Optimization of headspace single-drop microextraction technique for extraction of light hydrocarbons (C$_6$–C$_{12}$) and its potential applications

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ABSTRACT

In this study, headspace single-drop microextraction (HS-SDME) coupled with gas chromatography-flame ionization detection (GC-FID) was tested to determine C$_6$–C$_{12}$ light hydrocarbons (LHs) in petroleum and aqueous samples. Several significant experimental parameters, such as drop solvent type, drop volume, sample solution ionic strength, agitation speed and extraction time were optimized. Under optimum extraction conditions, specifically, a 1.5 µl microdrop of *n*-hexadecane, 30 min extraction of a 5 ml aqueous sample placed in a 10 ml vial, and stirring at 1000 rpm at room temperature, the reproducibility and accuracy of this method were found to be satisfactory. Two examples using this method indicated that HS-SDME is a simple, efficient and promising technique for the determination of volatile C$_6$–C$_{12}$ LHs in complex matrices.

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1. Introduction

C$_6$–C$_{12}$ light hydrocarbons (LHs) are abundant components of crude oils, especially in light oils or condensates. Various LH parameters have been established for identifying source and type of petroleum, evaluating their thermal maturity and making petroleum correlations (Halpern, 1995; Thompson, 1979, 1983; Ten Haven, 1996; Obermajer et al., 2000). The quantitative analysis of C$_6$–C$_{12}$ LHs involves a broad range of samples, which include natural gases, condensates, crude oils, soils and various aqueous samples. Due to compositional complexity of petroleum and possible matrix effects, sample pretreatment is necessary to determine the C$_6$–C$_{12}$ LHs in some samples, especially for soils and aqueous samples.

For oil and condensate samples, because the C$_6$–C$_{12}$ LH fraction is liquid at room temperature, direct headspace sampling is not feasible. Thus, direct injection of whole oil is frequently used to introduce analytes into the GC inlet (e.g. George et al., 2002). However, because petroleum is a complex mixture unlike natural gas, the direct injection will unavoidably contaminate the inlet system of the instrument, degrade column performance and introduce interferencing compounds. As for the dilution of whole oil sample, addition of diluent such as *n*-pentane or *n*-hexane will also cause interference to some extent (Whiticar and Snowdon, 1999). For solid or aqueous samples, extraction and concentration of target analytes is necessary prior to analysis, especially for low concentration samples. Liquid–liquid extraction (LLE) is the most common method used to extract analytes from aqueous solutions. However, conventional LLE is not only time consuming, labor

intensive and requires large amounts of toxic and environmentally hazardous organic solvents, but also can cause losses of volatile components. Therefore, other analytical techniques should be tested as potential methods to extract LHs in oils and other matrices.

Recently, the development of fast, simple and solvent-free sample preparation methods has become an important trend in chemical analysis (Psillakis and Kalogerakis, 2003). The headspace solid-phase microextraction (HS-SPME), as a rapid, simple and solvent-free extraction technique, has been used to analyze gasoline range hydrocarbons in oils (Harris et al., 1997) and seabed sediments (Abrams et al., 2009). The HS-SPME method, compared to traditional LLE, limits loss of LHs during the sampling procedure since it incorporates extraction, concentration and injection into a single step, which, in turn, makes it more time efficient. Additionally, headspace sampling eliminates interference from the complex sample matrix. However, there are still some drawbacks to this method, including fiber fragility, expensive device requirements, limited fiber choice, short life (each fiber can be used for only 50–100 analyses) and carry over between analyses.

Liquid phase microextraction (LPME) was developed as another rapid, simple, inexpensive and environmentally friendly extraction technique (Jeannot and Cantwell, 1996, 1997; Psillakis and Kalogerakis, 2001). Single-drop microextraction (SDME) is the simplest operational mode of the LPME technique, in which the whole extraction procedure is performed only with a microsyringe. A drop of solvent is utilized as the collection phase, replacing the coated fiber in HS-SPME. The analytes are extracted by the microdrop of organic solvent (about 1–3 µl) suspended from the tip of a microsyringe needle and either exposed to the headspace of a stirred sample solution (HS-SDME) (Theis et al., 2001) or immersed

into the stirred aqueous sample (direct SDME) (He and Lee, 1997; Wang et al., 1998). The extract is then directly injected into a gas chromatography system for analysis. HS-SDME is suitable for the extraction of volatile and semi-volatile organic compounds and allows avoidance of the interference of complex sample matrices. Additionally, HS-SDME has several advantages over HS-SPME. For example, it does not need any special apparatus. A wide variety of solvents and trapping agents can be chosen as a microdrop to meet different needs. Moreover, unlike the fibers of SPME, drops of SPME can be renewed for each extraction. Therefore, this extraction technique has been widely applied in various fields and involved in a broad range of sample types, including human serum, pharmaceutical preparations, vegetables, engine oils, degradation products of asphaltenes as well as various water samples (Przyjazny and Kokosa, 2002; Kokosa and Przyjazny, 2003; Shariati-Feizabadi et al., 2003; Bahramifar et al., 2004; Lambropoulou and Albanis, 2004; Yamini et al., 2004; Shahdousti et al., 2007; Li et al., 2010).

To date, few papers on the application of HS-SDME technique in petroleum geochemistry have been published (Li et al., 2010). The purpose of this study is to research the applications of HS-SDME technique in the extraction of C_6–C_{12} light hydrocarbons (LHs) from petroleum and petroleum-related aqueous samples by optimizing its extraction conditions.

During the drilling process, mud is usually pumped down the well to keep the drill bit cool, facilitate the movement of cuttings to the surface and prevent clogging and friction (Haworth et al., 1985). The drilling mud often carries drill cuttings and formation fluids and gases to the surface. Monitoring the levels and nature of these gases and fluids is important as this can provide information about the formation and fluid characteristics of the borehole. Mud gas logging (MGL) technique, has been routinely used in petroleum exploration and production (Haworth et al., 1985; Whittaker, 1991). More recently, stable isotope analysis was combined with the MGL into a new technique called Mud Gas Isotope Logging (MGIL) (Ellis et al., 2003, 2007). However, both MGL and MGIL are used to analyze only gas components of drilling mud. The analysis of C_6–C_{12} LHs in drilling mud can provide a supplement for understanding type, origin and evolution of deep seated fluids. Both low concentration of LHs and compositional complexity of matrices hinder the determination of the C_6–C_{12} LHs in drilling mud by using conventional methods. Therefore, the drilling mud sample was employed in this study to test the practicability of HS-SDME technique in a relatively complex aqueous phase.

2. Materials and methods

2.1. Reagents and chemicals

n-Hexane (n-C_6, 99%), n-heptane (n-C_7, HPLC grade, 99+%), n-octane (n-C_8, 98+%), n-nonane (n-C_9, 99%), n-decane (n-C_{10}, 99%), n-undecane (n-C_{11}, 99%), n-dodecane (n-C_{12}, 99+%), benzene (99%), ethylbenzene (99%), o-xylene (99%), methylcyclohexane (MCH, 99%), n-hexadecane (n-C_{16}, 99%), o-xylene-d_{10} (98+%) and n-octane-d_{18} (n-C_8D_{18}, 99%) were all purchased from Alfar Aesar China (Tianjin) Co., Ltd. Methanol (ACS, HPLC) was obtained from Burdick & Jackson. Toluene (99%) and sodium chloride were obtained from Qianhui Chemicals and Glassware Co., Ltd. (Guangzhou, China). All other reagents in this study were of analytical grade. The water used in the experiment was pure water from an ultrapure water purification system and was re-boiled and cooled to room temperature prior to use.

A mixed stock solution was prepared by dissolving n-C_6, benzene, n-C_7, MCH, toluene, n-C_8, ethylbenzene, o-xylene, n-C_9, n-C_{10}, n-C_{11}, and n-C_{12} in methanol, with the corresponding

concentrations of each component being 306, 362, 280, 292, 348, 288, 350, 366, 298, 288, 580, and 554 µg/ml, respectively. The stock solution was stored at 4 °C and diluted with boiled water for use in the working solutions. An extraction solvent containing an appropriate concentration of n-C_8D_{18} as an internal standard (IS) was used as the extractant for HS-SDME.

2.2. Samples

A crude oil from the Well Hade 23 in the Tarim Basin, China was used to examine the applicability of the HS-SDME method for samples containing high concentration of LHs.

During the drilling operation, rock cuttings that circulated to the surface were collected and placed in 946 ml cans at regular intervals from the mud pit. The cuttings were then covered with water, leaving one-third of the can empty. Next, the can was sealed, allowing gases contained in the cuttings to be liberated into the headspace. Finally, the collected headspace cans were transported to the laboratory for analysis. A batch of such headspace cans was collected from a drilling well in the South China Sea.

2.3. HS-SDME procedure

Fifty microliters of the diluted stock solution or sample were spiked into a 10 ml glass vial with 5 ml of water, a magnetic stir bar and an aluminum cap seal containing a PTFE-faced silicone septum. The vial was then placed on a magnetic stirrer (Jiangsu Guohua, China). A 10 µl microsyringe (SGE Analytical Science, Australia) was used as both the extraction and injection syringe. After a certain volume of extraction solvent containing 472 µg/ml n-C_8D_{18} as the internal standard was drawn into the microsyringe, the syringe needle was inserted through the rubber septum of the sample vial until its tip was about 0.5 cm above the surface of the working or sample solution. The micro syringe was fixed above the extraction vial by a metal clamp during the extraction. The syringe plunger was then carefully and slowly depressed until the micro drop of extraction solvent was suspended at the needle tip. After the extraction, the micro drop was retracted back into the needle carefully and slowly and directly injected into the gas chromatography system for analysis.

2.4. Gas chromatography (GC)

GC analyses were performed on an Agilent 7890 GC instrument equipped with a split/splitless injector, an HP-PONA fused silica capillary column (50 m × 0.20 mm × 0.50 µm), and a flame ionization detector (FID). Temperatures for both injection and detection were set at 300 °C. Nitrogen (⩾99.999%) was used as the carrier gas at a flow rate of 1.0 ml/min. The injection was operated in the split mode (100:1 for oils, 30:1 for drilling mud samples). The GC oven temperature was initially held for 5 min at 35 °C, then programmed to 50 °C at a rate of 1.5 °C/min and finally programmed at 8 °C/min to 300 °C, which was held for 5 min. Quantification of C_6–C_{12} LHs was performed by the integration of the peak areas. The response factors of LHs relative to the internal standard (n-C_8D_{18}) were calculated based on the peak area ratios of each C_6–C_{12} hydrocarbon to the internal standard.

3. Results and discussion

3.1. Optimization of HS-SDME conditions

For HS-SDME, the critical factors that affect extraction efficiency include solvent type, drop volume, sample ionic strength, agitation speed and extraction time (Kokosa and Przyjazny, 2003).

Firstly, the stability of the drop during extraction is fundamental to the choice of extraction solvent. The boiling point of solvent must be high enough to avoid evaporation, but it must be compatible with GC analysis. To select an appropriate solvent, 1-butanol, 1-octanol, chloroform and n-hexadecane were tested as extractants. Results showed that n-hexadecane was the most suitable extraction solvent because of its relatively low volatility, no interfering peaks, good affinity with the C_6–C_{12} LHs, and good separation of its GC peak from those of the C_6–C_{12} LHs. Fig. 1 shows a typical chromatogram after HS-SDME extraction of C_6–C_{12} LHs using n-hexadecane as the extraction solvent.

Previous studies have indicated that the drop volume influences the amount of extracted analytes and that the extraction efficiency is enhanced with an increase in drop volume (Shariati-Feizabadi et al., 2003; Bahramifar et al., 2004). However, larger drops are difficult to manipulate and a large injection volume will lead to bad separation in the chromatography analysis. Therefore, a microdrop volume of 1–3 µl is usually used (Lambropoulou and Albanis, 2004; Yamini et al., 2004; Bahramifar et al., 2004). In this work, different drop volumes of n-hexadecane (1.0, 1.5, 2.0, and 2.5 µl) were used to examine the extraction efficiency of HS-SDME. In addition to difficulties in maintaining the stability of suspended microdrops during the extraction, peak tailing and bad separation were observed in the chromatogram when the microdrop volume was more than 2 µl. Hence, a 1.5 µl microdrop was selected in succeeding experiments.

Other HS-SDME conditions, such as ionic strength, agitation speed and extraction time, were optimized according to the relative peak areas of each compound obtained from twelve experiments conducted under different conditions. The extraction conditions of these experiments are listed in Table 1. Twelve parallel working solutions at concentrations of 3.06 µg/ml (n-hexane), 3.62 µg/ml (benzene), 2.80 µg/ml (n-heptane), 2.92 µg/ml (methylcyclohexane), 3.48 µg/ml (toluene), 2.88 µg/ml (n-octane), 3.50 µg/ml (ethylbenzene), 3.66 µg/ml (o-xylene), 2.98 µg/ml (n-nonane), 2.88 µg/ml (n-decane), 5.80 µg/ml (n-undecane) and 5.54 µg/ml (n-dodecane) in water were used in this optimization procedure. Fig. 2 shows the relative peak areas of each C_6–C_{12} LHs per microliter injection volume under different experimental conditions. The results of experiments 1–3 demonstrate that ionic strength has varying effects on the extraction of different types of hydrocarbons. The 30% (w/v) NaCl concentration is favorable for the extraction of aromatic hydrocarbons, while 15% (w/v) NaCl is good for C_9–C_{12} alkanes, and 0% NaCl is good for C_6–C_8 alkanes.

Table 1
Extraction conditions of HS-SDME.

Experiment	NaCl (W/V) (%)	Stirring speed (rpm)	Extraction time (min)
1	0	1000	20
2	15	1000	20
3	30	1000	20
4	30	750	20
5	30	500	20
6	30	250	20
7	0	1000	30
8	0	1000	40
9	15	1000	30
10	15	1000	40
11	30	1000	30
12	30	1000	40

Experiments 3–6 indicate that the extraction efficiencies of C_6–C_{12} LHs all decrease with decreasing stirring speeds. As for extraction time, it depends on ionic strength and analytes (Fig. 2). For instance, experiments 1, 7 and 8 show that longer extraction time has little impact on extraction efficiencies for all concentrations of NaCl. Increases in ionic strength can obviously improve the extraction efficiencies of LHs, especially for C_9–C_{12} n-alkanes. However, more time is required to reach the equilibrium of extraction (experiments 2, 9 and 10). Experiments 3, 11 and 12 reveal that the optimum extraction time is 30 min under the 30% (w/v) NaCl concentration. Although the relative peak areas of each C_6–C_{12} measured under the tenth and eleventh experimental conditions are large, their reproducibilities under the two experimental conditions are bad. Furthermore, since the main LHs used for geochemical indicators fall in the range of C_6–C_8 alkanes, no addition of NaCl is selected in this study. Consequently, the condition in the seventh experiment is selected as optimal, i.e., 1.5 µl of n-hexadecane, 1000 rpm stirring rate, 30 min extraction time and 0% NaCl concentration for the determination of LHs in the following work.

3.2. Evaluation of HS-SDME

Validation procedures of the HS-SDME method for quantitative analysis of C_6–C_{12} LHs were performed under the optimized conditions described in Section 3.1. The working solutions for the calibration study were prepared by spiking boiled pure water with the stock solution over concentration ranges of 10.5–1836, 6.70–2172, 1.41–1680, 1.47–1752, 1.75–2088, 1.45–1728, 1.76–2100,
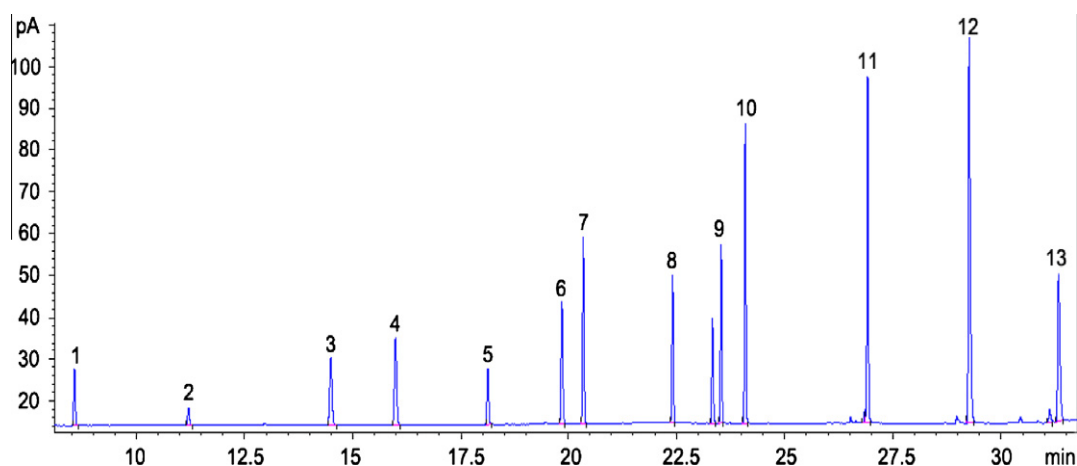

Fig. 1. Typical gas chromatogram of C_6–C_{12} light hydrocarbons extracted from the working solution by HS-SDME method using n-hexadecane as an extraction solvent. 1 = n-hexane (130 µg/l), 2 = benzene (154 µg/l), 3 = n-heptane (119 µg/l), 4 = methylcyclohexane (124 µg/l), 5 = toluene (148 µg/l), 6 = n-octane-d_{18} (IS, 472 µg/ml), 7 = n-octane (123 µg/l), 8 = ethylbenzene (149 µg/l), 9 = o-xylene (156 µg/l), 10 = n-nonane (127 µg/l), 11 = n-decane (123 µg/l), 12 = n-undecane (247 µg/l), 13 = n-dodecane (236 µg/l).
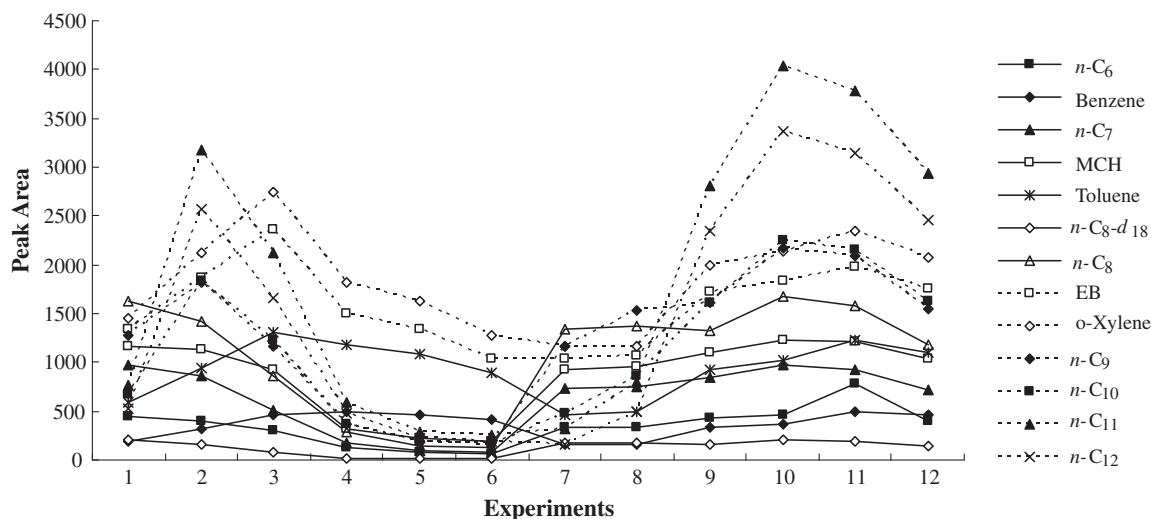
Fig. 2. Peak areas of C_6–C_{12} light hydrocarbons per microliter using the HS-SDME method under different extraction conditions at concentrations of each compound as *n*-hexane (3.06 μg/ml), benzene (3.62 μg/ml), *n*-heptane (2.80 μg/ml), methylcyclohexane (2.92 μg/ml), toluene (3.48 μg/ml), *n*-octane-d_{18} (0.48 μg/ml), *n*-octane (2.88 μg/ml), ethylbenzene (3.50 μg/ml), o-xylene (3.66 μg/ml), *n*-nonane (2.98 μg/ml), *n*-decane (2.88 μg/ml), *n*-undecane (5.80 μg/ml) and *n*-dodecane (5.54 μg/ml) in the water.

1.84–2196, 1.50–1788, 2.38–1728, 4.79–3480 and 4.57–3324 μg/l in the water for *n*-hexane, benzene, *n*-heptane, methylcyclohexane, toluene, *n*-octane, ethylbenzene, o-xylene, *n*-nonane, *n*-decane, *n*-undecane and *n*-dodecane, respectively. The calibration curves were constructed using ratios of peak area of each C_6–C_{12} LHs to the internal standard (A_{Cn}/A_{IS}) versus the corresponding concentration ratios (C_{Cn}/C_{IS}). Linearity was evaluated according to the correlation coefficients of the regression equations of the calibration curves. The calculated calibration curves showed good linearity for all C_6–C_{12} LHs, with the correlation coefficients (R^2) ranging from 0.9953 to 0.9999 (Table 2).

Reproducibility of the method was examined by extracting five parallel working solutions at the concentrations of 158 μg/l (*n*-hexane), 187 μg/l (benzene), 144 μg/l (*n*-heptane), 150 μg/l (methylcyclohexane), 179 μg/l (toluene), 148 μg/l (*n*-octane), 180 μg/l (ethylbenzene), 189 μg/l (o-xylene), 154 μg/l (*n*-nonane), 148 μg/l (*n*-decane), 299 μg/l (*n*-undecane) and 285 μg/l (*n*-dodecane) in water under optimized experimental conditions. As shown in Table 2, relative standard deviations (RSD, %) vary between 3.8% and 6.1%, indicating that the reproducibility of this extraction method is satisfactory.

HS-SDME is a non-exhaustive extraction technique. However, the large decrease of the acceptor to donor phase ratio permits large enrichment factors (Pena-Pereira et al., 2009), as was shown in this work. The concentration enrichment (*E*) is calculated by the following equation for each analyte:

$$E_i = \frac{C_{i,a}}{C_{i,s}}$$

where E_i is the concentration enrichment of the compound *i*. The terms $C_{i,a}$ and $C_{i,s}$ are the concentrations of *i* originally present in the sample and the concentration of the compound finally collected in the acceptor solution, respectively. The calculated enrichment factors range from 200 to 4095 for C_6–C_{12} LHs from 5 ml water (Table 2). Detection limits between 0.26–4.33 μg/l (Table 2) were calculated according to the signal that differed 10 times from the blank average signal.

3.3. Applications

For high concentration oils, the sample need be diluted with methanol prior to HS-SDME. Approximately 40 μl of the oil sample from the Tarim Basin was added to a 4 ml glass vial and weighed. The vial was then filled with a certain volume of methanol, tightly capped and extracted ultrasonically for 10 min. Three replicate extractions were performed on the methanol solution by using the optimized extraction conditions of HS-SDME. In this case, the matrix effect of crude oil must be negligible, because the dilution factor is close to 10,000. To check the performance of the HS-SDME method, a direct injection of the whole oil was conducted. Fig. 3 shows the distribution of C_6–C_{12} LHs in the crude oil achieved by the HS-SDME method and the direct injection method. Compared

Table 2
Quantitative results of HS-SDME.

| Analyte	Equation	R^2	Linear range (μg/l)	RSD (%, $n = 5$)	LOD (μg/l)	Enrichment factor
n-C_6	$y = 1197.6x + 0.0962$	0.9989	10.5–1836	6.1	1.71	535
Benzene	$y = 474.71x + 0.0027$	0.9997	6.70–2172	4.1	4.33	200
n-C_7	$y = 2922.7x + 0.0433$	0.9993	1.41–1680	5.9	0.70	1378
MCH	$y = 3457.6x + 0.0468$	0.9991	1.47–1752	5.8	0.60	1557
Toluene	$y = 1467.9x + 0.0092$	0.9997	1.75–2088	4.1	1.40	685
n-C_8	$y = 5290.6x + 0.0658$	0.9997	1.45–1728	5.2	0.39	2698
Ethylbenzene	$y = 3222.1x + 0.0158$	0.9997	1.76–2100	4.2	0.64	1546
o-Xylene	$y = 5909.8x + 0.0299$	0.9999	1.84–2196	3.8	0.35	3662
n-C_9	$y = 7258.3x + 0.0299$	0.9999	1.50–1788	5.6	0.28	3662
n-C_{10}	$y = 8041.8x + 0.0651$	0.9999	2.38–1728	3.9	0.26	4095
n-C_{11}	$y = 7080.1x + 0.0644$	0.9995	4.79–3480	4.8	0.29	3321
n-C_{12}	$y = 5078.3x + 0.165$	0.9953	4.57–3324	3.8	0.41	2209
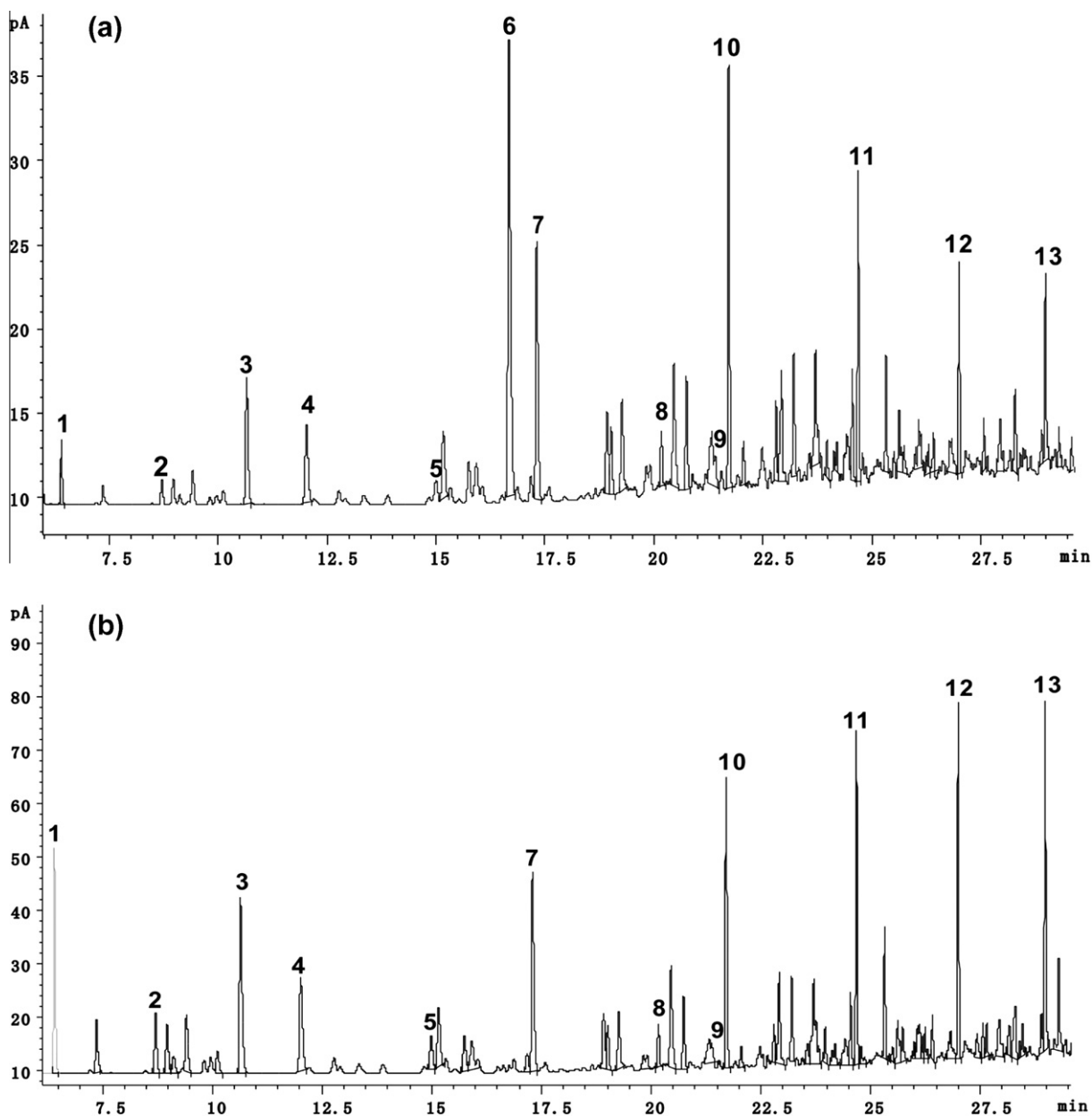
Fig. 3. Gas chromatograms of the $C_6–C_{12}$ light hydrocarbons extracted from the Tarim Basin oil by using: (a) the HS-SDME method and (b) the direct injection method. 1 = *n*-hexane, 2 = benzene, 3 = *n*-heptane, 4 = methylcyclohexane, 5 = toluene, 6 = *n*-octane-d_{18} (IS), 7 = *n*-octane, 8 = ethylbenzene, 9 = o-xylene, 10 = *n*-nonane, 11 = *n*-decane, 12 = *n*-undecane, 13 = *n*-dodecane.

with the LH distribution from the direct GC injection (Fig. 3b), the concentrations of *n*-hexane, benzene and $C_{10}–C_{12}$ *n*-alkanes are low when analyzed by HS-SDME (Fig. 3a). This may be explained by relatively higher or lower boiling points for these compounds, such that a higher boiling point does not favor the volatilization of $C_{10}–C_{12}$ *n*-alkanes from the donor phase, while a lower boiling point allows *n*-hexane and benzene to escape easily from the acceptor solution. This kind of effect from the HS-SDME method could be corrected by calibration curves. In addition, the result of three replicated analyses shows that the HS-SDME technique has a good reproducibility, RSD (%) being less than 5% for most target compounds.

The drilling mud was taken as an example of a low concentration and aqueous phase in this study. Headspace gas analyses of the drilling mud samples from a well in the South China Sea showed several intervals with relatively higher concentrations in

$C_2–C_5$ gaseous hydrocarbons, inferring the presence of oil or gas layers. A mud sample from one of these intervals was selected to determine the $C_6–C_{12}$ LHs using the optimized HS-SDME technique. Firstly, 5 ml of liquid from the drilling mud was transferred into a 10 ml glass vial equipped with a magnetic stir bar. Then, the other procedures were the same as above. Fig. 4 shows the gas chromatogram obtained from the drilling mud. Abundant $C_6–C_{12}$ LHs were found in the drill mud sample, indicating that this interval may be an oil layer.

Although the uptake of the $C_6–C_{12}$ LHs using HS-SDME may be affected by the complex mud matrix, the percent recovery determination of surrogates added to the matrix can give some indication of the degree of the matrix effect. Alternatively, the dilution with organic free pure water for the oil based mud sample with high concentration hydrocarbons will minimize the matrix effect. Therefore, further study will be needed for real geological applications.
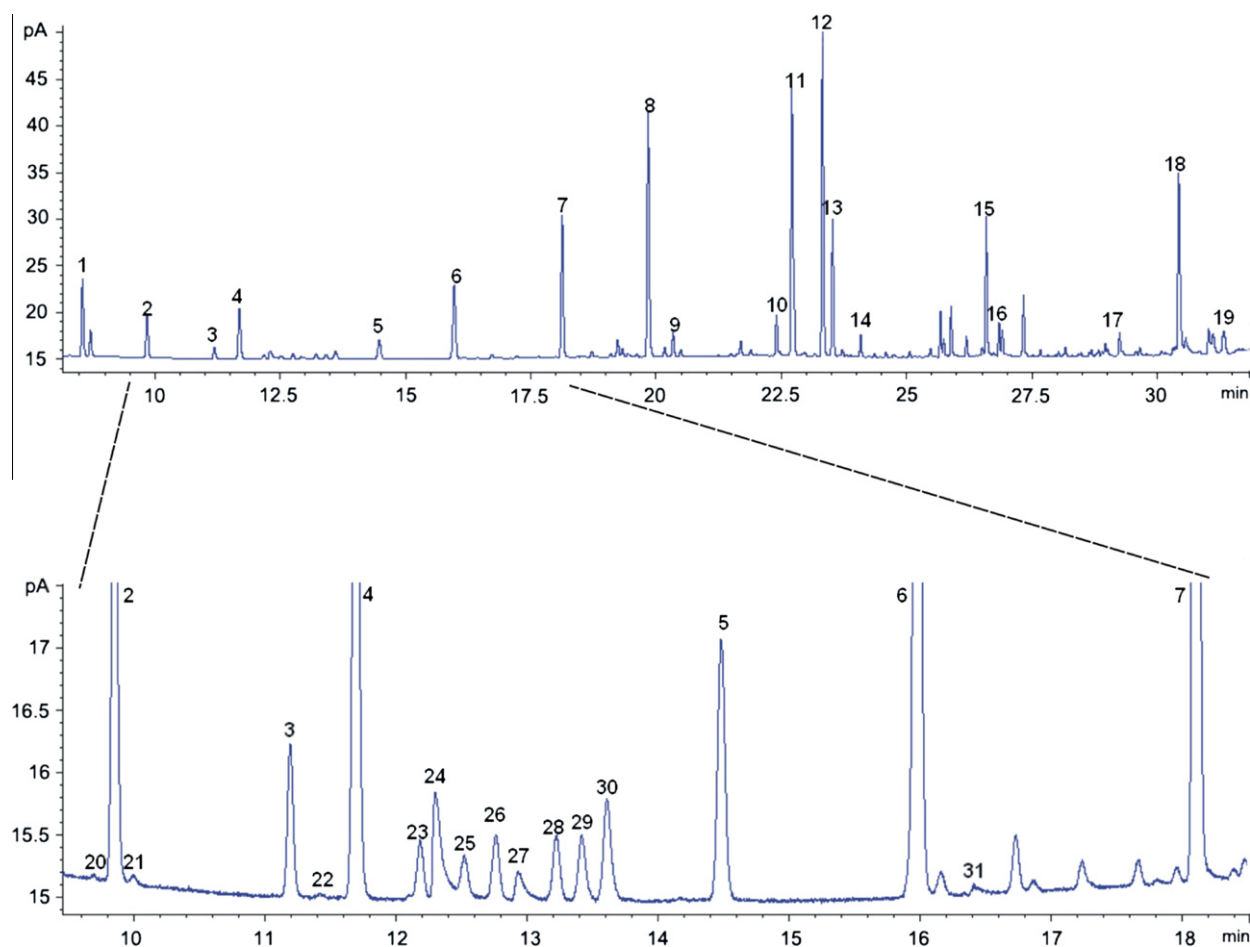
Fig. 4. Gas chromatogram of C_6–C_{12} light hydrocarbons extracted from the drilling mud sample. 1 = *n*-hexane, 2 = 2,4-dimethylpentane (24DMP), 3 = benzene (Ben), 4 = cyclohexane (CH), 5 = *n*-heptane, 6 = methylcyclohexane (MCH), 7 = toluene (Tol), 8 = *n*-octane-d_{18} (IS), 9 = *n*-octane, 10 = ethylbenzene (EB), 11 = m + p-xylene, 12 = o-xylene-d_{10} (IS), 13 = o-xylene, 14 = *n*-nonane, 15 = 1,2,4-trimethylbenzene (124TMB), 16 = *n*-decane, 17 = *n*-undecane, 18 = naphthalene (Na), 19 = *n*-dodecane, 20 = 2,2-dimethylpentane (22DMP), 21 = 2,2,3-trimethylbutane (223TMB), 22 = 3,3-dimethylpentane (33DMP), 23 = 2-methylhexane (2MH), 24 = 2,3-dimethylpentane (23DMP), 25 = 1,1-dimethylcyclopentane (11DMCP), 26 = 3-methylhexane (3MH), 27 = cis 1,3-dimethylcyclopentane (c13DMCP), 28 = trans 1,3-dimethylcyclopentane (t13DMCP), 29 = 3-ethylpentane (3EP), 30 = trans 1,2-dimethylcyclopentane (t12DMCP), 31 = ethylcyclopentane (ECP).

4. Conclusions

In this work, the HS-SDME method was optimized for the extraction of C_6–C_{12} LHs from the aqueous phase. *n*-Hexadecane was found to be a suitable extraction solvent. Extraction conditions were optimized and 1.5 µl extraction solvent, 1000 rpm stirring rate, 30 min extraction time and no NaCl were selected. Under the optimized extraction conditions, calibration curves with good linearity and reproducibility were obtained, with the correlation coefficients ranging between 0.9953 and 0.9997, and RSD (%) values ranging from 3.8% to 6.1% (n = 5). The enrichment factors for C_6–C_{12} LHs ranged from 200–4095. Based on the advantages of HS-SDME method, i.e., less organic solvent and time consumption, no sample carry over, simple operation and high enrichment, we believe that it is an alternative method for the extraction of volatile C_6–C_{12} LHs in complex matrices. Two examples using this method indicated that the HS-SDME can be used for the determination of the C_6–C_{12} LHs in petroleum and drilling muds. In addition, combined with ultrasonic extraction (methanol as an extraction solvent), it can also be easily expanded to the determination of C_6–C_{12} LHs in solid samples, such as soils. Therefore, HS-SDME is a simple, efficient and promising technique for the determination of volatile C_6–C_{12} LHs in complex matrices.

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