



A new application of headspace single-drop microextraction technique for compound specific carbon isotopic determination of gasoline range hydrocarbons

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ABSTRACT

In this study, headspace single-drop microextraction (HS-SDME) coupled with gas chromatography–isotope ratio mass spectrometry (GC–IRMS), was employed to determine compound specific carbon isotopic values ($\delta^{13}\text{C}$) of gasoline range hydrocarbons. The reproducibility of the method was found to be satisfactory. By comparison with the $\delta^{13}\text{C}$ values of the twelve target compounds determined using direct injection of their $n\text{-C}_{16}$ solution, no obvious isotopic fractionation was observed during the HS-SDME procedures. Some parameters that could affect the carbon isotopic fractionation, such as ionic strength of working solutions and inlet split ratio, were examined. The results also suggest that these factors had no significant effect on the carbon isotopic determination of gasoline range hydrocarbons. The application of HS-SDME to a crude oil sample proved that this method could be a promising tool for the determination of carbon isotopic values of gasoline range hydrocarbons in oils or aqueous samples.

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1. Introduction

Gasoline range hydrocarbons ($\text{C}_6\text{--C}_{12}$) have attracted increasing attention from organic geochemists in the past decades. As a main component of petroleum, they consist of different compound classes (n -alkanes, isoalkanes, cycloalkanes and aromatics) and comprise 20–40% of most crude oils (Harris et al., 1999). Thus, information derived from this major fraction in oil is considered more representative for the petroleum fluid than that from biomarkers, which are usually present in trace amounts in oil (Tissot and Welte, 1984; Odden et al., 1998). Many previous studies have established that gasoline range hydrocarbons can provide useful information regarding genetic associations and alteration of oils (Mango, 1990; ten Haven, 1996; Thompson, 1979, 1983). Although gasoline range hydrocarbons are more susceptible to biodegradation and evaporation, most of them are stable under thermal stress and can be found in fluids of high thermal maturities, where high molecular weight biomarkers such as steranes and terpanes tend to be present at very low concentrations or may even be absent. In such cases, oil–oil and oil–source correlations using high molecular weight biomarkers are found to be problematic. Therefore, gasoline range hydrocarbons have been widely utilized to identify oil families, assess the thermal maturity of oils and condensates, determine the source of mixed oils and identify alteration in crude oils due to water washing, biodegradation and evaporative fractionation (ten Haven, 1996; Obermajer et al., 2000; George et al., 2002; Pasadakis et al., 2004; Zhang et al., 2005; Chang et al.,

2007). Environmental chemists are also interested in gasoline range hydrocarbons for studying oil spills and other petroleum related contaminations in various water bodies (rivers, lakes, coastal waterways and groundwater) and soils. Oil-source correlation is important for the study of oil spills, as it usually provides forensic evidence for the investigation of spill events.

The molecular characteristics of gasoline range hydrocarbons are susceptible to secondary alteration, such as biodegradation, evaporation and water washing, which can render them inapplicable to oil correlation (Kaplan et al., 1997; Mansuy et al., 1997; Wang and Fingas, 1995; Wang et al., 1999). Compound specific isotope analysis (CSIA) is a valuable method for oil characterization and correlation (Bjørøy et al., 1994; Clayton and Bjørøy, 1994; Chung et al., 1998; Odden et al., 1998; Rooney et al., 1998; Whiticar and Snowdon, 1999), because stable carbon isotopic values ($\delta^{13}\text{C}$) are not as susceptible to the effects of secondary processes. The method has been successfully used to identify the source of contaminants and to elucidate the processes controlling their fate and transport (Kelley et al., 1997; Gray et al., 2002; Kolhatkar et al., 2002; Smallwood et al., 2002; Zwank et al., 2003). Early investigations using gas chromatography–isotope ratio mass spectrometry (GC–IRMS) mainly involved carbon isotope analysis of the C_{13+} n -alkanes in oils (Bjørøy et al., 1994; Mansuy et al., 1997). Subsequently, this technique was applied to the gasoline range fraction of oils and condensates (Chung et al., 1998; Odden et al., 1998; Harris et al., 1999; Whiticar and Snowdon, 1999) and volatile organic contaminants (Slater et al., 1999; Kolhatkar et al., 2002) by developing various sample pretreatment techniques.

A few solvent free or low solvent sample preparation techniques, such as purge and trap (P&T) (Whiticar and Snowdon, 1999; Kolhatkar et al., 2002; Zwank et al., 2003) and solid phase

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microextraction (SPME) (Dias and Freeman, 1997; Harris et al., 1999), have been used for CSIA of volatile organic compounds. P&T is a common extraction method which provides reproducible results and permits low method detection limits for volatile organic compounds. It has been used in conjunction with GC–IRMS for CSIA (Kelley et al., 1997; Harris et al., 1999; Whiticar and Snowdon, 1999; Kolhatkar et al., 2002). However, Smallwood et al. (2001) identified carbon isotopic signatures of methyl tertiary butyl ether (MTBE) in aqueous samples using P&T coupled on-line with a GC–IRMS system, and found a large and reproducible shift in carbon isotopic values (+0.66‰). Zwank et al. (2003) demonstrated that the $\delta^{13}\text{C}$ values varied significantly for extraction efficiencies below 40%, but approached the original isotopic signatures with increasing extraction efficiencies.

SPME, a simple, rapid and environmentally friendly method for organic matter analysis, has also been used in combination with CSIA (Dias and Freeman, 1997; Harris et al., 1999; Gray et al., 2002; Zwank et al., 2003). Some studies have shown that the common SPME method (direct immersion of the fiber into a sample solution) does not cause carbon isotopic fractionation (Dias and Freeman, 1997; Zwank et al., 2003; Huang et al., 2005). Headspace solid phase microextraction (HS-SPME) is a sample preparation method that extracts organic compounds from the headspace of a sample by the equilibrium partitioning of analytes among the three phases (liquid, headspace and fiber). Observed isotope shifts have been found during the HS-SPME procedure in several studies (Harris et al., 1999; Gray et al., 2002).

Headspace single-drop microextraction (HS-SDME) is another rapid, simple, inexpensive and non-hazardous sample preparation technique (Jeannot and Cantwell, 1997). In contrast to P&T and SPME, it does not need a specific apparatus except for a microsyringe. It is suitable for the extraction of volatile and semi-volatile organic compounds and has been successfully applied in various fields (Przyjazny and Kokosa, 2002; Shariati-Feizabadi et al., 2003; Bahramifar et al., 2004; Lambropoulou and Albanis, 2004; Yamini et al., 2004; Tan et al., 2005). Recently, the work by Fang et al. (2011) has proved that the HS-SDME method is a promising tool for the determination of volatile C_6 – C_{12} light hydrocarbons in petroleum and aqueous samples. However, to the best of our knowledge, few papers on the application of HS-SDME technique in isotope analysis have been published. Therefore, the occurrence of carbon isotopic fractionation during the HS-SDME procedure is unclear.

The purpose of this study is to investigate whether or not the HS-SDME method causes carbon isotopic fractionation of gasoline range hydrocarbons. First, the $\delta^{13}\text{C}$ values of 12 target compounds were determined by direct injection of their n - C_{16} solution. Next, these compounds were dissolved in water and their carbon isotopic values were determined using HS-SDME coupled with GC–IRMS. Comparison of the results obtained by the two methods allowed for the assessment of the extent of any isotopic fractionation. Some parameters that could affect the carbon isotopic analysis, such as ionic strength of working solutions and injection split ratio, were also explored in this study. Finally, to test the applicability of the method, the $\delta^{13}\text{C}$ values of gasoline range hydrocarbons in a real crude oil sample were analyzed by the HS-SDME method and were compared with the result obtained by the whole oil direct injection.

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+%), methylcyclohexane (MCH, 99%), n -hexadecane (n - C_{16} , 99%), benzene (99%), ethylbenzene (99%) and o -xylene (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. One mixed stock solution was prepared by dissolving n - C_6 , n - C_7 , MCH, n - C_8 , n - C_9 , n - C_{10} , n - C_{11} and n - C_{12} in methanol. Another was prepared by dissolving benzene, toluene, ethylbenzene and o -xylene in methanol. The stock solutions were stored at 4 °C and diluted with boiled water for use as the working solutions. The n - C_{16} solvent was used as the extractant for HS-SDME.

2.2. Headspace single-drop microextraction (HS-SDME)

Appropriate volumes of the prepared stock solutions or sample solutions were spiked into a 10 ml glass vial with 5 ml of water, a magnetic stir bar and an aluminium cap seal containing a rubber 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. First, a 1.2 μl volume of n - C_{16} as extraction solvent was drawn into the microsyringe. Then, 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 syringe plunger was depressed slowly and a 1.2 μl solvent droplet was suspended from the needle tip. During extraction, the microsyringe was fixed above the extraction vial using a metal clamp. After the extraction, the droplet was retracted into the needle and injected directly into the GC–IRMS system for analysis. Based on the study by Fang et al. (2011), the extraction parameters selected in this work were 1.2 μl of n - C_{16} (extraction solvent), 1000 rpm stirring rate (agitation speed), 30 min extraction time, 0% (w/v) NaCl concentration for the extraction of alkanes and 30% (w/v) NaCl concentration for the extraction of aromatics.

2.3. Gas chromatography–isotope ratio mass spectrometry (GC–IRMS)

GC–IRMS analyses were performed on a VG Isoprime instrument. For the analyzing of working solutions, the Agilent 6890 GC was equipped with a DB-5 capillary column (30 m \times 0.25 mm \times 0.25 μm) with helium as the carrier gas. It was held isothermally for 5 min at 40 °C before heating from 40 to 250 °C at 4 °C/min (5 min hold). For the crude oil analysis, gasoline range compounds were separated on a DB-5MS fused silica capillary column (50 m \times 0.25 mm \times 0.25 μm). The compounds were separated using a temperature program of 40 °C for 2 min, ramped 2 °C/min to 130 °C and then ramped to 290 °C at 20 °C/min (5 min hold). The combustion furnace was run at 880 °C. Carbon isotope ratios for individual hydrocarbons were calculated using CO_2 as a reference gas that was automatically introduced into the IRMS at the beginning and end of each analysis, and the data are reported in per mil (‰) relative to the VPDB standard. A standard mixture of n -alkanes (n - C_{12} to n - C_{32}) from Indiana University with known isotopic composition and a n - C_{16} solution of 12 pure compounds, including 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} , were used daily to monitor the performance of the instrument and test the accuracy of the $\delta^{13}\text{C}$ values of gasoline range hydrocarbons.

3. Results and discussion

3.1. $\delta^{13}\text{C}$ values of pure compounds

To eliminate the possible effect of the complicated matrix and coelution, 12 pure standards (i.e., *n*-C₆, benzene, *n*-C₇, MCH, toluene, *n*-C₈, ethylbenzene, *o*-xylene, *n*-C₉, *n*-C₁₀, *n*-C₁₁ and *n*-C₁₂) were selected for this study. A 1 μl portion of the *n*-C₁₆ solution, containing an appropriate concentration of these compounds, was directly introduced into the GC–IRMS system. The split ratio of the GC inlet was 50:1. This mixture was run seven times by GC–IRMS to determine the accuracy and precision of the instrument. Average $\delta^{13}\text{C}$ values and standard deviations (SD‰) for each compound are shown in Table 1. The analyses are highly reproducible, as indicated by the narrow range of the standard deviations (0.16–0.56‰) for the $\delta^{13}\text{C}$ values of individual hydrocarbons. Exceptions to this are *n*-C₈ and ethylbenzene, whose standard deviations are slightly higher than 0.5‰. Average values determined for the seven runs were considered as the standard values of $\delta^{13}\text{C}$ of each compound and were used in the succeeding studies. Prior to the CSIA analysis of the working solutions and the oil sample using HS–SDME, this *n*-C₁₆ solution containing the 12 target compounds and the Indiana standard mixture were analyzed daily by direct injection, to check the performance of the instrument.

3.2. $\delta^{13}\text{C}$ values obtained by HS–SDME

Working solutions were prepared by spiking boiled pure water with 10 μl of stock solutions. As the optimum extraction parameters for alkanes and aromatics are different in the NaCl concentration of the working solutions (0% w/v NaCl concentration for alkanes and 30% w/v NaCl for aromatics), the alkanes and the aromatics were analyzed separately and each fraction was analyzed five times. Fig. 1 shows a typical *m/z* 44 chromatogram of alkanes and aromatics extracted by HS–SDME. The isotopic results are shown in Tables 2 and 3. Deviations in the tables are calculated by subtracting the “standard” values determined by direct injection from the average values of five HS–SDME injections. As shown in the tables, all standard deviations (SD‰) of these target compounds are in the acceptable range of analytical error ($\leq 0.5\%$) and show good reproducibility. Compared with the standard values, the isotopic deviations of the alkanes and aromatics vary between -0.6% and 0.3% , and almost all fall in the range of analytical error. These results confirm that the HS–SDME technique has good reproducibility in the CSIA of gasoline range hydrocarbons, and does not cause any significant carbon isotopic fractionation. Therefore, the method can be used in the carbon isotope analysis of gasoline range hydrocarbons.

3.3. Effect of analytical conditions

The effect of analytical and instrument parameters on HS–SPME such as flow rates, temperature programs and combustion conditions on the carbon isotope ratios of gasoline range hydrocarbons has been demonstrated (Harris et al., 1999). As part of this study, the effects of solution ionic strengths and injection split ratios were tested.

A number of studies have indicated that the addition of salt can increase the activity coefficients of hydrophobic compounds in water and affect the extraction efficiency of HS–SDME (Li et al., 2010). This may result in isotopic fractionation between the aqueous and organic phases. To identify this effect, the $\delta^{13}\text{C}$ values of the selected alkanes and aromatics were determined after HS–SDME from 30% w/v and 0% w/v NaCl aqueous solutions, respectively. Each analysis was performed three times. The results are listed in Tables 4 and 5. Standard deviations (SD%) vary between 0.04‰ and 0.48‰, showing good reproducibility. Similarly, compared with the standard values, most of the deviations are lower than 0.5‰, except the values of *n*-C₆ (-0.7%) under the 30% w/v NaCl condition. The slight deviation may result from the incomplete extraction of *n*-C₆ which has been observed by the comparison of the HS–SDME method with the direct injection (Fang et al., 2011). Consequently, although the ionic strength of the solution can influence the extraction efficiency of analytes, no variation is evident in the carbon isotopic values.

Due to the dynamic range limit of IRMS, the amount of analyte introduced into the IRMS system should be controlled to an appropriate range to obtain reliable isotope data. In addition to varying the injection volume, changing the split ratio of the GC injector is a simple method for adjusting the amount of individual gasoline range hydrocarbons. Some studies indicated that the split ratio could cause isotopic fractionation in light gases (Baylis et al., 1994). However, Harris et al. (1999) investigated the $\delta^{13}\text{C}$ values of 16 gasoline range analytes at different split ratios and found no detectable isotopic fractionation. To examine this effect, the same *n*-C₁₆ solution containing the 12 pure compounds was analyzed by direct injection at different split ratios (100:1, 50:1, 20:1, 10:1 and 3:1). The peak heights of each compound were kept within the linear range of the IRMS by adjusting the injection volume and the concentration of samples. For each split ratio, duplicate analyses were performed. The average values are given in Table 6. Compared with the standard values, which were obtained under a split ratio of 50:1, deviations for almost all other split ratios fell within the acceptable analytical error range, except *n*-C₇ in split ratio of 10:1 (0.7‰) and MCH in split ratio of 3:1 (0.8‰), which are slightly higher than 0.5‰ (Table 6). This demonstrates that injection split ratio has minimal isotope effect on the gasoline range hydrocarbons.

Table 1
Carbon isotope values of 12 pure target compounds determined by direct injection.

Compound	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Average (‰)	SD (‰)
<i>n</i> -C ₆	-47.1	-47.3	-47.7	-47.6	-47.4	-47.2	-47.6	-47.4	0.23
Benzene	-25.0	-25.5	-25.0	-25.2	-25.5	-25.2	-25.2	-25.2	0.22
<i>n</i> -C ₇	-40.4	-40.2	-40.3	-40.0	-40.4	-40.9	-40.6	-40.4	0.28
MCH	-29.2	-29.8	-29.8	-29.1	-29.9	-29.4	-29.5	-29.5	0.31
Toluene	-29.8	-29.8	-29.6	-30.2	-29.3	-29.6	-29.6	-29.7	0.26
<i>n</i> -C ₈	-46.6	-45.6	-46.6	-47.09	-45.8	-46.0	-46.1	-46.2	0.56
Ethylbenzene	-28.4	-27.6	-28.0	-28.4	-29.17	-28.8	-28.6	-28.4	0.52
<i>o</i> -Xylene	-28.2	-27.7	-27.7	-28.4	-28.8	-28.4	-27.9	-28.2	0.39
<i>n</i> -C ₉	-49.4	-49.7	-49.5	-49.3	-49.5	-49.7	-49.4	-49.5	0.16
<i>n</i> -C ₁₀	-36.3	-35.8	-36.6	-36.5	-36.3	-35.7	-36.6	-36.2	0.33
<i>n</i> -C ₁₁	-28.3	-28.0	-28.5	-28.8	-28.6	-28.1	-28.3	-28.4	0.27
<i>n</i> -C ₁₂	-32.5	-32.2	-32.7	-32.5	-32.9	-32.7	-33.0	-32.6	0.27

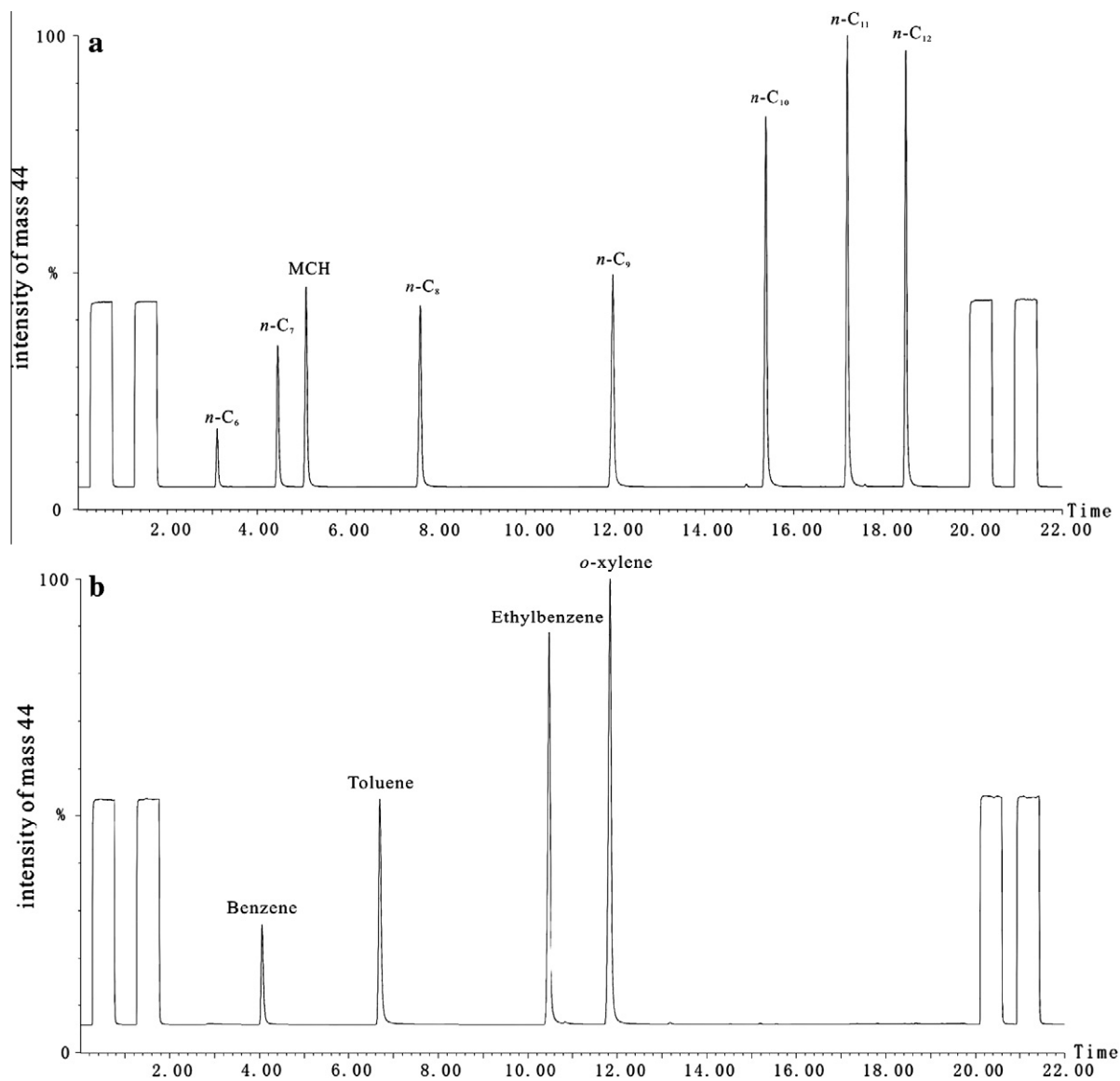


Fig. 1. (a) Typical m/z 44 chromatogram of target alkanes extracted by HS-SDME. (b) Typical m/z 44 chromatogram of target aromatics extracted by HS-SDME.

Table 2
Carbon isotope values of alkanes obtained by HS-SDME (0% w/v NaCl solution).

Compound	Standard values (‰)	Run 1	Run 2	Run 3	Run 4	Run 5	Average (‰)	SD (‰)	Deviation (‰)
$n-C_6$	-47.4	-47.7	-48.0	-48.2	-48.2	-47.7	-48.0	0.25	-0.6
$n-C_7$	-40.4	-40.5	-40.3	-40.6	-40.1	-40.4	-40.4	0.16	0.0
MCH	-29.5	-30.1	-29.9	-29.4	-30.1	-29.9	-29.9	0.28	-0.4
$n-C_8$	-46.2	-46.7	-46.2	-46.4	-46.3	-46.2	-46.4	0.19	-0.2
$n-C_9$	-49.5	-49.9	-49.7	-49.6	-49.5	-50.0	-49.7	0.20	-0.2
$n-C_{10}$	-36.2	-35.8	-36.5	-36.2	-36.4	-36.1	-36.2	0.28	0.0
$n-C_{11}$	-28.4	-28.1	-28.3	-28.3	-28.2	-28.2	-28.2	0.11	0.2
$n-C_{12}$	-32.6	-32.2	-32.3	-32.0	-32.2	-32.7	-32.3	0.25	0.3

Table 3
Carbon isotope values of aromatics obtained by HS-SDME (30% w/v NaCl solution).

Compound	Standard values (‰)	Run 1	Run 2	Run 3	Run 4	Run 5	Average (‰)	SD (‰)	Deviation (‰)
Benzene	-25.2	-25.9	-24.9	-25.9	-25.3	-25.4	-25.5	0.43	-0.3
Toluene	-29.7	-29.9	-30.2	-29.9	-29.8	-30.1	-30.0	0.16	-0.3
Ethylbenzene	-28.4	-28.6	-28.7	-28.6	-28.6	-28.7	-28.6	0.05	-0.2
<i>o</i> -Xylene	-28.2	-28.6	-28.6	-28.2	-28.6	-28.4	-28.5	0.17	-0.3

Table 4
Carbon isotope values of alkanes obtained by HS-SDME (30% w/v NaCl solution).

Compound	Standard values (‰)	Run 1	Run 2	Run 3	Average (‰)	SD (‰)	Deviation (‰)
<i>n</i> -C ₆	-47.4	-47.6	-48.2	-48.5	-48.1	0.48	-0.7
<i>n</i> -C ₇	-40.4	-40.0	-40.0	-40.5	-40.2	0.26	0.2
MCH	-29.5	-29.7	-29.5	-29.4	-29.5	0.12	0.0
<i>n</i> -C ₈	-46.2	-46.3	-46.1	-45.8	-46.1	0.28	0.1
<i>n</i> -C ₉	-49.5	-49.4	-50.0	-49.4	-49.6	0.33	-0.1
<i>n</i> -C ₁₀	-36.2	-36.2	-36.4	-35.7	-36.1	0.36	0.1
<i>n</i> -C ₁₁	-28.4	-28.0	-28.4	-27.8	-28.1	0.32	0.3
<i>n</i> -C ₁₂	-32.6	-31.7	-32.3	-32.0	-32.0	0.28	0.4

Table 5
Carbon isotope values of aromatics obtained by HS-SDME (0% w/v NaCl solution).

Compound	Standard values (‰)	Run 1	Run 2	Run 3	Average (‰)	SD (‰)	Deviation (‰)
Benzene	-25.2	-26.0	-25.4	-25.6	-25.7	0.32	-0.5
Toluene	-29.7	-29.1	-29.6	-29.7	-29.5	0.30	0.2
Ethylbenzene	-28.4	-28.7	-28.6	-28.7	-28.7	0.05	-0.3
<i>o</i> -Xylene	-28.2	-28.2	-28.1	-28.2	-28.2	0.04	0.0

Table 6
Results obtained by different injection split ratios.

Analytes	Standard values (‰)	Split ratio				Deviation (‰)			
		100:1	20:1	10:1	3:1	100:1	20:1	10:1	3:1
<i>n</i> -C ₆	-47.4	-47.7	-47.4	-47.5	-47.1	-0.3	0.0	-0.1	0.3
Benzene	-25.2	-25.3	-25.2	-24.8	-24.9	-0.1	0.0	0.4	0.3
<i>n</i> -C ₇	-40.4	-40.3	-40.3	-39.7	-40.0	0.1	0.1	0.7	0.4
MCH	-29.5	-29.3	-29.4	-29.4	-28.7	0.2	0.1	0.1	0.8
Toluene	-29.7	-30.1	-29.5	-29.5	-29.2	-0.4	0.2	0.2	0.5
<i>n</i> -C ₈	-46.2	-45.8	-46.0	-45.8	-46.4	0.4	0.2	0.4	-0.2
Ethylbenzene	-28.4	-28.8	-28.7	-28.3	-28.1	-0.4	-0.3	0.1	0.3
<i>o</i> -Xylene	-28.2	-28.1	-28.4	-28.1	-28.1	0.1	-0.2	0.1	0.1
<i>n</i> -C ₉	-49.5	-49.4	-49.6	-49.1	-49.3	0.1	-0.1	0.4	0.2
<i>n</i> -C ₁₀	-36.2	-36.0	-36.3	-35.8	-36.3	0.2	-0.1	0.4	-0.1
<i>n</i> -C ₁₁	-28.4	-28.3	-28.5	-28.3	-28.1	0.1	-0.1	0.1	0.3
<i>n</i> -C ₁₂	-32.6	-32.5	-32.6	-32.3	-32.3	0.1	0.0	0.3	0.3

Based on our studies, a method detection limit for benzene, toluene, ethylbenzene and *o*-xylene of about 0.1–0.6 ppm can be obtained using the HS-SDME technique coupled with GC-IRMS. It may be lowered by changing the injection split ratio, increasing the sample volume, decreasing the headspace volume and so on.

3.4. Application of HS-SDME to a real oil sample

A crude oil from the HD23 well in the Tarim Basin, China was analyzed to examine the applicability of the proposed HS-SDME coupled with GC-IRMS in the determination of $\delta^{13}\text{C}$ values of gasoline range hydrocarbons. Meanwhile, carbon isotope composi-

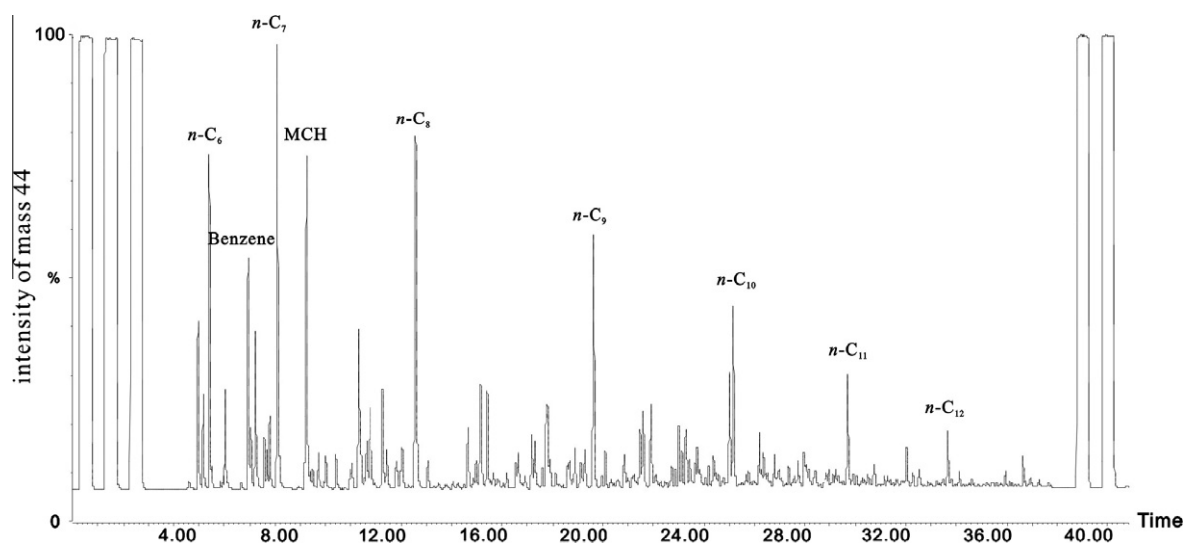
**Fig. 2.** The m/z 44 chromatogram of the HD23 crude oil by using HS-SDME coupled with GC-IRMS.

Table 7
 $\delta^{13}\text{C}$ values of gasoline range hydrocarbons in the HD23 crude oil obtained using two different methods.

Analytes	HS-SDME				Whole oil injection			
	Run 1	Run 2	Average (‰)	SD (‰)	Run 1	Run 2	Average (‰)	SD (‰)
<i>n</i> -C ₆	-31.9	-31.9	-31.9	0.02	-32.1	-32.4	-32.2	0.16
Benzene	-29.8	-29.8	-29.8	0.01	-30.1	-30.4	-30.2	0.20
<i>n</i> -C ₇	-32.4	-31.7	-32.0	0.46	-32.2	-32.2	-32.2	0.04
MCH	-30.4	-30.3	-30.4	0.13	-30.4	-30.3	-30.3	0.04
<i>n</i> -C ₈	-31.5	-31.3	-31.4	0.17	-31.8	-31.7	-31.8	0.03
<i>n</i> -C ₉	-33.9	-33.6	-33.8	0.22	-34.2	-34.2	-34.2	0.01
<i>n</i> -C ₁₀	-33.7	-33.3	-33.5	0.31	-33.7	-33.2	-33.5	0.35
<i>n</i> -C ₁₁	-34.5	-34.5	-34.5	0.04	-34.9	-34.9	-34.9	0.03
<i>n</i> -C ₁₂	-34.3	-34.7	-34.5	0.27	-34.2	-34.0	-34.1	0.16

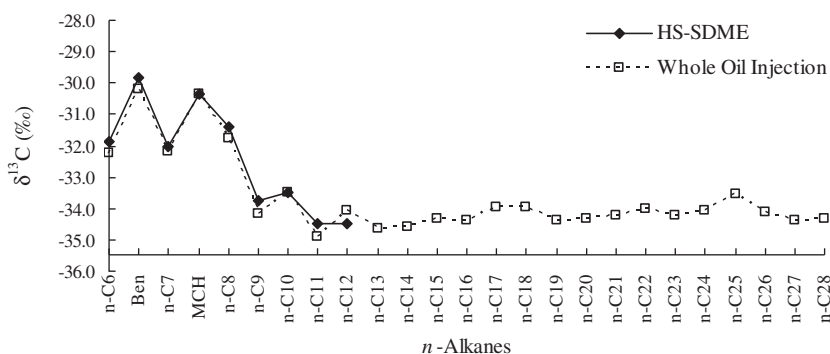


Fig. 3. Stable carbon isotopic composition of individual hydrocarbons in the HD23 crude oil obtained using two different methods.

tions of hydrocarbons in the oil were also determined by using the direct injection of the whole oil. Fig. 2 shows the *m/z* 44 chromatogram of the crude oil obtained using the HS-SDME sampling method coupled with GC-IRMS. As suggested by Harris et al. (1999), good baseline separation is a prerequisite to a precise and reproducible isotopic measurement of gasoline range hydrocarbons. Nine gasoline range compounds in the crude oil were identified based on the retention time. The gas chromatogram shows that peak resolution is good for the nine hydrocarbons (Fig. 2). Table 7 lists the results of duplicate analyses. Ratios of nine compounds (*n*-C₆, benzene, *n*-C₇, MCH, *n*-C₈, *n*-C₉, *n*-C₁₀, *n*-C₁₁ and *n*-C₁₂) show good reproducibility within 0.01–0.46‰ standard deviations using HS-SDME method.

As shown in Table 7 and Fig. 3, the $\delta^{13}\text{C}$ values of the nine gasoline range hydrocarbons determined by the HS-SDME method are similar to the result from the direct injection. This indicates that the HS-SDME method may be an efficient extraction way for the determination of carbon isotopic values of the gasoline range hydrocarbons. As a rapid sample preparation technique, HS-SDME is useful for the extraction of volatile or semi-volatile organic hydrocarbons. However, it is poor in the extraction of C₁₃₊ hydrocarbons and loses the opportunity to simplify a sample into different fractions using some “offline” sample separation techniques such as silica gel chromatography, molecular sieving, etc. Therefore, whole oil injection or other “offline” sample preparation methods are a good choice for the determination of C₁₃₊ hydrocarbons.

4. Conclusions

The HS-SDME technique is a simple, inexpensive and effective sample preparation method that may be coupled with GC-IRMS to determine the compound specific carbon isotope values of gasoline range hydrocarbons. Repeated analyses indicate that this method has good reproducibility and causes no obvious isotopic

fractionation. Comparison experiments indicate that the ionic strength of working solutions and the injection split ratio have no evident effect on the $\delta^{13}\text{C}$ values of the selected gasoline range hydrocarbons.

The application of HS-SDME to crude oil and the comparison with the results of the whole oil direct injection prove that this method could be a promising tool for the determination of carbon isotopic values of gasoline range hydrocarbons in oils or aqueous samples.

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