

Research Article

Determination of δ^{13} C of Trace Hydrocarbons in Natural Gas Using Syringe Solid Phase Extraction (SSPE) Coupled with Gas Chromatography/Isotope Ratio Mass Spectrometry (GC/IRMS)

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Sample preparation technique, for the analysis of δ^{13} C ratios in oil and gas samples, has gradually been recognized as one of the most crucial steps of the whole analytical process. In this study, a new convenient method, syringe solid phase extraction (SSPE), was proposed for measuring δ^{13} C in natural gas samples. Based on conditional experiments of temperature and time, SSPE fitted with activated carbon adsorbent was applied with a gas chromatography/isotope ratio mass spectrometry (GC/IRMS) system for trace carbon isotope analysis. The results showed that isotopic fractionation was not clearly observed during the adsorption and desorption process, and the δ^{13} C ratios measured by SSPE-GC/IRMS were in good agreement with the known δ^{13} C ratios of CH₄~C₅H₁₂ measured by GC/IRMS with the accuracy all within ±0.48‰. A natural gas sample was applied to verify the efficiency of this new method, and the obtained results confirmed that SSPE-GC/IRMS is a reliable technique characterized with simplicity, efficiency, and reliability.

1. Introduction

Compound-specific isotope analysis (CSIA) features with a gas chromatograph (GC) interfaced to an isotope ratio mass spectrometry (IRMS) are a reliable sample pretreatment tool for normal level carbon isotope analysis of hydrocarbons in environmental forensics, archaeology, ecology, and gas geochemistry [1–11]. This technique had been widely used in oil and gas geochemistry, for the obtained carbon isotopic ratios can be applied to identify gas genetic origin, characterize gas maturity, and correlate gas with their source rocks. It remains one of fundamental and promising techniques for oil-gas exploration and exploitation of normal level hydrocarbon compounds [10–16].

In general, trace hydrocarbons refer to small molecule volatile hydrocarbons such as $C_1 \sim C_8$ hydrocarbons in oil and gas geochemistry [17]. Those compounds are widely distributed in natural gas, crude oils, source rocks, sediments, oilfield water, and other types of reservoir fluids. Besides, their δ^{13} C ratios contain abundant geochemical information and are considered as an effective proxy associated with oilgas formation and evolution [18, 19]. However, it is difficult to analyze them directly by CSIA features with GC/IRMS, for those hydrocarbons are always beyond the detection limit of the instrument or very easy to escape during the preparation process [20].

To achieve the analysis of these particular hydrocarbon compounds for various applications, many previous works have been carried out, and some novel and practical methods such as purge and trap (P&T) and solid phase microextraction (SPME) have been put forward, and these highly efficient techniques made remarkable achievements for preconcentration of trace volatile or semivolatile organic compounds [21–25]. Though these works greatly improved the detection limit for most trace compounds, these often exhibited selectivity for some hydrocarbon compounds during the extraction process, making the whole analysis quite unfeasible. Therefore, for more intensive measurements of trace light hydrocarbons, the feasibility of these techniques remain to be discussed; the rapid isotopic analysis of trace hydrocarbons is still far from being realized. So, it is quite necessary to develop a new method for the efficient measurement of these compounds for geochemical applications.

In this study, a new technique, syringe solid phase extraction (SSPE), was proposed for the enrichment of trace hydrocarbon compounds with high capacity. In addition, with the consideration of fractionation, the integrated study of time and temperature during the adsorption and desorption process is carried out to determine the optimized experimental condition.

2. Experimental

2.1. Sample Preparation

2.1.1. Standard Sample Preparation. The SSPE preconcentration method was tested by a standard sample; composition of the gas are indicated in Table 1. It consists methane, ethane, propane, isobutane, normal butane, isopentane, and normal pentane, all of them were at trace levels after diluting with helium. The carbon isotopic ratios of different hydrocarbon compounds were also listed in Table 1, and all the δ^{13} C were determined by the GC/IRMS system. The determination was assessed by a number of duplicated injections, and the statistical results on these injections of the accuracy were calculated with standard deviations.

2.1.2. Geological Sample Preparation. A natural gas sample from Xiamaling Formation (XML), Sichuan Basin (Table 2), was applied to validate the extract efficiency of the SSPE technique with isobutane, isopentane, pentane, and heptane at the trace level, and all the δ^{13} C were determined by the GC/IRMS system.

2.2. Syringe Solid Phase Extraction (SSPE). The improved technique is called syringe solid phase extraction, which consists of three parts: the syringe, the three-way valve, and the extraction part (Figure 1). The syringe was used to hold helium and the natural gas. The three-way valve was used to switch different channels to realize the adsorption and desorption process. And the extraction part, the core part of SSPE technique, was designed to substitute the coated fiber of SPME technique. Adsorbents were filled in the tiny metal tube, and the target compounds can be adsorbed and desorbed by the needle plugging with the aid of the peristaltic pump and the microfurnace.

TABLE 1: Composition and carbon isotopic ratios of the standard sample.

Compound	Formula	δ^{13} C (V-PDB, ‰) (<i>n</i> = 6)	$P_1(\%)$	P_2 (%)
Methane	CH_4	-41.84 ± 0.21	50.271	0.084
Ethane	C_2H_6	-29.45 ± 0.17	22.931	0.038
Propane	C_3H_8	-26.70 ± 0.32	7.013	0.012
Isobutane	$i-C_4H_{10}$	-26.48 ± 0.31	11.284	0.019
Normal butane	$n-C_4H_{10}$	-25.58 ± 0.29	4.418	0.007
Isopentane	$i-C_5H_{12}$	-24.78 ± 0.36	3.352	0.006
Normal pentane	$n-C_5H_{12}$	-23.12 ± 0.33	0.731	0.001

 δ^{13} C ratios were all measured by direct injection, and all the ratios were calculated by average values of 6 duplicated injections under the same condition. P_1 : hydrocarbon content of direct injection (each peak area of the hydrocarbon represents their content); P_2 : hydrocarbon content after diluting with helium.

TABLE 2: Composition and peak area of natural gas sample from XML.

Compound	δ^{13} C (V-PDB, ‰)	Peak area (mV)
CH ₄	-48.20	1.02
C_2H_6	-44.31	1.10
C ₃ H ₈	-41.33	0.99
$i-C_4H_{10}$	—	—
$n-C_4H_{10}$	-37.28	0.91
i-C ₅ H ₁₂	_	—
$n-C_5H_{12}$	-35.42	0.43
C ₆ H ₁₄	_	

In this study, SSPE was applied to extract hydrocarbon compounds from natural gas, and all the applications were accomplished by using the metal tube containing adsorbents. In order to select a proper adsorbent, 11 different adsorbents were prepared. Each adsorbent was purified by the microfurnace at 400°C for 5 minutes. The prepared diluted natural gas (diluted with helium) sample was sealed in a glass container (600 mL). Firstly, the SSPE needle should be exposed into the bottle to extract the natural gas sample for 10 minutes at a rate of 3 mL/min. Then, the extracted hydrocarbon compounds should be desorbed for 5 minutes at 300°C. And finally, for the analysis of δ^{13} C ratios, the needle needed to be inserted into the GC injection port.

2.3. Optimized Condition Setting

2.3.1. Adsorbents. 3A, 4A, 5A, 13X, Al_2O_3 , silica gel, GDX-101, graphene (TORAY, Japan), 2,6-diphenylfuran porous polymer resin (Tenax), and two types of activated carbon were prepared as the adsorbents of SSPE. Furthermore, in order to validate the extract efficiency, carbon molecular sieve/polydimethylsiloxane/carboxen (CAR/PDMS/carboxen, Geofluids



FIGURE 1: Diagram of SSPE structure and its operation procedure. The SSPE process has four steps: (1) heat the metal tube to ensure the adsorbent is completely purified; (2) extract the target hydrocarbon compounds through the natural gas sample; in this step, the sorbent is exposed to the sample and target analytes are separated from the sample matrix and adsorbed on the sorbents; (3) desorb the hydrocarbon compounds with the microfurnace; and (4) inject the hydrocarbons into the GC inlet.

75 μ m, Supelco, USA) was selected as the fiber coating of the SPME technique.

2.3.2. Temperature. Six temperature (-20°C, 0°C, 20°C, 40°C, 60°C, and 80°C) were applied to the selection of an optimized adsorption temperature. Similarly, to evaluate the efficiency of desorption temperature, this study compared 10 different desorption temperatures (50~500°C, every two adjacent temperatures were at an interval of 50°C).

2.3.3. Time. Ten adsorbent time (1~10 minutes, every two adjacent time were at an interval of 1 minute) were set to evaluate the efficiency characteristics of adsorption time. And the concentration efficiency of 10 desorption time (0.5 minutes, 1 minute, 1.5 minutes, 2 minutes, 3 minutes, 4 minutes, 5 minutes, 6 minutes, 7 minutes, and 8 minutes) was used to measure the desorption time.

2.4. GC-IRMS. A GC-C-IRMS system (Gas Chromatography-Combustion, Agilent 6890, Agilent Technologies, USA; GC Combustion III; Isotope Ratio Mass Spectrometry, Finnigan Delta plus XP, Thermo Fisher, Bremen, Germany) was used to evaluate the SSPE efficiency. Helium (\geq 99.999%) was applied as carrier gas at 4 mL/min. Separation of hydrocarbon compounds was performed on HP-Plot Q (Agilent, 19095P-Q04, 30 m × 0.53 mm × 40 μ m) column. The temperature of HP-Plot Q column was held at 30°C for 4 minutes, then turned up to 100°C at the rate of 8°C/min and maintained for 4 minutes, and finally increased to 240°C at the rate of 8°C/min and then maintained for 30 minutes. The inlet temperature of the GC was set at 240°C, and all injections were set at split mode at the split ratio of 4:1. The furnace was maintained at 940°C to ensure the individual compound completely oxidized when it flowed through the oxidation ceramic reactor filled with twisted wires (Ni/CuO/Pt). Three standard pure CO₂ gases were used as reference gas for the calculation of δ^{13} C of specific compounds. All δ^{13} C signatures of analytes are reported relative to the Vienna Pee Dee Belemnite (V-PDB) and expressed as δ^{13} C = {[13 C/ 12 C]_{sample}/[13 C/ 12 C]_{standard} - 1} × 1000.

3. Results

3.1. Adsorbent Selection. All peak areas of hydrocarbon compounds obtained from the 11 adsorbents are listed in Figure 2(a). For all adsorbents, activated carbon exhibited the best adsorption efficiency, and 4A molecular sieve showed poor adsorptive capacity. Additionally, enrichment coefficient (K) was also considered (Figure 2(b)), which was expressed as the ratio of the concentration (P (%)) of the



FIGURE 2: Comparison of adsorption efficiency and enrichment coefficient (*K*) of the 11 adsorbents on CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} , and C_5H_{12} . A: 4A; B: 3A; C: graphene; D: silica gel; E: GDX-101; F: Tenax; G: activated carbon 1; H: AlO; I: 5A; J: 13X; K: activated carbon 2.

same hydrocarbon between the extracted analyte and their corresponding compounds in the gas sample. The result also illustrated that the activated carbon has the best enrichment coefficient. Therefore, it indicated that the activated carbon was suitable for the extraction of hydrocarbons in natural gas, and the following tests were all using activated carbon as adsorbents.

3.2. Temperature Optimization

3.2.1. Adsorption Temperature. Comparing all the adsorption temperature in Figure 3(a), it can be seen that the adsorbent has the best adsorption efficiency at 20°C. The δ^{13} C of CH₄, C₂H₆, C₄H₁₀, and C₅H₁₂ varied in a wide range, for the obtained SD-1 were relatively larger than that of the uncertainties of the instrument ± 0.5‰ (CH₄ was 0.97, C₂H₆ was 0.53, i-C₄H₁₀ was 0.70, n-C₄H₁₀ was 0.79, i-C₅H₁₂ was 1.80, and n-C₅H₁₂ was 1.08), whereas C₃H₈ were quite different, with the SD-1 value of 0.40 (Table 3). Additionally, the δ^{13} C of CH₄, C₂H₆, i-C₄H₁₀, n-C₄H₁₀, and n-C₅H₁₂ were distributed as follows: CH₄: -43.8~-41.2‰, C₂H₆: -31.4~-30.0‰, i-C₄H₁₀: -26.3~-24.5‰, n-C₄H₁₀: -26.4~-24.7‰, i-C₅H₁₂: -27.3~-22.3‰, and n-C₅H₁₂: -24.0~-21.1‰ (Table 3).

3.2.2. Desorption Temperature. At different desorption temperature, the amount of hydrocarbon compounds released by thermal desorption varies greatly (Figure 3(b)). C_4H_{10} and C_5H_{12} could not be thermally desorbed when desorption temperature was below 200°C. Thermal desorption has better adsorption efficiency at the range of 250~350°C. It can be

observed that the standard deviations of the δ^{13} C distribution of CH₄~C₅H₁₂ vary in a relatively wide range if CH₄ was 0.44, C₂H₆ was 0.51, C₃H₈ was 0.46, i-C₄H₁₀ was 0.61, n-C₄H₁₀ was 0.44, i-C₅H₁₂ was 0.61, and n-C₅H₁₂ was 0.81, for their δ^{13} C ratios were at a relatively large range (Table 3). The δ^{13} C ratios of CH₄ were comprised between -42.7 and -41.1‰, C₂H₆ was distributed from -30.4 to -28.4‰, C₃H₈ was clustered between -28.3 and -27.0‰, i-C₄H₁₀ was ranged from -27.4 to -25.7‰, n-C₄H₁₀ was clustered between -27.1 and -26.0‰, i-C₅H₁₂ was located in the range of -25~-23.6‰, and n-C₅H₁₂ ratios were ranged from -25.1 to -22.8‰.

3.3. Time Optimization

3.3.1. Adsorption Time. As shown in Figure 3(c), the best enrichment efficiency of the adsorption time was between 2 and 5 minutes, and the adsorption efficiency of CH₄ remains a relatively stable level with adsorption time changing, but the change of $C_2H_6\sim C_5H_{12}$ was more obvious than that of CH₄, especially $C_2H_6\sim C_4H_{10}$. Unlike temperature, $\delta^{13}C$ of CH₄ $\sim C_5H_{12}$ had a relatively good reproducibility at different adsorption times, which means adsorption time has a relatively little effect on $\delta^{13}C$ ratios; the standard deviations of CH₄ $\sim C_5H_{12}$ were all with 0.41‰ (Table 3).

3.3.2. Desorption Time. C_5H_{12} could not be desorbed before 1.5 minutes, and the adsorption amount of CH_4 and C_5H_{12} remained in a stable level of the whole desorption process, whereas the changes of the amount of $C_2H_6 \sim C_4H_{10}$ were Geofluids



FIGURE 3: Peak areas at different experimental conditions: (a) the adsorption peak areas with adsorption temperatures ranging from 0 to 40° C; (b) the adsorption peak areas at different desorption temperatures from 250 to 350° C; (c) the adsorption peak areas at different adsorption temperatures from 250 to 350° C; (c) the adsorption peak areas at different adsorption temperatures areas at different desorption peak areas at different adsorption peak areas at different adsorption peak areas at different desorption temperatures.

TABLE 3: δ^{13} C ratios of standard natural gas sample and its SDs at different conditions.

Compound	SD-A	Ads temper	orption rature (°	C)	Deso temper	orption ature (°0	C)	Adsorpti	on time	(s)	Desorpti	on time	(s)
-		$M(n=\hat{6})$	SD-1	SD-2	M(n = 10)	SD-1	SD-2	M(n = 10)	SD-1	SD-2	$M \ (n=10)$	SD-1	SD-2
CH ₄	-41.84	-42.40	0.97	0.40	-41.88	0.44	0.03	-41.55	0.24	0.20	-41.52	0.24	0.23
C_2H_6	-29.45	-30.85	0.53	0.99	-29.78	0.57	0.23	-30.08	0.32	0.44	-29.75	0.80	0.21
C_3H_8	-26.70	-26.96	0.40	0.18	-27.99	0.46	0.91	-27.05	0.42	0.25	-27.62	0.41	0.65
$i-C_4H_{10}$	-26.48	-25.72	0.70	0.54	-27.03	0.61	0.39	-26.87	0.16	0.28	-21.31	0.33	3.66
$n-C_4H_{10}$	-25.58	-25.39	0.79	0.13	-25.37	0.44	0.15	-25.60	0.39	0.02	-23.98	0.36	1.13
$i-C_5H_{12}$	-24.78	-24.97	1.80	0.13	-20.13	0.61	3.29	-25.26	0.41	0.34	-17.25	0.28	5.32
$n-C_5H_{12}$	-23.12	-22.92	1.08	0.14	-19.71	0.81	2.41	-23.47	0.28	0.25	-16.9	0.44	4.40

SD-A: the average ratios of the standard natural gas sample, V-PDB, ‰; *M*: average ratios at different experimental conditions, V-PDB, ‰; SD-1: standard deviations obtained from average ratios at different experimental conditions; SD-2: standard deviations between STDA and *M*.

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Compound		Adsorp	ption te	mperat.	ure (°C)	_				Desorp	tion ter	nperatu	re (°C)							Adsorp	tion tin	ne (min)							De	orption	time (n	(uit			
I I I I I I I I I I I I I I I I I I I	-20	0	20	40	60	80	50	100	150	200	250	300	350	400	450	500	1	2	3	4	5	9	2	5	10	0.5		1.5	2	3	4	5	9	7	8
CH_4	-44	-42	-42	-41	-42	-43	-41	-41	-41	-41	-42	-41	-42	-41	-42	-43	-42	-41 -	41	42 -4	12	41	42	2 -4	2 -41	-45	-42	-42	-42	-42	-42	-42	-41	-42	41
C_2H_6	-31	-31	-30.0	-31	-31	-31	-30	-30	-30	-30	-30	-30	-30	-30	-30	-28	-30	-30 -	30	30 -0	30	30	30 -3		0 -30	-32	-30	-29	-29	-30	-30	-30	-29	-29	-30
C_3H_8	-27	-27	-27	-28	-27	-27	-28	-27	-28	-28	-28	-27	-28	-28	-28	-27	-28	-28 -	27	27 -2	56	26 -	27 -2		7 -27	-28	-28	-29	-27	-28	-28	-28	-28	-28	-28
$i-C_4H_{10}$	-25	-26	-26	-26	-25	-26	I	I	-26	-27	-27	-27	-27	-27	-26	-26	-27	- 27	27	27 -2	27	27	27 -2	5	7 -27	-27	-27	-27	-27	-27	-27	-27	-27	-27	-27
$n-C_4H_{10}$	-24.7	-25.0	-25.8	-26.4	-24.4	-26.0	I	-26.4	-26.0	-27.0	-26.9	-26.1	-27.0	-26.9 -	- 1.72	26.3 -	25.5 -	25.4 -2	6.2 -2	5.5 -2	5.0 -2	5.8 -2	5.2 -25	5.4 -25	.9 -26.	1 -25.	-25.4	-25.8	-25.1	-25.5	-25.1	-25.3	-25.1	-25.5	25.7
$i-C_5H_{12}$	-27	-22	-24	-25	-27	-24	I	I	I	-25	-25	-25	-25	-24	-24	-24	-25	-25 -	25	25 -2	25	25	25 -2	9	5 -26	Ι	Ι	-25	-25	-25	-26	-26	-25	-25	-25
$n-C_5H_{12}$	-22.4	-23.8	-23.5	-22.8	-21.1	-24.0	Ι	Ι	Ι	-24.9	-24.6	-23.1	-24.6	-24.6 -	-24.3 -	22.8 -	24.0 -:	23.9 -2	3.6 -2	3.3 -2	3.2 -2	3.2 -2	3.5 -23	3.5 -23	.3 -23.	2 —	Ι	-24.1	-24.9	-23.5	-24.9	-25.2	-24.8	-25.1 .	24.5
ATe: adso	rntio	n tem:	nerati	Tre: L	Te: d	esorni	hion to	emne	rature	: ATi:	adsor	rntion	time:	DTi:	desor	ntion	time																		

TABLE 4: δ^{13} C ratios of standard sample at different temperatures (°C) and times (min).

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larger, and the best adsorption time located in the interval of $2 \sim 5$ minutes (Figure 3(d)). Comparing the results obtained by adsorption time, it can be seen that except for C_2H_6 (SD-1 was 0.80), the reproducibility of the measurements of 10 desorption times is also satisfied with the uncertainties of the instrument, with the standard deviations all within 0.44‰ (Table 3).

4. Discussion

4.1. Determination of Optimization Conditions. The balance of trace hydrocarbon compounds between adsorbents is critical to optimal condition [26, 27]. Thermal dynamic conditions such as temperature and time are important factors affecting the adsorption efficiency. As temperature increases, both the diffusion ability of the molecules and relative motion between molecules increase; meanwhile, the adsorption rate of adsorbents is faster [20, 26-28]. However, an increase in temperature causes the lower partition coefficient of compounds between the matrix and the adsorbent, thus limiting the amount of the concentrated compound [20, 28]. It is obvious that the SD-1 values of adsorption temperature (0.53~1.80‰, except for C₃H₈) and desorption temperature (CH₄: 0.44, C₂H₆: 0.57, C₃H₈: 0.46, C₄H₁₀: 0.61, C₄H10: 0.44, C₅H₁₂: 0.61, and C₅H₁₂:0.81) vary greatly, and almost all the standard deviation values are beyond the limit uncertainty of instrument 0.5‰ (Table 3). Thus, this conditional test provided compelling evidence that δ^{13} C exhibits a considerable influence on isotopic fractionations. Select temperature from Figures 3(a) and 3(b) as follows: 20°C for adsorption temperature and 300°C for desorption temperature, and compare the δ^{13} C with the average ratios of the standard natural gas sample (Tables 3 and 4), the obtained results are all within 0.47‰ (within 0.50‰). That is, the selected temperatures show little effect on isotopic fractionations, and they can be used as efficiency temperature.

Similarly, equilibrium time is also an important condition that affects the extraction efficiency [28, 29]. Though many researchers may have an empirical understanding of these impacts, there is little explicit clear experiment [20, 30]. The extraction amounts of hydrocarbons remain a relatively stable level after reaching equilibrium, whereas a large change appeared before that state. Different from temperature, except for 0.80‰ of C_2H_6 obtained from desorption time, other SD-1 values of adsorption time and desorption time are all within 0.44‰, which means time may have smaller effects on isotopic fractionations. Additionally, choose the maximum extraction efficiency time to estimate the effect on isotope fractionation, all obtained standard deviations are within 0.5‰ (Figures 3(c) and 3(d)).

The optimized experimental conditions are determined as follows: adsorb the sample at 20°C for 3 minutes and then desorb it at 300°C for 3 minutes. The obtained results of δ^{13} C values are in good agreement with the δ^{13} C ratios of direct injection (original standard natural gas, without helium dilution) and SPME (Figure 4). The δ^{13} C values obtained by these three methods are in good agreement without obvious fractionations (the standard deviations between DI and SSPE are as follows: ±0.15‰ for CH₄, ±0.14‰ for



FIGURE 4: Validation of SSPE. DI: direct injection for original standard natural gas sample; SPME: solid phase microextraction for diluted standard natural gas; SSPE: syringe solid phase for diluted standard natural gas.

 C_2H_6 , ±0.19‰ for C_3H_8 , ±0.03‰ for i- C_4H_{10} , ±0.19‰ for n- C_4H_{10} , ±0.49‰ for i- C_5H_{12} , and ±0.45‰ for n- C_5H_{12}). Therefore, this method is a reliable method for trace hydrocarbon preconcentration.

4.2. Geological Sample Verification. After determining the optimization conditions, geological samples are applied to verify the efficiency of SSPE technique, and chromatograms of a natural gas sample obtained by DI, SPME, and SSPE are detected and identified (Figure 5, Table 5). Simultaneously, similar experiments are carried out with SPME technique, and their peak intensities show that the adsorption efficiency of SSPE is higher than SPME (Figures 5(b) and 5(c)). From data given in Table 4, it can be seen that the δ^{13} C values are all within a reasonable range without carbon isotope fractionation (SD values are all within 0.48), and the intensity of each hydrocarbon obtained by the SSPE method is higher than DI and SPME with the highest intensity of 30000 mV (intensities of DI and SPME are all lower than 2000 mV). Therefore, comparing these values obtained from DI, SPME, and SSPE, it is found that this established SSPE method is reliable for carbon isotope analysis.

4.3. Legacy Issues and Future Prospects. This study facilitates in trace hydrocarbons in natural gas where some barriers and baffles restrict its measurement [25]. For instance, isotopic fractionations appeared obviously with a high temperature (e.g., higher than 350°C), but the mechanism still remains to be solved. So, further insight from this problem needs to be followed up. In addition, considering that the whole sample preconcentration process is completely by manual operation, it is meaningful to expect future improvements for this technique. By optimizing the automation of SSPE technique, better accuracy and precision can be obtained. Additionally,



FIGURE 5: Geological sample analysis of DI, SPME, and SSPE: (a) direct injection of $30 \,\mu$ L natural gas sample; (b) SSPE extracted for 30 minutes; (c) SSPE extracted for 3 minutes at 20°C and then desorbed for 3 minutes at 300°C. 1: CH₄; 2: C₂H₆; 3-1: C₃H₆; 3: C₃H₈; 4-1: i-C₄H₁₀; 4-2: C₄H₈; 4: n-C₄H₁₀; 5-1: i-C₄H₁₀; 5-2: C₅H₁₀; 5: C₅H₁₂; 6-1: i-C₄H₁₀; 6: C₆H₁₄; 7: C₇H₁₆.

TABLE 5: δ^{13} C ratios (‰), S (mV), and SD (‰) obtained from DI, SPME, and SSPE.

Commenced	Direct	injection		Solid phase mi	croextraction	S	yringe solid ph	ase extraction
Compound	$\delta^{13}C$	Peak area	$\delta^{13}C$	Peak area	Standard deviation	$\delta^{13}C$	Peak area	Standard deviation
CH ₄	-48.20	1.02	_	_	_	-47.76	12.50	0.31
C_2H_6	-44.31	1.10	-44.82	0.24	0.36	-44.99	91.70	0.48
C_3H_8	-41.33	0.99	-42.86	0.28	1.08	-41.02	241.44	0.21
$i-C_4H_{10}$	—		-36.89	0.41	—	-39.42	35.90	—
$n-C_4H_{10}$	-37.28	0.91	-40.78	2.40	2.48	-36.84	170.06	0.31
i-C ₅ H ₁₂	—	—	-38.58	0.58	—	-37.95	9.37	—
$n-C_{5}H_{12}$	-35.42	0.43	-37.76	2.64	1.65	-35.15	29.54	0.19
$C_{6}H_{14}$	—		-34.58	3.56	—	-36.53	2.82	—

the conditions highlighted in this study can also be applied to simplified studies on source rocks, oilfield water, and other samples for further study.

5. Conclusions

The SSPE-GC/IRMS technique based on SPME-GC/IRMS was conducted on standard and geological samples with different adsorbents, temperatures, and times to determine the optimized experimental condition and achieve the analyzed trace hydrocarbon isotope. For this purpose, the content and δ^{13} C were analyzed. The following conclusions can be drawn:

- (1) Activated carbon was selected as the reliable adsorbents, and the optimized condition was determined; adsorb sample at 20°C for 3 minutes and then desorb it at 300°C for 3 minutes. The quality data such as precision and accuracy are acceptable for this technique with the uncertainty of the measurement lower than 0.48 in all cases of the natural gas, which is in accordance with the requirements of the GC-IR/MS
- (2) Apply a sample of Xiamaling formation, Sichuan Basin, for the detection of the SSPE technique; the results showed satisfying extraction efficiency
- (3) The lower detection limits for trace light hydrocarbons required by this technique are achieved and validated, and the requirement of uncertainty was also fulfilled for all hydrocarbons. More hydrocarbons, at the lower content level, than other previous methods proposed in the literature based on the use of SPME-GC-IR/MS have been detected. More hydrocarbons, at the lower content level, than other previous methods proposed in the literature based on the use of SPME-GC-IR/MS have been detected. This technique is quick and simple and increases the selectivity and sensitivity of analysis. And furthermore, the proposed technique is versatile, for it can be applied to detect other samples besides natural gas samples

Data Availability

The data used to support the findings of this study are available from the corresponding author and first author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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