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Determination of Organic Sulfur Contaminants Using Hollow Fibre-protected Liquid-phase Micro-extraction Coupled with Gas Chromatography

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A simple and solvent-minimized sample preparation technique based on hollow fibre-protected liquid-phase micro-extraction has been developed for extraction of fifteen organic sulfur compounds (OSCs) from aqueous samples. The analysis of the extracted OSCs was performed by gas chromatography equipped with mass spectrometry and/or flame photometric detectors. 3.3 µl of organic solvent located in the lumen of hollow fibre was used to extract OSCs from 8 ml of an aqueous sample. Several parameters influencing extraction efficiency such as salt concentration, stirring speed, temperature, sample volume, organic phase volume and extraction time were studied and optimized using super-modified simplex method. Under optimized conditions, including extraction solvent (toluene) extraction time (15 min), salt addition (4% w/v), stirring rate (1200 rpm), sample volume (8 ml SV), organic solvent volume (3.3 µl) and extraction temperature (35 °C), the limits of detection varied from 0.1 to 8.7 µg l^{-1} and 0.7 to 99.4 µg l^{-1} for GC-FPD and GC-MS, respectively. The calibration graphs were linear over three orders of magnitude for most of the studied OSCs. The relative standard deviations for inter- and intra-day analysis were in the range of 5-10%, and the relative recoveries of the analytes from three different real water samples were more than 83%. The results were compared with those obtained using direct single drop micro-extraction and headspace single drop micro-methods. The proposed method is reliable and can be considered useful for routine monitoring of the organic sulfur compounds in surface water samples.

Keywords: Hollow fiber, Liquid-phase micro-extraction, Organic sulfur

INTRODUCTION

Over the years, organosulfur compounds (OSCs) have been extensively investigated in matrices, because detailed chemical characterization of OSCs can often provide basic information of an environmental sample. OSCs derived from petroleum sources play a huge role in analytical chemistry mainly as pollutants and as markers for many processes, such as pipeline corrosion, environmental pollution and viscosity [1]. Together with certain aliphatic compounds and several polycyclic aromatic hydrocarbons (PAHs), OSCs are important marker compounds in environmental forensic work, establishing the source of a spilled crude oil. Among the detection systems available for liquid chromatography, tandem mass spectrometry (MS/MS) has gained special attention for the identification and confirmation of several OSCs, despite the difficulty of their ionization, and the photoionization of 16 OSCs was investigated using a krypton lamp in a PhotoMate TM source [2-6].

OSCs are present at trace levels in different waters, foods, beverages and fragrances that are responsible for taste and odor [6-11]. They are the source of malodorous conditions in municipal sewage systems [12-14]. Although sulfur compounds contribute, in a positive way, to powerful aroma and taste, they are frequently the cause of off-flavors and odors, because of their low sensory thresholds and often-unpleasant characteristics. Hence, there is an

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increasing demand for developing methods for determining such contaminations in food and environment [15-20].

Numerous methods have been developed to determine the OSCs in various samples [17-30]. Most of them are based on gas chromatography (GC) equipped with different selective detectors such as mass spectrometry (MS) [17,23], sulfur chemiluminescence detector (SCD) [24], pulsed flame photometric detector (PFPD) [22], atomic emission detector (AED) [25] and flame photometric detector (FPD) [14,21,26-29]. Also, high performance liquid chromatography (HPLC) has been applied to determine OSCs [30].

The determination of OSCs at trace levels in the environmental samples is difficult due to their low concentration and complex matrices. Consequently, a separation or pre-concentration step is essential to achieve a desired performance. Conventional sample preparation methods for these compounds are liquid–liquid extraction (LLE) [31], solid phase micro-extraction (SPME) [7,28] and purge and trap (P&T) [32,33].

Conventional LLE consumes high costs and potentially hazardous organic solvents. In addition, for a trace analysis, a large volume of sample is often required, and its handling can be extremely time-consuming and tedious. P & T, also known as the dynamic headspace method, removes volatile compounds from the sample matrix by passing an inert gas such as helium or nitrogen through the matrix. This method is, however, more time-consuming and needs expensive equipment. In contrast, SPME is a simple and solvent-free technique. However, the high cost, limited lifetime of the fiber, and possible carry-over between analyses are of the drawbacks of the SPME technique [34].

Simple, solvent-minimized techniques such as single-drop micro-extraction (SDME) [35-42] and hollow fiber-based liquid phase micro-extraction (HF-LPME) [43-50] have recently been developed. These techniques are very inexpensive, and the drop is renewable at negligible cost. High precision and sensitivity are obtained in a short time analysis. In HF-LPME, a hollow fiber containing an organic solvent in the lumen is inserted into the tip of the syringe needle and is used for the extraction of the analytes. The protection of the solvent provided by the hollow fiber avoids the inherent problems of SDME. In addition to the simplicity and low cost of these techniques, the main advantage is that there are no carry-over problems.

Due to the importance of OSCs in aqueous sample flavor, and their impact as off-flavors and odors, the present study proposes a sensitive method for rapid and routine determination of these substances. The objective of this study is to identify and quantify fifteen OSCs as the target analytes in natural aqueous sample in near crude petroleum land (Khark Island of Iran). The results of extraction and determination of OSCs are compared with those obtained from HS-SDME and direct-SDME coupled to GC-FPD and/or GC-MS.

To the best of our knowledge, HF-LPME has not yet been employed for the extraction and pre-concentration of OSCs from aqueous samples.

EXPERIMENTAL

Reagents

The standard compounds listed in Table 1 (with purity more than 98%) were purchased from Acros Organics (Geel, Belgium), Fluka (Buchs, Switzerland), Merck (Darmstadt, Germany) and Sigma-Aldrich (St. Louis, MO, USA) Companies. Table 1 shows the structures of the studied OSCs standards. The boiling points of the OSCs varied in the range of 120-366 °C. Tetrahydrothiophene was used as an internal standard (IS). Other reagents used in the present study were of analytical reagent grade and were obtained from Merck Company. The reagent water used was purified with a Milli-Q system from Millipore (Bedford, MA, USA). Standard stock solutions of each OSCs (1 mg ml^{-1}) were prepared in methanol and stored in the freezer at -10 °C. A 2 mg l^{-1} fresh standard solution containing fifteen OSCs was weekly prepared in methanol and stored at 4 °C.

Sample Preparation

Extraneous water of east vent (ExEV), entrance water (EnSR) and extraneous water of Sardasht's Refinery (ExSR) were collected from Khark Island (Khark, Iran). The samples were collected in sterile plastic flasks during a period of 10 weeks and stored at -4 °C until the analysis. They were used immediately after thawing at room temperature.

Table 1. List of OSCs Standards and Related Information

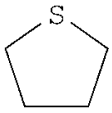
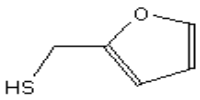
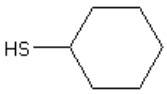
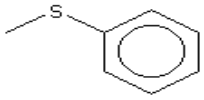
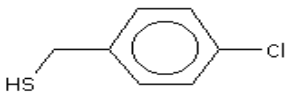
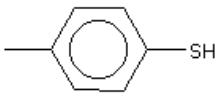
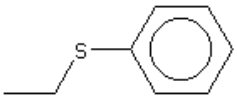
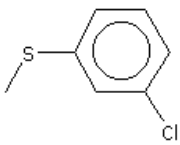
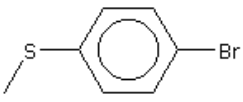
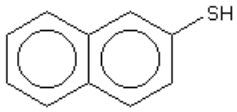
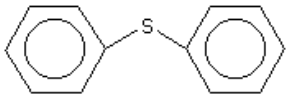
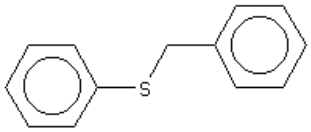
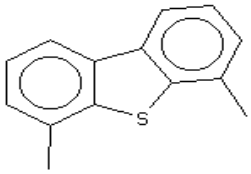
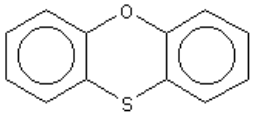
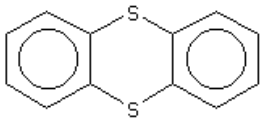
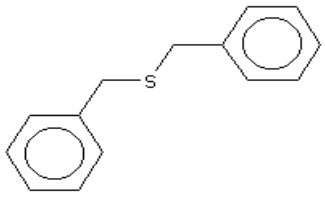
Entry	Compound	Formula	Structure	Abbreviation	Bp or M. p. (°C)[b]
1	Tetrahydrothiophene	C_4H_8S		TI[a]	120 (Bp)
2	2-Furfurylthiol	C_5H_6OS		2FT	155 (Bp)
3	Cyclohexyl thiol	$C_6H_{12}S$		CT	159 (Bp)
4	Methyl phenyl sulfide	C_7H_8S		MPS	188 (Bp)
5	4-Chlorobenzyl mercaptan	C_7H_7ClS		4CBM	121 (Bp)
6	4-Methylthiophenol	C_7H_8S		4MTP	195 (Bp)
7	Ethyl phenyl sulfide	$C_8H_{10}S$		EPS	205 (Bp)
8	3-Chlorothioanisole	C_7H_7ClS		3CT	234 (Bp)
9	1-Bromo-4-(methylthio)benzene	C_7H_7BrS		BMTB	255 (Bp)

Table 1. Continued

10	2-Naphthalenethiol	$C_{10}H_8S$		2NT	286 (Bp)
11	Diphenyl sulfide	$C_{12}H_{10}S$		DPS	NA[c]
12	Benzyl phenyl sulfide	$C_{13}H_{12}S$		BPS	197[d] (Bp)$^{0.036\ bar}$
13	4,6-Dimethyldibenzothiophene	$C_{14}H_{12}S$		DMDBT	~340 (Bp)
14	Phenoxathiin	$C_{12}H_8OS$		PX	150 (Bp)
15	Thiaanthrene	$C_{12}H_8S_2$		TH	366 (Bp)
16	Dibenzyl sulfide	$C_{14}H_{14}S$		DBS	44 - 47 (Mp)

[a]Internal Standard (IS). [b]B. p., boiling point; M. p., melting point. [c]Not available. [d]Boiling point at pressure of 0.036.

The real water samples were filtered through a 0.45 µm cellulose acetate syringe filter (Osmonics, Warren, Indiana, USA)

Procedures

Hollow fiber liquid-phase micro-extraction. All the LPME experiments were performed using Accurel Q3/2 polypropylene hollow fiber membrane (600-µm I.D., 200-µm wall thickness, 0.2-µm pore size) from Membrana GmbH (Wuppertal, Germany). The whole fiber was cut into small segments with length of 1.8 cm. One end of each resulting hollow fiber was heat-drawn to fit on the micro-syringe needle. A Hamilton 85RN (26S/51 mm/needle type 2) 5 µl syringe (Hamilton Bonaduz AG, Bonaduz, Switzerland) was employed to introduce the extracting solvent into the lumen of the hollow fiber, to suspend the hollow fiber, and also to inject the extracted analytes at the end of extraction into the GC injection port. Extraction and injection processes were performed in the following steps: (1) 8 ml of the aqueous sample solution was transferred into a 10 ml glass vial containing a 8 mm × 3 mm magnetic stirring bar; (2) the vials were placed on a multiple-station magnetic stirrer (Ikamag RO 5 power, IKA -WERKE GmbH and Co., KG, Staufen, Germany); (3) a carefully measured portion of 3 µl of the extracting solvent (toluene) was injected into the hollow fiber; (4) the fiber together with a small part of the supporting syringe needle was submerged in the sample solution; (6) the vial was covered with Parafilm and stirred for a prescribed time period; (7) at the end of the extraction time, the hollow fiber was removed from the sample solution and the extracting solvent was withdrawn into the syringe; (8) finally, 1 µl of the extracting solvent was injected into the GC injection port. To obtain suitable signals in the optimization experiments, relatively high concentration of OSCs in aqueous solution (200 µg l^{-1}) was used. All the experiments were done at room temperature and the sample solution was stirred at a rate of 800 rpm for 15 min

HS-SDME and direct-SDME. In HS-SDME experiments, syringe needle was inserted through the silicone septum of a 10 ml extraction vial and the end of needle was located about 1 cm above the surface of the stirred solution. After extraction in a prescribed time period, the drop was retracted into the micro syringe and injected into the GC for analysis. A fixed concentration of IS (Tetrahydrothiophene) was prepared in the extracting solvent. The analytical signal was the peak area ratio of the analytes to the internal standard.

Direct single-drop micro-extraction was performed in a 10 ml vial containing 8 ml of the sample solution which was placed on a magnetic stirrer. The extraction was performed by suspending 3.3 µl of organic solvent (toluene) on the tip of a 10 µl micro-syringe immersed in the stirred solution. Following sample extraction, the micro drop was withdrawn into micro syringe and 1 µl of the extracting solvent was injected into the GC injection port. The extraction conditions for HS-SDME and Direct-SDME were the same as for HF-LPME.

GC-FPD Analysis

Separation and identification of OSCs were carried out on a Chrompack CP9000 gas chromatograph (Middleburg, The Netherlands), equipped with a flame photometric detector (FPD) and a Chrompack CP-Sil8 CB fused-silica capillary column with a 25 m × 0.32 mm I.D. and 0.25 µm film thickness. The injector and detector's temperatures were 250 and 280 °C, respectively. The GC split valve was closed for 0.5 min and then was opened. Nitrogen was used as a carrier gas to give 1 ml min^{-1} column flow and 6 ml min^{-1} split line flow. The detector gases flow rates were 100 ml min^{-1} of air, 90 ml min^{-1} of hydrogen and 20 ml min^{-1} of nitrogen as a makeup gas. The initial oven temperature was 50 ºC and increased to 100 ºC at a rate of 15 ºC min^{-1} followed by a second ramp (10 ºC min^{-1}) to a temperature of 250 ºC which was hold for 1 min followed by a third ramp (5 ºC min^{-1}) to a final temperature of 280 ºC which was hold for 2 min.

The analytical signal was taken as the peak area ratio of OSCs to internal standard and relative peak areas were used for quantitative calculations.

GC/MS Analysis

The GC/MS analysis was carried out using a Thermoquest-Finnigan gas chromatograph equipped with a fused silica capillary DB-1 column (60 m × 0.25 mm I.D.;

film thickness 0.25 μm) coupled with a TRACE mass (Manchester, UK). The transfer line temperature was 250 ºC. The ionization energy was 70 eV with a scan time of 1 s and mass range of 35-465 amu. Nitrogen was used as carrier gas to give 1.1 ml min^{-1} column flow and 55 ml min^{-1} split line flow.

Oven temperature was increased from 60 ºC to 250 ºC at the rate of 4 ºC min and finally was hold at 250 ºC for 10 min. The components of the OSCs were identified by comparison of their mass spectra with those of a computer library or with authentic compounds. Data obtained were confirmed by comparison of their retention indices, either with those of authentic compounds or with data published in the literature.

RESULTS AND DISCUSSION

Extraction Solvent

The selection of organic solvent immobilized in the pores of hollow fiber is a critical factor in permitting HF-LPME to achieve the highest enrichment factor. Ideally, the extraction solvent should be immiscible in water, its polarity should be matched to that of the fiber, and be stable enough over the extraction time [51-55].

Seven water-immiscible solvents including toluene, hexane, dichloromethane, benzyl alcohol, carbon tetrachloride, n-octane and tetrachloroethylene were evaluated. 5 ml of aqueous samples was spiked with all of the OSCs at 20 μg l^{-1}, and extraction was conducted at stirring rate of 800 rpm and extraction time of 10 min. The final choice of solvent was based on extraction efficiency and gas chromatographic behavior of the solvent. The extraction efficiency of HF-LPME was followed by peak areas of OSCs in different solvents. The average of peak areas and RSDs% for triplicate extraction of OSCs using different solvents are shown in Table 2. Toluene was chosen for further studies, because it could extract all of the studied OSCs and exhibited low solvent loss during the extraction time. Suitable extraction efficiencies were also obtained from dichloromethane, however, the solvent could not wet the micro-pores of fiber very well and thus higher RSDs were obtained [56].

Simultaneous Optimization of Extraction Time, Salt Addition, Stirring Rate, Sample volume, Organic Solvent Volume and Extraction Temperature Using Simplex Optimization Procedure

Simplex optimization is a stepwise strategy. This means that the experiments are performed one by one. The exception is the starting simplex, in which all experiments can be run in parallel. The principles for a simplex optimization are illustrated in literature [57].

The effective factors such as extraction time (ET), salt addition (SA), stirring rate (SR), sample volume (SV), organic solvent volume (OSV) and extraction temperature (ET) were optimized by the super-modified simplex method (SMS) [57,58]. SMS program was started by introducing lower and upper boundary conditions for the above six variables: Et, 5-50 min; SA, 0-5 w/v%; SR, 0-1200 rpm; SV, 1-20 ml; OV, 1-5 μl; ET, 10-60 ºC. The initial simplex consisted of the first seven vertices (one more than the number of variables) that were chosen randomly. Experiments 1-7 in Table 3 show the values of the six parameters that were designated as the initial simplex conditions. Experiment number 18 (Fig. 3) indicates the optimum conditions with the highest relative peak area value of the analyte to internal standard (Tetrahydro-thiophene). The simplex was halted at experiment 22, as there was no further significant improvement towards maximization of the relative peak area value, as shown in Fig. 3. The optimum conditions were found to be ET, 15 min; SA, 4 w/v%; SR, 1200 rpm; SV, 8 ml; OV, 3.3 μl; ET, 35 °C. It was found that the optimum conditions by the simplex optimization are similar to those obtained by the univariate method [59-64]. These optimum conditions were applied in further experiments. Figure 1 exhibits chromatograms under the optimum conditions for ExEV, EnSR and ExSR real water samples. Figure 2 shows some of the common available organic compounds (AOCs) in real samples identified by their retention time in a solution of a pure compound and by comparing mass spectra (SCAN mode) and retention times with those of standard references.

Method Performance

Using the optimal extraction conditions, repeatability,

Table 2. Efficiency of Different Organic Solvents Evaluated for Extraction of Fifteen OSCs by HF-LPME

	Peak area ($\times 10^7$) (RSD%, n = 3)						
Compound	Hexane	Benzyl alcohol	Carbon tetrachloride	Toluene	Tetrachloroethylene	n-Octane	Dichloromethane
2FT	1.62 (13.90%)	1.53 (22.60%)	1.85 (13.90%)	1.84 (8.51%)	1.43 (11.20%)	1.57 (9.41%)	1.86 (10.43%)
CT	1.89 (14.40%)	1.79 (23.90%)	-	2.06 (11.00%)	-	-	2.01 (11.26%)
MPS	1.85 (14.80%)	0.44 (44.30%)	-	1.81 (10.02%)	1.68 (14.60%)	1.41 (2.73%)	1.82 (10.18%)
4CBM	1.60 (16.20%)	0.88 (41.10%)	0.27 (10.20%)	1.77 (7.66%)	1.85 (9.01%)	-	1.78 (9.96%)
4MTP	1.40 (14.10%)	1.29 (22.70%)	2.22 (14.30%)	1.56 (6.96%)	0.87 (15.40%)	1.37 (7.31%)	1.62 (9.06%)
EPS	1.68 (14.60%)	0.43 (45.70%)	-	1.79 (6.75%)	-	1.38 (8.31%)	1.78 (9.95%)
3CT	1.85 (13.90%)	1.69 (29.70%)	-	2.11 (7.80%)	1.41 (2.73%)	-	1.99 (11.15%)
BMTB	0.87 (15.40%)	0.65 (46.70%)	1.17 (38.20%)	0.91 (9.30%)	-	-	1.10 (6.16%)
2NT	2.13 (17.30%)	1.98 (27.80%)	1.06 (37.70%)	2.51 (8.97%)	0.83 (7.54%)	2.04 (9.62%)	2.26 (12.66%)
DPS	0.87 (21.30%)	0.57 (50.70%)	-	0.96 (6.92%)	-	0.78 (8.25%)	1.08 (6.06%)
BPS	0.33 (28.40%)	-[a]	-	0.21 (9.41%)	1.75 (7.51%)	0.15 (8.90%)	0.56 (3.12%)
DMDBT	0.31 (23.30%)	0.17 (62.70%)	1.29 (7.53%)	0.34 (8.08%)	-	0.27 (10.20%)	0.73 (4.10%)
PX	1.54 (14.35%)	0.86 (34.20%)	-	1.68 (8.21%)	-	1.38 (7.81%)	1.81 (10.15%)
TH	1.77 (14.25%)	-	1.36 (14.65%)	1.95 (8.3%)	0.86 (34.20%)	1.57 (7.91%)	2.01 (11.26%)
BH	1.36 (14.65%)	1.17 (38.20%)	-	1.51 (9.53%)	-	1.29 (7.53%)	1.62 (9.06%)

[a]Not detected.

reproducibility, the precision, linearity and limit of detection of the extraction method followed by GC-FPD and/or GC-MS analysis were investigated using spiked water samples. The results are shown in Table 4. The linear dynamic range was given for each of the analytes. The correlation coefficients of the calibration curves (R^2) ranging from 0.986-0.999 for GC-FPD and ranging from 0.996-0.999 for GC-MS imply that the analytes have shown good linearity within these concentration ranges except 4CBM, and allowed the quantification of the agents at ppb levels by HF-LPME. Further, the limits of detection differ substantially for the various OSCs. For most of the agents, the detection limit is lower than 3.8 μg l^{-1} (except 4CBM, 4.6; 3CT, 4.2; BPS, 5.8; DMDBT, 6.5 and TH, 8.7 μg l^{-1}) for GC-FPD and lower than 37.6 μg l^{-1} (except 4CBM, 58; 3CT, 56.1; BPS, 78.8; DMDBT, 51.5 and TH, 99.4 μg l^{-1}) for GC-MS. Figure 5a shows HF-LPME- GC-FPD chromatogram of OSCs after extraction from spiked

Table 3. The Progress of SMS Towards Optimum in the Analysis of OSCs by HF-LPME

Experimental number	Factors						Relative Peak Area													
	SV (ml)	OV (µl)	SE (w/v%)	SR (rpm)	TI (min)	TE (°C)	2FT	CT	MP	4CBM	4MTP	EPS	3CT	BMTB	2NT	DPS	BPS	DMDBT	PX	TH	BS
1	8	2	4	650	18	20	0.4	1.7	0.9	0.5	0.9	1.9	0.9	0.7	1.0	0.6	0.5	0.8	1.3	0.8	0.7
2	13	2	4	650	23	30	0.6	2.3	1.3	0.7	1.2	2.6	1.2	1.0	1.3	0.9	0.6	1.1	1.8	1.1	1.0
3	8	2	3	950	23	20	0.3	1.2	0.7	0.4	0.6	1.4	0.6	0.5	0.7	0.5	0.3	0.6	1.0	0.6	0.5
4	8	3	4	950	23	35	0.4	1.6	0.9	0.5	0.8	1.8	0.8	0.7	0.9	0.6	0.4	0.8	1.2	0.8	0.7
5	13	3	4	950	18	20	0.1	0.4	0.2	0.1	0.2	0.5	0.2	0.2	0.3	0.2	0.1	0.2	0.3	0.2	0.2
6	15	1	3	950	18	30	0.2	0.6	0.3	0.2	0.3	0.7	0.3	0.3	0.4	0.2	0.2	0.3	0.5	0.3	0.3
7	13	1	3	850	13	20	0.1	0.3	0.1	0.1	0.1	0.3	0.1	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.1
8	8	3	4	650	16	33	0.8	3.1	1.7	0.9	1.6	3.5	1.6	1.4	1.8	1.2	0.8	1.5	2.4	1.5	1.4
9	6	3.5	4	500	13	40	0.6	2.4	1.3	0.7	1.3	2.7	1.3	1.1	1.4	0.9	0.7	1.2	1.9	1.2	1.1
10	13	3.3	4	950	21	38	0.7	2.9	1.6	0.9	1.5	3.3	1.5	1.3	1.7	1.1	0.8	1.4	2.3	1.4	1.3
11	8	3.8	3	1050	15	30	1.0	4.1	2.2	1.2	2.1	4.6	2.1	1.8	2.3	1.5	1.1	2.0	3.2	2.0	1.8
12	6	4.7	3	1250	11	31	0.8	3.4	1.8	1.0	1.8	3.8	1.8	1.5	1.9	1.3	0.9	1.6	2.6	1.6	1.5
13	6	3	3	780	19	44	0.5	1.9	1.0	0.5	1.0	2.1	1.0	0.8	1.1	0.7	0.5	0.9	1.4	0.9	0.8
14	11	3	4	720	13	38	0.8	3.0	1.6	0.9	1.6	3.4	1.6	1.3	1.7	1.1	0.8	1.4	2.3	1.4	1.3
15	12	4.4	3	650	16	41	0.4	1.4	0.8	0.4	0.7	1.6	0.7	0.6	0.8	0.5	0.4	0.7	1.1	0.7	0.6
16	9	2.6	3	870	18	33	1.1	4.3	2.3	1.2	2.2	4.8	2.2	1.9	2.4	1.6	1.2	2.0	3.3	2.0	1.9
17	15	3.2	4	850	15	23	1.0	4.2	2.3	1.2	2.2	4.7	2.2	1.8	2.4	1.6	1.1	2.0	3.2	2.0	1.8
18	8	3.3	4	1200	15	35	1.2	4.8	2.6	1.4	2.5	5.4	2.5	2.1	2.7	1.8	1.3	2.3	3.7	2.3	2.1
19	6	3.5	5	1250	13	38	1.1	4.5	2.5	1.3	2.4	5.1	2.4	2.0	2.6	1.7	1.2	2.2	3.5	2.2	2.0
20	6	3.1	4	850	9	27	0.6	2.5	1.3	0.7	1.3	2.8	1.3	1.1	1.4	0.9	0.7	1.2	1.9	1.2	1.1
21	11	3.2	4	920	18	35	0.5	1.9	1.0	0.5	1.0	2.1	1.0	0.8	1.1	0.7	0.5	0.9	1.4	0.9	0.8
22	8	3.4	4	1150	19	26	0.4	1.7	0.9	0.5	0.9	1.9	0.9	0.7	1.0	0.6	0.5	0.8	1.3	0.8	0.7

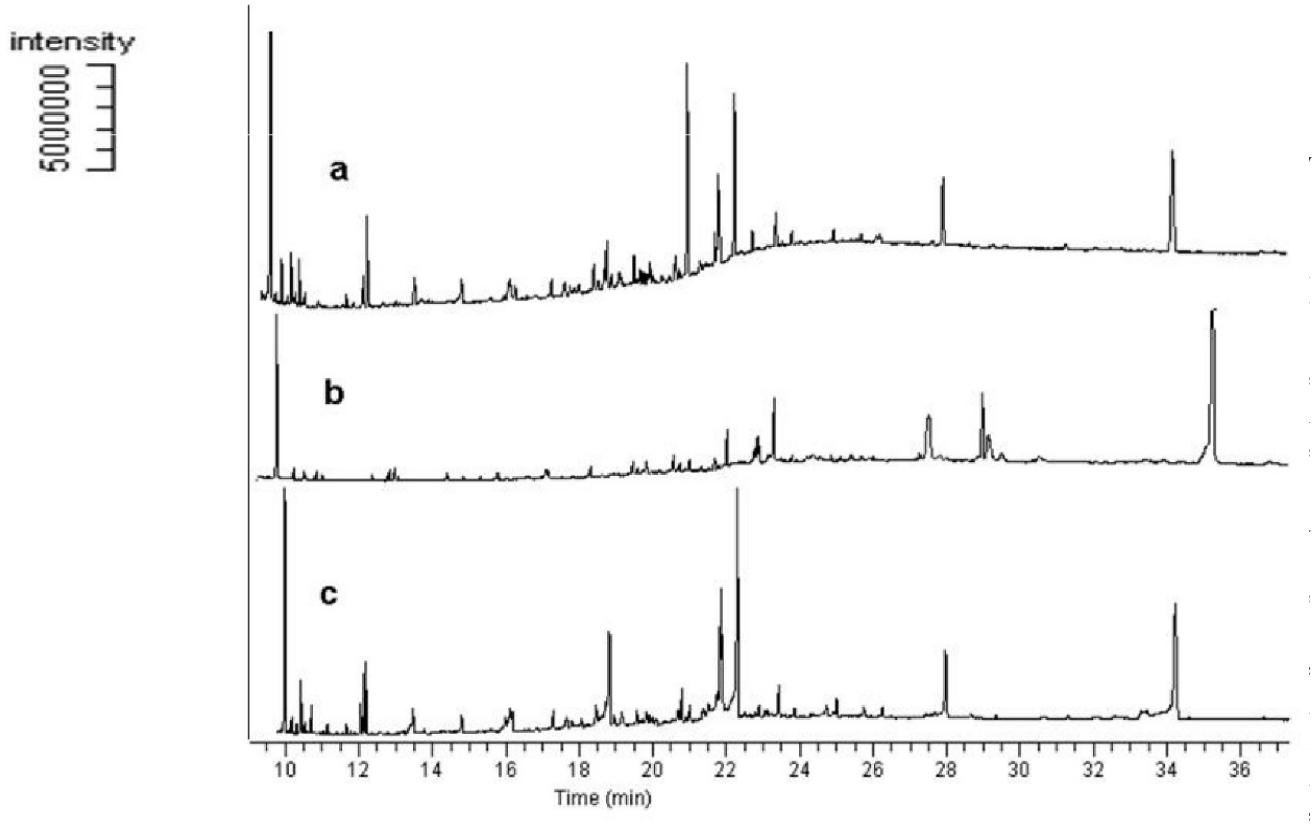


Fig. 1. Chromatogram of AOCs obtain by HF-LPME under optimized conditions a) unspiked the ExEV water b) unspiked the EnSR water c) unspiked the ExSR water.

distilled water sample at ppb levels.

The proposed method displayed good reproducibility to determine the spiked OSCs in the water samples at 10 µg l^{-1} concentration levels with intra-day R.S.D. values in the range of 4.93-8.65% and inter-day R.S.D. values of 4.98-9.75% (for 5 consecutive days).

Real Samples

Totally three water samples were taken from different locales in Khark Island.

Drinking water (entrance water (EnSR) and extraneous water of Sardasht's Refinery (ExSR)). Obvious observations and elementary experiments showed pollutions of iron kind (the color of water) and organic products (the taste and smell of water). The sample water was taken from the output of Sardasht's refinery. The water into a concentration of 20 µg l^{-1} in the vial. Figure 4b-c shows the HF-LPME-GC chromatogram for ExEV sample for FPD and MS detectors, respectively. Table 5 also shows that the relative recoveries from the three real water samples were greater than 83%.

Comparison of HF-LPME with Direct-SDME and HS-SDME

HF-LPME is advantageous over SDME and HS-SDME in terms of ease of operation, sensitivity and reproducibility. SDME requires careful and elaborate manual operations, causing those problems of drop dislodgement/stability which have been reported [56]. We have also compared the enrichment factor (EF) of OSCs by both techniques and

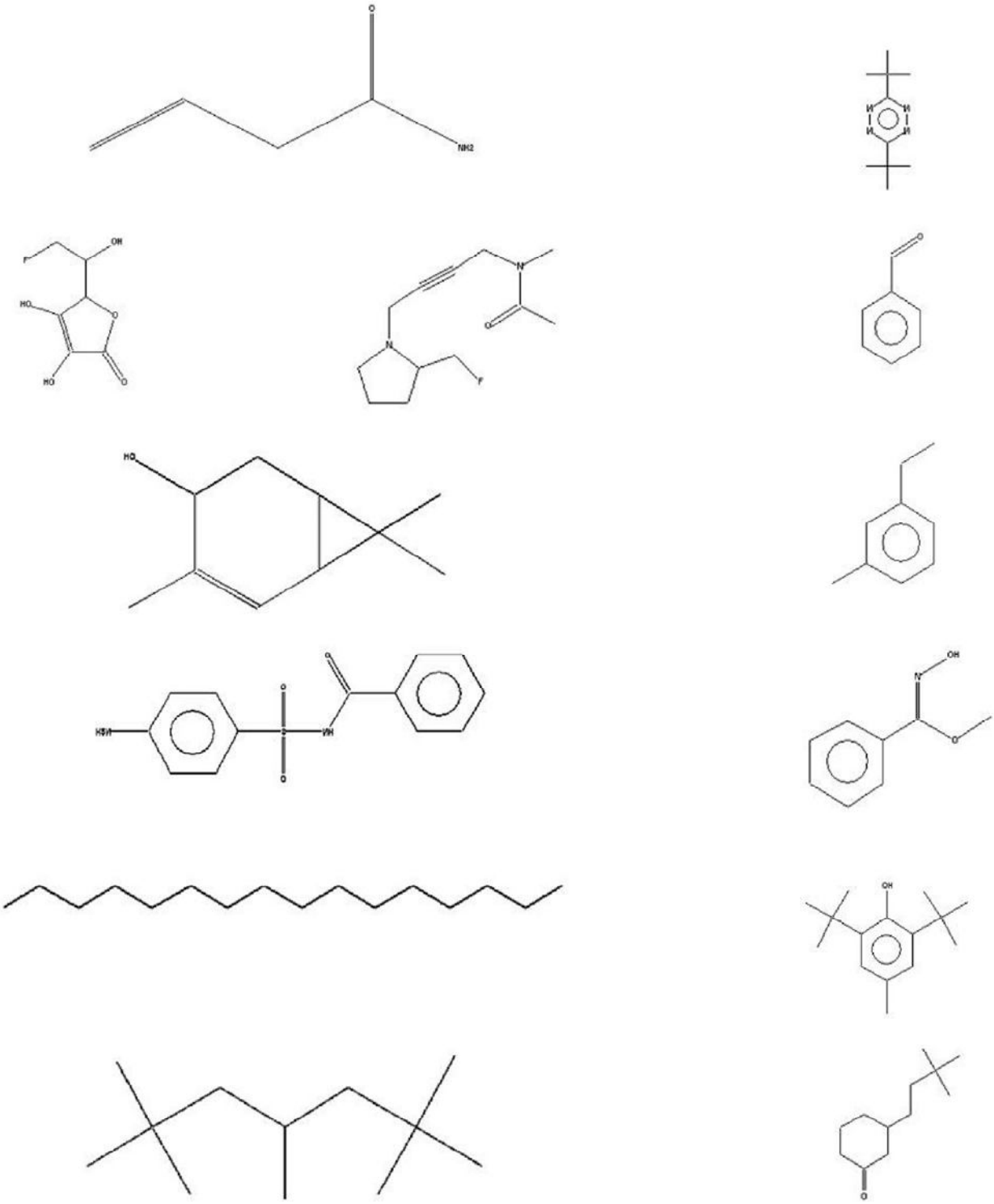


Fig. 2. Some of AOCs in real samples that were identified by their retention time in a solution of a pure compound and by comparing mass spectra (SCAN mode) and retention times with those of standard references.

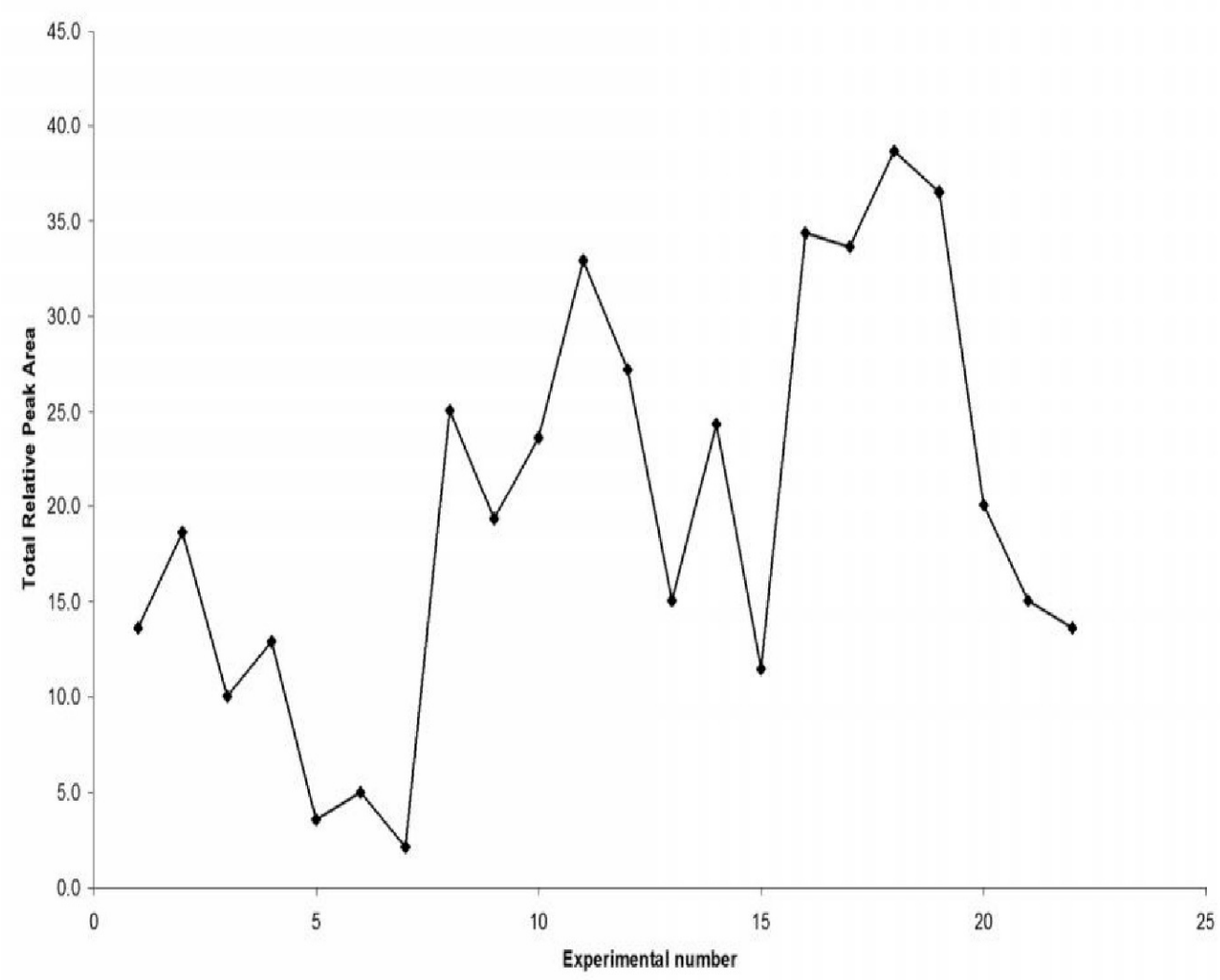


Fig. 3. Simplex algorithm that shows experiment number 18 indicates the optimum conditions with the highest relative peak area value and experiment 22 is the terminal point.

found that, in addition to convenient operation, HF-LPME had better enrichment factor and precision than that of SDME (Table 5). Enrichment factors (EF) are calculated by the ratio of GC-MS signals after and before micro-extraction. All analytes were spiked in water at the concentration of 50 µg l^{-1} and extracted by HF-LPME and SDME. HS-SDME is applied for the analysis of semi-volatile and volatile compounds. Analytes 2FT, CT, MP, 4CBM and 4MTB were spiked in water and extracted by HF-LPME and HS-SDME under optimal conditions. With HF-LPME, enrichment factors for 2FT, CT, MP, 4CBM and 4MTB were 240, 210, 254, 253 and 250, respectively; whereas, with HS-SDME, corresponding EFs were 49, 13, 41, 29 and 28.

CONCLUSIONS

HF-LPME provides a novel, rapid and easily used

Table 4. Performance of the Validation Analysis

OSCs	LOD ($\mu g\ l^{-1}$)[a]		Linear dynamic range ($\mu g\ l^{-1}$)		[b]R^2		RSD (%)[d]	
							Intra-day	Inter-day
	FPD	MS	FPD	MS	FPD	MS	FPD	FPD
2FT	2.1	17.6	10-100	250-1000	0.9995	0.9996	7.28	7.03
CT	0.1	0.7	15-50	150-950	0.9987	0.9831	8.65	9.75
MP	3.6	32.2	15-50	150-950	0.9856	0.9951	7.40	8.80
4CBM	4.6	58.0	-	-	0.9974[c]	0.9981[c]	5.83	7.08
4MTB	0.63	5.9	30-80	300-1000	0.9879	0.9974	4.93	4.98
EPS	2.1	25.7	5-50	250-1000	0.9967	0.9940	5.70	6.10
3CT	4.2	56.1	10-100	150-1000	0.9957	0.9977	7.21	5.96
BMTB	2.8	37.6	20-100	200-1000	0.9863	0.9986	8.93	7.03
2NT	2.5	18.7	50-150	200-1000	0.9913	0.9928	7.75	6.26
DPS	3.6	28.7	10-100	150-1000	0.9874	0.9978	6.14	5.10
BPS	5.8	78.8	10-100	150-1000	0.9863	0.9957	4.94	7.75
DMDBT	6.5	51.5	10-100	150-1000	0.9896	0.9911	5.80	8.02
PX	3.8	34.1	10-100	150-1000	0.9998	0.9973	6.90	6.66
TH	8.7	99.4	10-50	150-1000	0.9993	0.9946	8.45	5.90
BS	1.5	18.2	15-50	100-1000	0.9890	0.9967	7.38	8.22

[a]LOD is based on signal-to-noise ratio of 3. [b]Linear range at concentrations of 1, 5, 10, 50, 100, 500 $\mu g\ l^{-1}$ for GC-FPD and 100, 250, 500, 750, 1000 $\mu g\ l^{-1}$ for GC-MS. [c]R^2 based on non-linear regressions. [d]Repeatability was investigated at a concentration of 20 $\mu g\ l^{-1}$ for each analyte (n = 5).

technique to extract residues of OSCs from aqueous samples. With optimized parameters, the method needs only 8 ml of sample and 3.3µl of extraction solvent. The low LOD (<8.7 $\mu g\ l^{-1}$ and < 99.4 $\mu g\ l^{-1}$ for GC-FPD and GC-MS, respectively) and low RSD (<9.7% and <18.2 % for GC-FPD and GC-MS, respectively) indicate that the technique has great potential and stability for analyzing different field samples with disposable fibers which can decrease matrix influence. This method allows a good recovery of fifteen OSCs from aqueous samples, and an easy and rapid determination with high sensitivity.

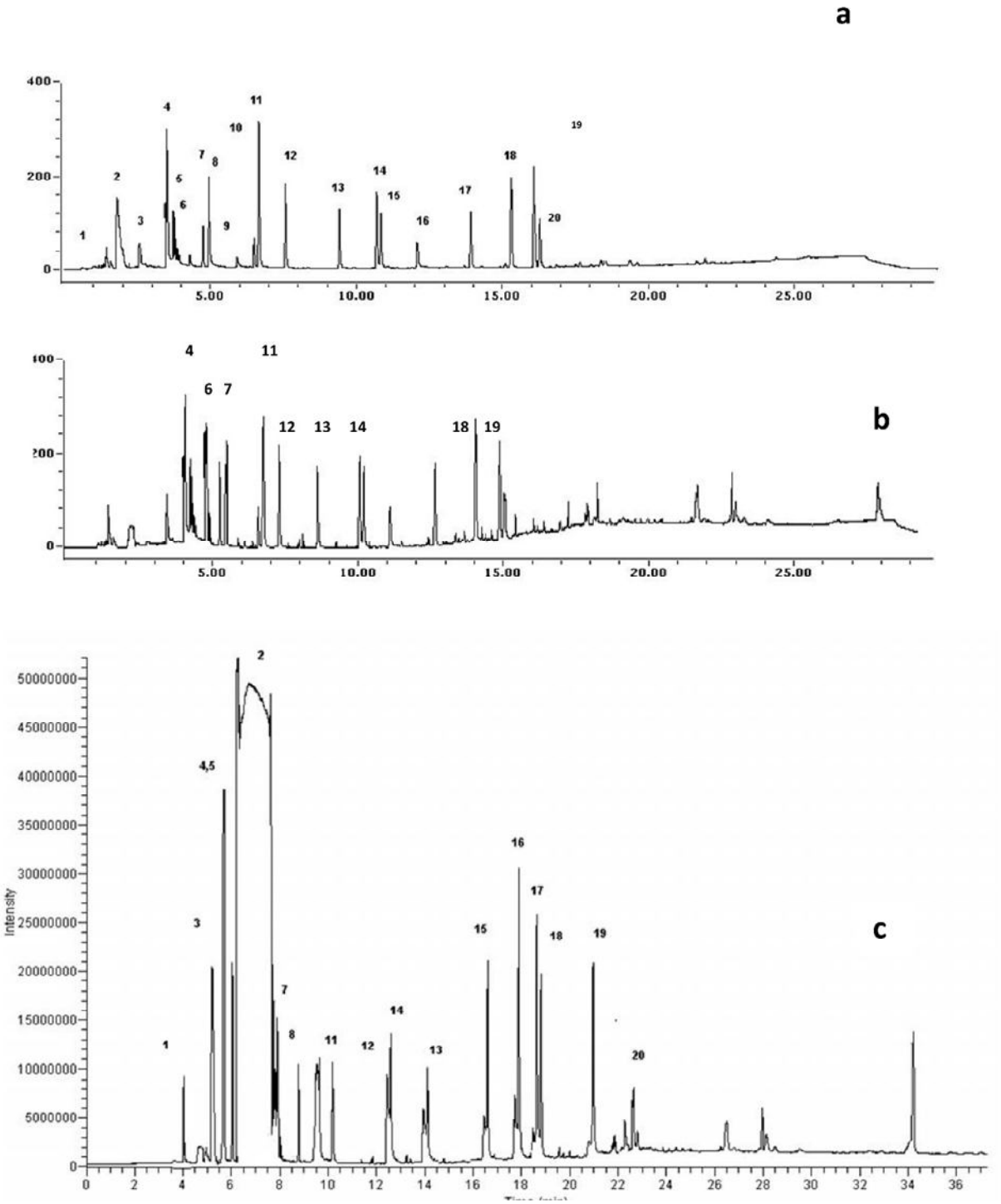


Fig. 4. a, b) HF-LPME-GC-FPD Chromatogram of OSCs obtained from spiked at concentrations of 20 µg l^{-1} in deionization water and ExEV, respectively, c) HF-LPME-GC-MS Chromatogram of OSCs obtained from spiked at concentrations of 40 µg l^{-1} in ExEV sample : (1) TI ^{IS}; (2) Toluene ; (3) FT; (4) CT; (5) MP; (6) peak 13^{A}; (7) CBM; (8) MTP; (9) peak 14^{A}; (10) peak 4^{A}; (11) EPS; (12) 3CT; (13) BMTB; (14) 2NT; (15) DPS; (16) BPS; (17) DMDBT; (18) PX; (19) TH; (20) BS. ^{A}Unidentified substance IS internal standard.

Table 5. Comparison of Performance of HF-LPME and Direct-SDME for 50 µg l^{-1} Spiked ExEV Water Sample. Recovery of 10 µg l^{-1} Spiked Extracts for Tree Real Samples (n = 3)

OSCs	HF-LPME		Direct-SDME		Recover (%)		
	EF	RSD (%)	EF	RSD (%)	ExEV	EnSR	ExSR
2FT	240	8.9	64	9.4	83	93	99
CT	210	5.1	48	7.3	102	115	121
MP	254	6.1	61	21.1	95	107	113
4CBM	253	13.4	54	17.0	97	109	115
4MTB	250	4.2	63	7.1	88	99	105
EPS	195	6.7	46	9.0	85	96	101
3CT	199	13.5	40	15.2	91	102	108
BMTB	192	18.2	87	20.1	96	108	114
2NT	181	6.9	49	14.1	86	97	102
DPS	78	6.0	18	9.4	110	124	121
BPS	43	10.6	10	14.4	105	118	125
DMDBT	63	14.2	13	16.6	83	93	99
PX	211	10.5	53	13.1	87	98	103
TH	267	3.6	64	5.2	94	106	112
BS	247	10.4	50	11.5	84	95	100

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