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Use of Switchable solvent liquid phase microextraction for determination of petroleum pollutants in water samples by gas chromatography–mass spectrometry

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Abstract

In this study, a switchable solvent liquid phase microextraction (SSLPME) followed by GC-MS detection was developed for preconcentration and determination of total petroleum hydrocarbons (TPHs) in water samples. The extraction technique uses 100 µL of a water-immiscible solvent (dipropylamine) that can be solubilized in the aqueous phase in 1:1 ratio using HCl as a reagent. Afterwards, phase separation is induced by the addition of sodium hydroxide. Optimization of the variables affecting this method was carried out in order to achieve the best extraction efficiency. The optimized conditions included: volume of the sample 5 mL, volume of extraction solvent 100 µL, and pH of sample: 12.0. Under the optimum experimental conditions, good limits of detection (0.3–1.21 µg L^{-1}), linearities (R^2 > 0.996), and repeatability of extraction (RSDs below 5.6%, n = 5) were obtained. Finally, the developed method was successfully applied to the determination of the target analytes in different types of natural water samples and acceptable recoveries (>84%) were obtained.

Keywords: Switchable solvent liquid phase microextraction (SSLPME), Total petroleum pollutants (TPHs), Dipropylamine, Water samples.

1. Introduction

In recent years, the pollution of air, soil and water by petroleum hydrocarbons is one of the most important environmental problems [1]. The most common functional categories of compounds found in petroleum products are n-alkanes, branched alkanes, cycloalkanes and aromatic compounds [2-3].

Normal alkanes from petroleum sources are an important feed stock for the petrochemical industries; the long chain alkanes can be processed into lubricant and fuel additives, plasticizers, industrial surfactants, flotation agents and solvents [4].

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants that are mainly formed during the incomplete combustion of organic materials (e.g. coal, oil, petrol, and wood) [5]. They are found in air, water, sediments, and plant and animal tissues. PAHs have been reported to be highly mutagenic and carcinogenic in humans [6]. Since PAH compounds are carcinogenic, identification and determination of these compounds in environmental waters are very important. Although their solubility in water is very low, concentrations in the $\mu g l^{-1}$ level are commonly encountered in the environment. Since these compounds are considered toxic at this level, their presence must be monitored [7-8].

Because of the importance of these compounds as environmental pollutants, monitoring petroleum hydrocarbons in waters is important for human health protection and environmental control. The most common techniques used for the analysis of total petroleum hydrocarbons (TPHs) compounds are gas chromatography (GC) [9-10] and high performance liquid chromatography (HPLC) [11-12]. Due to the low concentrations that need to be quantified in water samples, a sample preparation is required prior to chromatographic analysis.

Sample preparation is an essential part of analytical procedure. The main objective of sample preparation is to both clean up and enrich the analytes of interest from the sample and to convert the analytes into a form suitable for the analytical measuring instrument [13]. Traditional sample preparation techniques such as solid phase extraction (SPE) and liquid–liquid extraction (LLE) are considered time and require large amounts of toxic and expensive organic solvents.

Most environmentally friendly approaches to sample preparation are based on modifications of SPE and LLE with the focusing on reducing solvent consumption and increasing the extraction efficiency [14]. As a result of this, solid-phase microextraction (SPME) [15-16], and liquid-phase microextraction (LPME) [17] have been developed. Although SPME is a simple and solvent-free extraction technique, SPME fibers are frail, relatively expensive, and tend to degrade with repeated use [18]. To overcome these problems, simple, low-cost liquid-phase microextraction (LPME) has recently been introduced [17]. In LPME, extraction normally usually takes place into a small amount of a water-immiscible solvent (acceptor phase) from an aqueous sample containing analytes (donor phase).

Homogeneous liquid-phase microextraction (HLPME) utilizes the phenomenon of phase separation from a homogeneous solution and simultaneously extracts the target solutes into a very small organic phase [19]. In this method, the initial condition is a homogeneous solution and there is no interface between the water phase and the extraction solvent phase. Therefore, it has the advantage of extremely fast extraction speed due to the absence of obstacles from the surface contact between the aqueous phase and the organic phase during the extraction procedure. In these cases, phase separation is based on the phenomenon of salting out, the change of temperature and pH, and the formation of ion pairs. This method has been mainly studied as a powerful preconcentration method for separation of the desired component or instrumental analysis [20-22].

Jessop et al., have synthesized new type of solvent called generation “switchable” or “smart” solvents (SS) [23]. Switchable hydrophilic solvents (SHSs) are defined as solvents that change their physical properties reversibly and abruptly [24]. The SHS can be mixed with water samples and is easily separated from the aqueous phase by removing CO_2 from solution [25]. Alternatively, the hydrophilicity switch can be also triggered by changing the charge of the SHS through pH shift [26], which is particularly useful in the context of microextraction. The main advantages of using of SS are that allows the extraction of the analytes in a homogeneous phase without dispersive solvent and the ease of phase separation without additional equipment. SPs are environmentally friendly compounds [26-27].

In this work, a homogeneous liquid–liquid microextraction, based on the use of switchable hydrophilic solvents, was proposed for the determination of TPHs in water samples by GC-MS. The applicability

of this method with real samples was evaluated by analyzing water samples.

2. Experimental

2.1. Reagents and standard solutions

All reagents were of analytical grade and were used as received. 16 polycyclic aromatic hydrocarbons mixture standard containing 2000 µg/ml each component and 26 alkanes mixture standard containing 500 µg/ml each component were purchased from Dr. Ehrenstorfer (Reference Materials, Augsburg, Germany). The deionized water was prepared by Milli-Q water purification system (Millipore, Bedford, MA, USA). Working standard solutions were obtained by appropriate stepwise dilution of the stock standard solution with acetonitrile. All solutions were freshly were prepared and stored just in a in the refrigerator (4 ºC) for one month.

2.2. Instrumentation

GC/MS analysis was performed using an Agilent Technology model 7890A coupled with mass spectoscopy model 5975equ ipped and a BP-5 (nonpolar) capillary column (30 m×0.25 mm×0.25 µm film thickness). The oven temperature was maintained at 60 °C for 2 min and programmed to increase at 6 °C/min to 100 ° and then 10 °C/min to 290 °C for 15 min. Other operating conditions were as follows: carrier gas He, at a flow rate of 1 mL/min; injector temperature 290 °C; and splitless mode The operating conditions of the mass system were identical to those described above. The mass spectra were obtained at 70 eV. The mass range was from *m/z* 50-500 amu. Quantitative data were obtained from the electronic integration of the peak areas. Injections were performed using 10 µL Hamilton syringe (Bonaduz, Switzerland).

2.3. Extraction procedure

First, 5 mL of the sample solution was transferred to the extraction vial. Then, 100 µL water-immiscible solvent (DPA) and 100 µL HCl were added to the sample solution which formed a single phase. Then, 2 mL of NaOH solution (10 M) was added as a trigger to phase separation. The cloudy solution was immediately formed and the complete separation of the water and DPA occurred after about 2 minutes. Finally, DPA (40 µL) was collected from the surface of the sample solution and 1 µL of the collected DPA was directly injected to GC-MS using a 10 µL Hamilton syringe.

3. Results and discussion

In order to achieve the best extraction performance, different parameters affecting the extraction procedures were studied and optimized. All optimization studies were performed with 20 µg L^{-1} standards and optimum values were selected based on the highest mean of triplicate measurements based on peak areas.

Parameter optimization was performed using the one-at-a-time method. All of the experiments were performed at room temperature.

3.1. Optimization of conditions

In this work simultaneous microextraction of 42 petroleum pollutants was done. Since the structure of polycyclic compounds (16 compounds) and n-alkanes (26 compounds) are close to each other and had similar behavior during optimization, so in the optimization figures, the total area under the peaks of these compounds was used.

3.1.1. Selection of the extraction solvent

To achieve the high extraction performance with SSLPME, the extraction solvent should have the following characteristics: (1) the ability to extract the target compounds, (2) the ability to convert from the hydrophilic form to the hydrophobic form and vice versa by by pH shift, (3) having high solubility in water for the hydrophilic form and low solubility in water for the hydrophobic form of the switchable solvent.

Considering all criteria, the extraction abilities of dipropylamine (DPA) and triethylamine (TEA) were investigated in this section. Therefore, extraction was performed using 0.5 mL of each solvent. The results are shown in Figure 1. According to the extraction results, under the same conditions, DPA showed better extraction efficiency in comparison to TEA under the same conditions. Therefore, based on the quantitative recoveries, DPA was selected as the extraction solvent for further work.

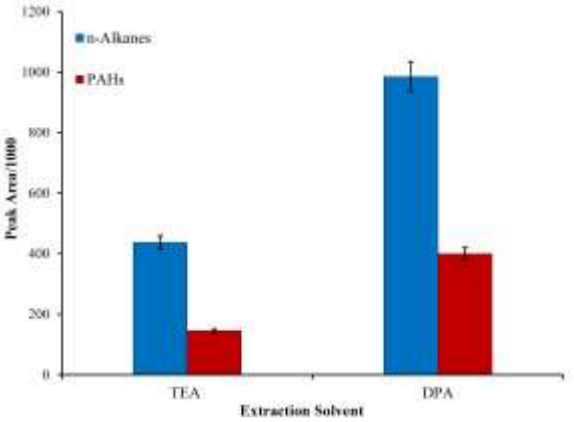

Figure 1. The influence of the extraction solvent on the extraction efficiency of n-alkanes and PAHs compounds obtained from SHSs. Extraction conditions: Volume of the water sample, 5 mL; Volume of the extraction solvent 0.5 mL, analyte concentration 20 µg L^{-1}, room temperature.

3.1.2. Effect of extraction solvent (acceptor phase) volume

In HLLME, the volume of extraction solvent is an important parameter because it affects EF. Therefore, to determine the optimal volume of extraction solvent, different volumes of DPA (50, 75, 100, 150, 200 µL) were studied while the other experimental conditions were kept constant. At volumes less than 100 µL of DPA, no cloudy condition is formed due to the partial dissolution of DPA in water. Solvent collection in volumes below 100 µL was difficult and non-reproducible. Hence, based on the obtained experimental data shown in Figure 2, 100 µL of DPA was used in all subsequent experiments.

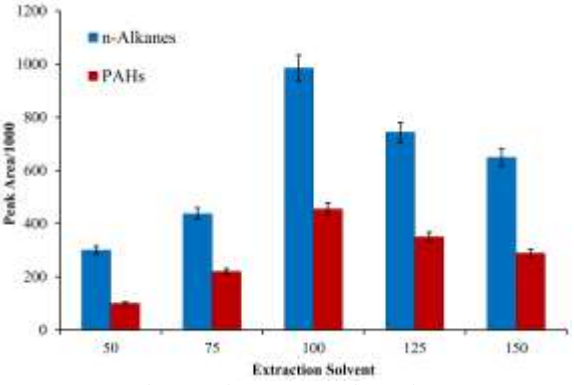

Figure 2. The influence of the volume of the of extraction solvent volume on the extraction efficiency n-alkanes and PAHs compounds. Extraction conditions: volume of the water sample 5 mL, concentration level at 20 µg L^{-1}, and room temperature.

3.1.3. Effect of sample (donor phase) volume

The low concentration of PAHs can be achieved by the high enrichment factor and is based on the use of maximum sample volume. Effect of sample volume on the analytical signals was investigated in the range of 2-6 mL to obtain the best results. In this step, the amount of spiked TPHs was kept same in all tested volumes. As the results show, the analytical signals increased with increasing sample volume but remained constant after 5 mL. Therefore, the sample volume of 5 mL was selected as the optimal volume for the subsequent extractions.

3.1.4. Effect of NaOH solution volume

NaOH is necessary for the separation of the phases in the presented microextraction system [24]. Hydrophilic protonated DPA can be converted to hydrophobic form by adding NaOH solution. To investigate the influence of the volume on the analytical signals, some experiments were performed by addition of different volumes of NaOH solution (10 M) in the range of 0.5 to 4 mL. Other experimental conditions were kept constant. The results showed that the analytical signals were increased up to 2 mL of NaOH solution while the separation of phases did not occur in lower volumes of NaOH solution. Further increase in volume of NaOH caused decrease in extraction efficiency because the hydrophobic DPA did not occur. Therefore, 2 mL of NaOH solution was used in all subsequent experiments.

3.1.5. Effect of pH of sample and extraction time

The effect of pH of sample solution on the analytical signal was studied within the range of 3.0–12.0. The results showed that the analytical signal is not affected by pH of the solution which is probably due to the using NaOH as a trigger that causes to change the pH of the sample to basic values as well as chemical structures of TPHs that do not have acidic or basic functional groups.

In this work, extraction time was defined as the interval time between injection of a mixture of DPA/HCl and exactly before starting the collection of DPA. If not stirred or centrifuged, phase separation takes at least 2.0 minutes after the addition of NaOH. Therefore, the effect of extraction time was investigated in the range of 2.0–10 min, and the results demonstrated that the extraction time has no significant influence on the analytical signal. Therefore, 2.0 minutes was selected as the optimum extraction time. On the other hand, in SHS-ME, extraction solvent completely dissolved in the

sample solution and the contact surface area between extraction solvent and sample solution is infinitely large. Therefore, transfer of the analytes from sample solution to extraction solvent is very fast and independent of time.

3.2. Extraction performance

The optimized SSLPME method was used for the determination of TPHs in water samples. The main analytical figures of merit are summarized in Table 1. The limit of detection (LOD) was obtained based on a signal to noise ratio (S/N) of 3. The limit of quantification (LOQ) was determined as the lowest concentration in the linear range that can be measured by the regression equation.

The enrichment factor (EF) was defined as the ratio of the final analyte concentration in the organic phase ($C_{org,\ final}$) and the initial concentration of analyte in the sample solution ($C_{s,\ initial}$):

$$EF = \frac{C_{org,\ final}}{C_{s,initial}} \qquad (1)$$

Extraction recovery (R%) was calculated according to the following equation for each analyte:

$$R\% = \left(\frac{V_o}{V_s}\right)\left(\frac{C_{org,\ final}}{C_{s,initial}}\right) \times 100 = EF \left(\frac{V_o}{V_s}\right) \times 100 \qquad (2)$$

Where V_O is the volume of organic phase, V_S is the volume of sample.

The repeatability of the method was evaluated at a concentration level of 20 µg L^{-1} and the RSDs (n=5) were in the range of 2.9–5.6%.

3.3 Real Sample Analysis

The proposed method was successfully applied for the determination of TPHs in various water samples. To construct the calibration curve, different concentrations of analytes were added to a water sample after verifying that it did not contain TPHs, and the calibration equation was constructed. Analytical characteristics of proposed SSLPME method for the determination of TPHs in water samples are summarized in Table 2. Also, Figure 3 shows obtained chromatograms of PAHs and n-Alkanes extracted from river water by SSLPME–GC–MS.

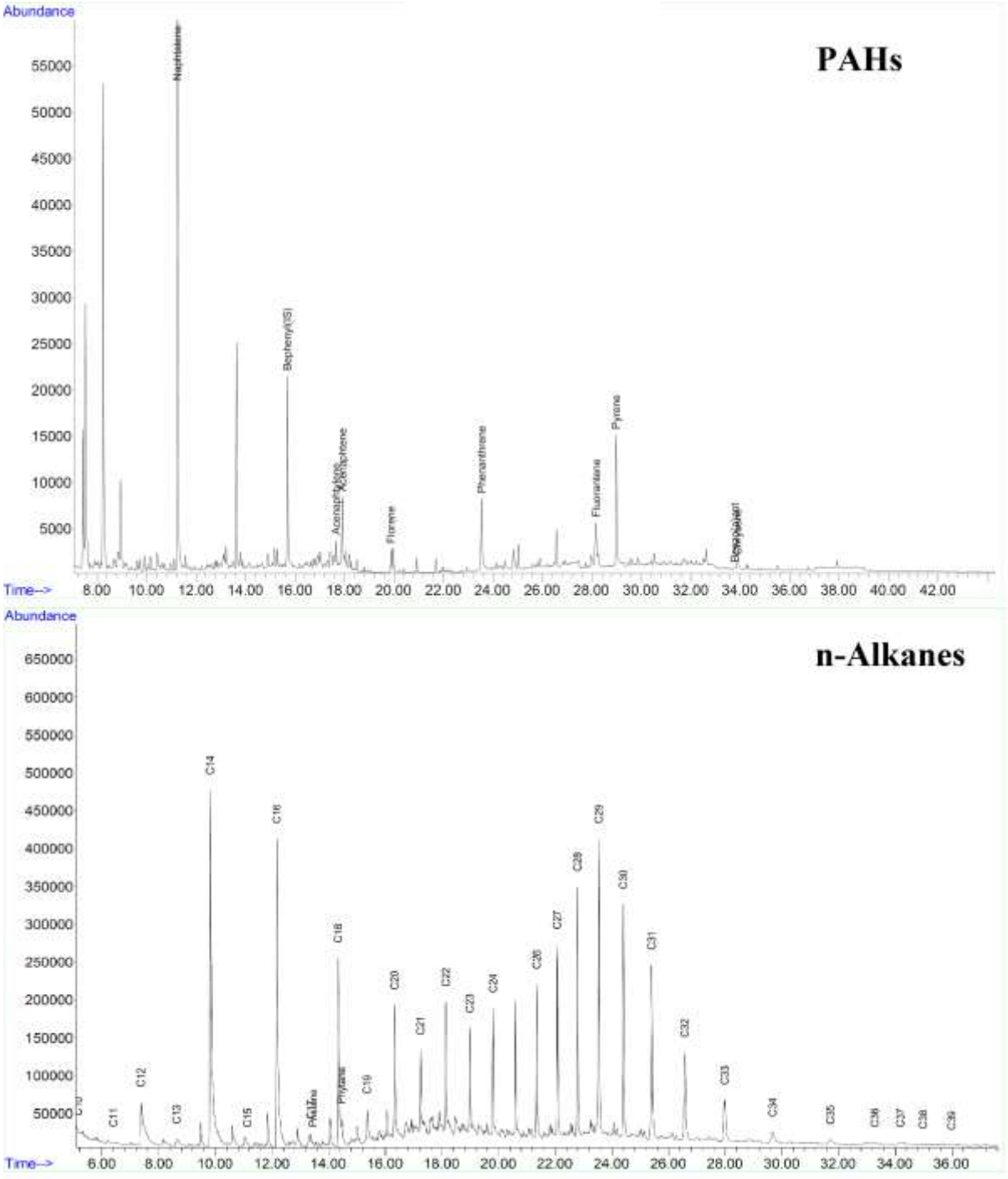

Figure 3. Chromatograms of PAHs and n-Alkanes extracted from river water by SSLPME–GC–MS.

Table 1. Some analytical performance data of SHSs method for petroleum pollutants

Compounds	Linearity (µg L^{-1})	R^2	LOD[a] (µg L^{-1})	RSD[b] % (n=5)	Recovery (%)
C10	1-5000	0.998	0.30	3.9	92
C11	1-5000	0.999	0.30	4.3	87
C12	1-5000	0.998	0.30	5.2	94
C13	1-5000	0.997	0.30	4.9	93
C14	1-5000	0.998	0.30	4.8	**95**
C15	1-5000	0.998	0.30	5.3	96
C16	1-5000	0.999	0.30	5.1	88
C17	1-5000	0.999	0.30	3.5	96

C18	1-5000	0.997	0.30	4.1	98
C19	1-5000	0.998	0.30	4.2	99
C20	1-5000	0.998	0.30	5.6	96
C21	1-5000	0.999	0.30	3.8	95
C22	1-5000	0.999	0.30	2.9	89
C23	1-5000	0.998	0.30	3.7	86
C24	1-5000	0.998	0.30	4.2	98
C25	1-5000	0.997	0.30	4.7	93
C26	1-5000	0.996	0.30	5.1	94
C27	1-5000	0.998	0.30	4.8	95
C28	1-5000	0.999	0.30	5.1	87
C29	1-5000	0.998	0.30	4.4	88
C30	1-5000	0.997	0.30	2.9	84
C31	1-5000	0.998	0.30	3.6	96
C32	1-5000	0.998	0.30	2.9	98
C33	1-5000	0.999	0.30	4.3	97
C34	1-5000	0.999	0.30	4.1	99
C35	1-5000	0.997	0.30	3.7	94
Naphthalene	1-5000	0.998	0.30	3.5	96
Acenaphthylene	1-5000	0.998	0.30	5.1	98
Acenaphthene	1-5000	0.999	0.30	4.4	89
Fluorene	1-5000	0.998	0.30	3.9	87
Phenanthrene	1-5000	0.999	0.30	3.6	86
Anthracene	1-5000	0.998	0.30	2.9	89
Fluoranthene	1-5000	0.997	0.30	4.3	88
Pyrene	1-5000	0.998	0.30	4.1	97
Benzo(a)anthracene	1-5000	0.998	0.30	3.5	86
Chrysene	1-5000	0.999	0.30	4.1	97
Benzo(b)fluoranthene	4-5000	0.999	1.21	5.5	85
Benzo(k)fluoranthene	1-5000	0.997	0.30	5.6	94
Benzo(a)pyrene	1-5000	0.998	0.30	3.8	93
Indeno(1,2,3-cd)pyrene	1-5000	0.998	0.30	3.9	96
Dibenzo(a,h)anthracene	4-5000	0.999	1.21	4.7	86
Benzo(g,h,i)perylene	2-5000	0.998	0.60	4.2	85
Benzo(k)fluoranthene	2-5000	0.999	0.60	5.1	88

[a] Limit of detection (signal-to-noise = 3)

[b] Relative standard deviations

Table 2. Real sample analysis with SHSs-GC-MS

Compounds	**Drinking water**			**River water**			**Sea water**		
	Cinitial ($\mu g\ L^{-1}$)	R[b] (%)	RSD[c] (%)	Cinitial ($\mu g\ L^{-1}$)	R (%)	RSD (%)	Cinitial ($\mu g\ L^{-1}$)	R (%)	RSD (%)
C10	ND[a]	98	3.6	ND	88	3.8	ND	88	3.8
C11	ND	98	3.8	ND	89	4.3	ND	88	5.1
C12	ND	96	3.3	16.11	98	3.8	ND	87	5.4
C13	ND	89	3.8	4.12	97	4.3	23.32	90	4.8
C14	ND	94	3.1	52.43	95	4.8	12.43	90	4.8
C15	ND	95	4.4	3.54	87	5.8	21.54	91	3.8
C16	ND	96	3.8	43.02	89	5.7	ND	91	3.8
C17	ND	98	3.8	3.76	98	4.3	6.76	92	4.3
C18	ND	88	3.7	48.98	99	4.7	8.98	88	3.8
C19	ND	89	4.3	12.87	85	3.8	12.87	87	4.3
C20	ND	93	2.7	34.03	89	5.1	ND	88	4.7
C21	ND	93	3.8	24.43	90	5.4	34.43	83	4.8
C22	ND	94	4.1	39.49	90	4.8	45.49	86	3.3
C23	ND	95	3.4	33.51	90	3.8	ND	86	4.8
C24	ND	95	2.8	38.44	93	3.8	ND	87	5.1
C25	ND	97	3.3	32.12	94	3.8	ND	87	5.4
C26	ND	96	2.7	27.87	96	4.3	ND	90	4.8
C27	ND	99	2.8	33.97	90	3.8	ND	90	5.8
C28	ND	88	4.3	43.09	86	4.3	11.76	86	5.7
C29	ND	96	3.8	37.64	91	4.7	27.54	87	4.3

C30	ND	94	2.3	31.12	90	3.8	ND	86	4.7
C31	ND	94	3.7	23.76	90	4.8	33.76	88	3.8
C32	ND	96	2.8	18.23	93	3.8	ND	89	5.1
C33	ND	97	2.4	12.23	88	5.7	ND	87	3.8
C34	ND	97	4.8	4.31	89	4.3	ND	84	3.8
C35	ND	99	3.8	3.23	87	4.7	ND	85	4.3
Naphthalene	ND	98	2.8	59.54	88	3.8	17.54	84	3.8
Acenaphthylene	ND	97	2.1	3.43	90	3.1	21.33	86	4.3
Acenaphthene	ND	89	3.4	12.54	87	3.8	32.54	84	4.7
Fluorene	ND	95	2.4	6.78	90	2.8	ND	85	4.8
Phenanthrene	ND	97	3.8	21.11	90	3.8	36.11	85	4.8
Anthracene	ND	89	3.8	ND	83	4.3	ND	80	3.8
Fluoranthene	ND	93	3.1	12.43	88	3.8	ND	81	3.8
Pyrene	ND	97	5.4	29.87	87	4.3	ND	82	3.8
Benzo(a)anthracene	ND	94	3.8	12.23	89	4.7	12.23	81	4.3
Chrysene	ND	89	5.8	13.54	83	4.3	13.54	83	4.7
Benzo(b)fluoranthene	ND	87	3.3	ND	82	3.8	ND	82	4.8
Benzo(k)fluoranthene	ND	92	4.7	ND	85	4.3	ND	81	5.4
Benzo(a)pyrene	ND	96	4.8	3.21	86	4.7	ND	80	4.8
Indeno(1,2,3-cd)pyrene	ND	98	5.4	ND	84	4.3	ND	81	3.8
Dibenzo(a,h)anthracene	ND	88	4.8	ND	81	3.8	ND	80	4.8
Benzo(g,h,i)perylene	ND	94	4.8	ND	86	4.3	ND	83	5.1
Benzo(k)fluoranthene	ND	97	5.1	ND	88	4.8	ND	82	5.4

[a]Not Detected

[b]Recovery (%, n=3)

[c]Relative standard deviations

3.4. Comparison of SSLPME with other methods

Since there's one report about simultaneous microextraction of petroleum pollutants (*n*-alkanes and PAHs) in water samples [9], the proposed method was compared with the other methods which were applied for the extraction of *n*-alkanes [3, 28-29] and PAHs [30-33] separately (Table 3). The extraction time of SSLPME and DLLME methods is shorter than the other microextraction methods. In headspace solvent microextraction (HSME) and hollow fiber liquid phase microextraction (HF-LPME) methods the extraction time is longer than SSLPME and DLLME according to the fact that less contact surface area increases the extraction time. The solid phase extraction (SPE), solid-phase microextraction (SPME) and headspace solid-phase microextraction (HSPME) methods are more expensive and time consuming. The main advantage of the SSLPME and DLLME method is its quite large surface area between the fine droplets of the extraction solvent and the water sample, and accordingly its fast extraction kinetics results in the rapid achieving of a state of equilibrium and higher enrichment factors. SSLPME method is faster than DLLME. In this method, the initial condition is a homogeneous solution and there is no interface between the water phase and the extraction solvent phase. Therefore, it has the advantage of extremely fast extraction speed due to the absence of obstacles from the surface contact between the aqueous phase and the organic phase during the extraction procedure.

Table 3. Comparison of the proposed method (SSLPME) with the other methods.

Compound	Method	LOD (μg L^{-1})	LDR (μg L^{-1})	RSD	Extraction time (min)	Ref.
n-Alkanes	HSME	0.1-4	0.5–400 to 5–200	≤7.2	8	[3]
	SPME	0.1–0.3	0.5–30	≤9.54	20	[28]
	HSPME	50–150	150–3000 to 450–4500	≤8.6	20	[29]
PAHs	SPME	0.001-0.029	0.01-10		45	[30]
	HSPME	0.03-0.3	0.1-50	≤10.2	30	[31]
	SPE	0.026–0.82	0.2-100 to 1–100	≤9.7	60	[32]
	LPME	0.35–0.60	1.2–12	≤6.0	20	[33-34]
n-Alkanes and PAHs	DLLME	0.1-0.96	1-200 to 4-200	≤8.8	4	[10]
	SSLPME	0.3-1.21	1-5000	≤5.6	2	Proposed method

4. Conclusion

The SSLPME method using Switchable hydrophilic solvents (SHSs) was applied for the simultaneous determination of 42 petroleum pollutants in water samples by GC-MS. The main advantages of using of SHSs are that allows the extraction of the analytes in a homogeneous phase without dispersive solvent and the ease of phase separation without additional equipment. It is simple and fast, and it does not require specialized laboratory equipment for phase separation. This method was successfully applied to the determination of petroleum pollutants in different water samples.

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The authors have declared no conflict of interest.

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