\mu g\,mL^{-1}$ with relative recoveries (R.R%).

		River water		Wastewater[b]
Method	Analytes	Spiked Conc. ($\mu g\,mL^{-1}$)	R.R%	Founded Conc. ($\mu g\,mL^{-1}$)
DI-SDME	Benzene	2	91.2	nd[a]
	Toluene	2	85.9	nd
	Ethylbenzene	2	90.9	nd
	Xylene	2	88.6	nd
HS-SDME	Benzene	2	96.9	nd
	Toluene	2	97.2	nd
	Ethylbenzene	2	99.9	0.0042
	Xylene	2	98.0	0.0012
HS-SDME with ultrasonic waves	Benzene	2	93.8	nd
	Toluene	2	93.2	nd
	Ethylbenzene	2	93.0	nd
	Xylene	2	89.8	0.0013

Notes: [a]Not detected. [b]We could find some of the analytes in the wastewater (without spiking the standards).

The method has comparative results with simple DI-SDME, and is applied for the real sample solutions.

3.5 *Real water analysis*

The above three techniques were applied to the determination of BTEX in river water and wastewater samples. The river water sample was collected from a local river near the university campus and wastewater was obtained from a research chemical institute, all from the city of Mashhad, Iran.

Both the river water sample and the wastewater were filtered through a filter paper before analysis. No BTEX compounds were detected in the river water sample; therefore river water samples were spiked with the BTEX compounds to assess matrix effects. LPME methods are non-exhaustive extraction procedure and the relative recovery (determined as the ratio of the concentrations found in natural and distilled water samples, spiked with the same amount of analytes), instead of the absolute recovery (used in exhaustive extraction procedures), was employed. Table 4 shows the recovery for BTEX compounds in spiked river water and wastewater samples.

It can be concluded from Table 4 that headspace methods have better results for BTEX compounds than the DI-SDME method.

4. Conclusions

LPME methods combined with GC-FID were successfully applied for the analysis of trace levels of BTEX in environmental water samples. The developed protocol proved to be a simple, rapid, inexpensive, precise and sensitive analytical procedure.

The proposed DI-SDME technique using surfactant is a promising method for the analysis of trace BTEX in many environmental matrices. The results obtained with the method described above indicate that surfactant assisted DI-SDME methodology is a good alternative extraction technique for BTEXs in water and offers highly interesting advantages from an analytical point of view, such as possibility of extracting and pre-concentrating the analytes of different polarities. Surfactants are less toxic and cheaper than the extractants used in LPME. The most commonly used surfactants are commercially available too.

The HS-SDME methods used in this work have higher efficiencies than DI-SDME for BTEX and also volatile organic compounds. Generally, for many complex samples, headspace extraction is the fastest and cleanest method for analysing volatile components in dirty matrixes. Headspace analysis also lends itself to automation for quality control or sample screening. This is made possible by modern instrumentation being able to reproducibly prepare samples in an efficient manner. In this case of SDME, the solvents should not even be water immiscible as in the case of direct LPME from water solutions. Headspace LPME should also be applied for the determination of volatile analytes in solid matrices.

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