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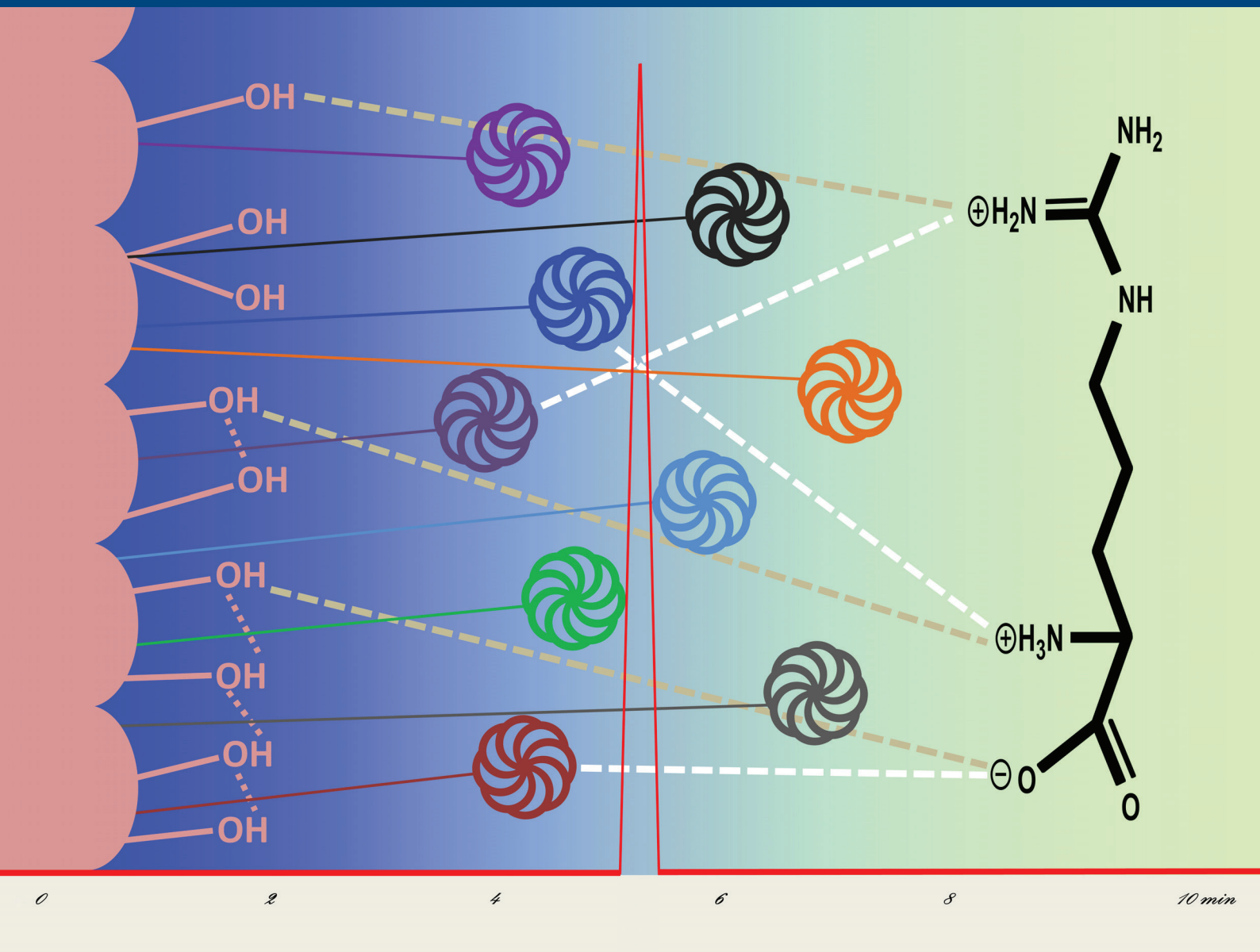

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SHORT COMMUNICATION

Simultaneous determination of compound-specific isotopic compositions of acyclic isoprenoids and *n*-alkanes in light crude oil

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Stable carbon and hydrogen isotope ratios of individual *n*-alkanes and acyclic isoprenoids are important tools in petroleum geochemistry. However, the analysis requires baseline separation and peak profiles using gas chromatography–isotope ratio mass spectrometry to obtain accurate compound-specific isotope data. Time-consuming isolation or purification is typically conducted to separate the compounds to avoid co-elution with other compounds or matrices in crude oils. We developed a simple gas chromatography separation method to simultaneously measure the compound-specific carbon or hydrogen isotope compositions of *n*-alkanes and acyclic isoprenoids. It was achieved by direct injection of the whole crude condensate and light oil or the saturated fractions of different types of crude oils using a 60 m DB-17ms column. This method simplifies the pre-treatment of compound-specific isotope analysis, saves manpower and time, and reduces the use of organic solvents to be more environmentally friendly.

KEYWORDS
acyclic isoprenoids, compound-specific isotopic analysis, gas chromatography– isotope ratio mass spectrometry, *n*-alkanes

1 | INTRODUCTION

Compound-specific carbon and hydrogen isotopic compositions of *n*-alkanes and acyclic isoprenoids, pristane (Pr) and phytane (Ph), from source rock extracts and crude oils provide valuable information for distinguishing crude oil classification, conducting oil–oil and oil–source rock correlations, and understanding in-reservoir processes that support field efforts in petroleum exploration and development [1–8]. Compound-specific carbon and hydrogen isotopic ratios of individual organic compounds can be determined by compound-specific isotope analysis (CSIA) using GC with isotope ratio mass spectrometry (IRMS). Reviews and multiple research papers have documented detailed information on analytical methods and the use of compound-specific carbon and hydrogen isotopic data [9–12].

In CSIA by GC-IRMS, baseline separation is essential for accurate and reproducible data [13]. However, *n*-alkanes often co-elute with branched/cyclic hydrocarbons (e.g., Pr and Ph) on conventional nonpolar columns (i.e., −1 or −5) [14]. Therefore, isolation of *n*-alkanes or acyclic isoprenoids is required before GC-IRMS analysis. Two steps are usually performed: (1) silica/alumina chromatography separation to obtain the saturated fraction and (2) molecular sieve or urea adduction techniques to isolate *n*-alkanes and branched/acyclic alkanes from saturated fractions [10, 11]. The entire process takes several hours and uses large amounts of organic solvents and

Article Related Abbreviations: CSIA, compound-specific isotope analysis; IRMS, isotope ratio mass spectrometry; Ph, phytane; Pr, pristane

hydrofluoric acid (HF) to collect *n*-alkanes [1]. Recent methods eliminate the use of HF and increase the recovery of hydrocarbons with low molecular weights [10, 15]. However, two analyses are needed to obtain the isotopic signatures of *n*-alkanes and acyclic isoprenoids; thus, the *n*-alkanes and branched/cyclic fractions are analyzed to obtain their carbon or hydrogen isotopic data.

Barrie et al. [12] designed a method to simultaneously obtain the compound-specific carbon ($\delta^{13}C$) signatures of *n*-alkanes (*n*-C_4 to *n*-C_{25+}) and acyclic isoprenoids via the direct injection of whole crude oil using a 50 m HP-PONA column. However, a method for the simultaneous determination of the compound-specific hydrogen (δD) isotopes of *n*-alkanes, Pr, and Ph in crude oil has not been reported. In this study, we developed an enhancement in peak resolution by separating *n*-alkanes, Pr, and Ph on a polar column instead of traditional nonpolar columns to simultaneously measure the compound-specific hydrogen isotopic signatures of the hydrocarbons directly from whole crude oils or their saturated fractions in a single GC-IRMS analysis.

2 | MATERIALS AND METHODS

2.1 | Chemicals and materials

GC residue analysis grade methanol, hexane, and dichloromethane (DCM) were purchased from CNW. Silica (200 mesh), alumina (100–200 mesh), and urea (AR, 99%) were obtained from Macklin. The silica was purified by extraction with DCM for 72 h and activated at 120°C for 2 h. The alumina was purified at 450°C for 4 h.

Four crude oil samples were used to test the separation method for the CSIA of $\delta^{13}C$ and δD (details are listed in Table S1). The saturated fractions were isolated from crude oil by silica/alumina LC using an *n*-hexane eluent. A subset of the saturated fractions was further treated with urea adducts to separate the *n*-alkanes and branched/cyclic alkanes.

2.2 | GC–isotope ratio MS analysis

The $\delta^{13}C$ and δD of the individual *n*-alkanes were obtained from whole crude oil (only for the condensate and light oil samples, P148 and PJB60, respectively) and the saturated fraction, and the *n*-alkane fraction was obtained from urea adduction. The Pr and Ph isotope signatures were obtained from whole crude oil (only for P148 and PJB60) and the saturated fraction, and the branched/cyclic fraction was obtained from urea adduction. Whole crude oils were injected directly without any organic solvent dilution, whereas the saturated fraction, *n*-alkanes, and branched/cyclic alkane fractions were diluted with hexane before GC-IRMS analysis.

The CSIA of $\delta^{13}C$ was performed on a GV isoprime IRMS instrument interfaced with an HP6890 GC via a GC5 combustion interface. The temperature of the combustion furnace was 850°C. The GC was fitted to a DB-17ms column (60 m × 0.25 mm × 0.25 μm) coated with 50% diphenyl and 50% dimethylpolysiloxane for the stationary phase. The initial GC oven temperature was set at 80°C (2 min), ramped to 310°C at 5°C/min, and held for 20 min. The CSIA of δD was performed on a Thermo Delta V ADVANTAGE interfaced with a Trace GC Ultra. The furnace temperature was set to 1420°C. The same column was used for the analysis. The GC oven was programmed from 80°C (2 min) to 220°C at 4°C/min and then ramped to 310°C at 5°C/min, with a final hold time of 25 min. Helium was used as the carrier gas at a constant flow rate of 1.0 and 1.2 ml/min for the CSIA of $\delta^{13}C$ and δD, respectively. The inlet temperature was set to 290°C. All samples or fractions were injected in split mode. One microliter of crude oil was injected at a split ratio of 50:1 and 10:1 to the CSIA of $\delta^{13}C$ and δD, respectively. The injection amounts of the other fractions were similar to those of the whole crude oil at different split ratios.

2.3 | Data quality

Carbon and hydrogen isotope values were certified with respect to Vienna Pee Dee Belemnite and Vienna Standard Mean Ocean Water isotope scales, respectively, and are reported in delta notation ($\delta^{13}C$ and δD, respectively). A standard composed of a mixture of *n*-alkanes with known compound-specific carbon and hydrogen isotopic values was measured to monitor the overall system precision and stability. A minimum of one standard analysis was conducted before and after each sample analysis; the absolute errors were controlled within ±0.5‰ for $\delta^{13}C$ and ±5.0‰ for δD analysis. Each sample or fraction was run at least three times, and the average value was reported (Tables S2 and S3). Repeatability was characterized by the SD of multiple measurements of the same fraction. Reproducibility was characterized by the RSD of the injections of different fractions of the same sample.

3 | RESULTS AND DISCUSSION

3.1 | Separation of *n*-alkanes and acyclic isoprenoids

The baseline separation of acyclic isoprenoids and *n*-alkanes was obtained using a DB-17ms column. There was no noticeable baseline bump for the condensate and

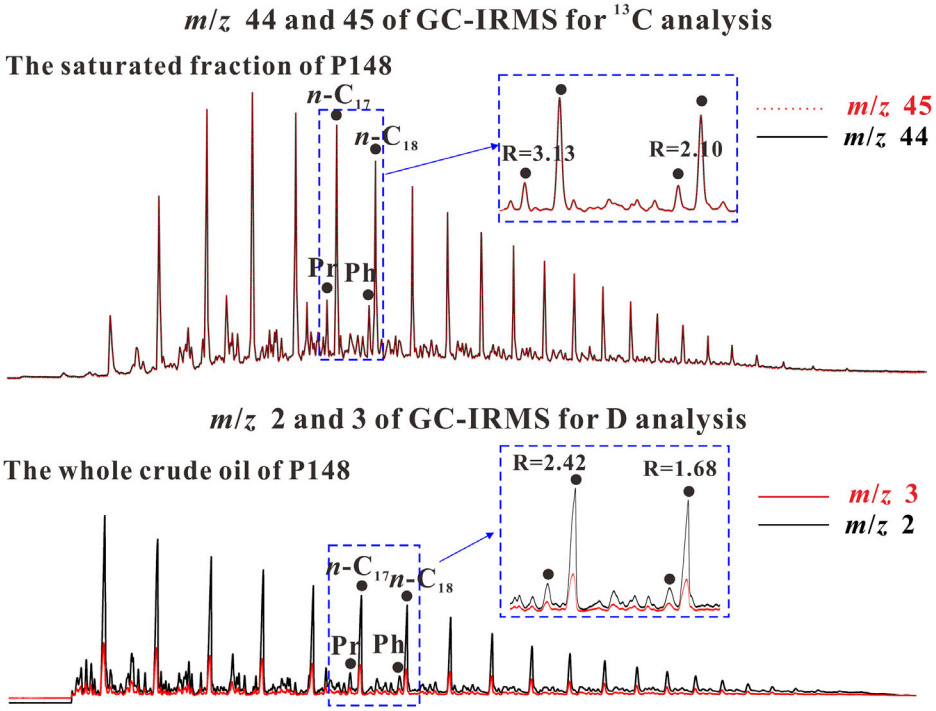

FIGURE 1 Example of GC-IRMS chromatograms of the saturated fraction of $\delta^{13}C$ analysis and the whole crude oil of δD (condensate, P148) analysis showing enhanced separation resolution between the Pr and *n*-C_{17} and Ph and *n*-C_{18}. Additional chromatograms are shown in the Supporting Information

light oils or the saturated fractions of the four samples (Figure 1 and Supporting Information). The resolution (R) [16] of compounds eluted between *n*-alkanes, including acyclic isoprenoids and other minor interfering components, is visible and baseline resolved. R, which was exemplified by P148, reached 3.13 for Pr and *n*-C_{17} on a DB-17ms column in the $\delta^{13}C$ analysis of the saturated fraction and 2.10 for Ph and *n*-C_{18}, respectively (Figure 1). For the D/H ratio analysis, larger injection volumes often cause imperfect chromatographic shapes, leading to inadequate resolution than the equivalent carbon isotope determination. However, R for Pr and *n*-C_{17} reached 2.42 and 1.68 for the Ph and *n*-C_{18} in the condensate (P148), respectively, obtaining the baseline separation. The perfectly normal chromatographic peak shapes of *n*-alkanes and acyclic isoprenoids (e.g., Pr and Ph) indicate a slight possibility of co-elution with other compounds (e.g., methylalkanes, cycloalkanes, and polycyclic biomarkers) in the crude oils and the saturated fractions (Figure 1), thus satisfying the requirements of GC-IRMS analysis.

3.2 | Compound-specific carbon isotopic compositions

The SD of compound-specific $\delta^{13}C$ values for multiple measurements in different fractions (including whole crude oil, saturated fractions, *n*-alkanes from urea adduction, and branch/cyclic hydrocarbons) varied within ±0.3‰ and ±0.7‰ (Table S2). Good repeatability indicates the stability of the GC-IRMS system and the designated methodology. The *n*-alkane data agreed well with all the individual sample components (Figure 2). The RSD of the fractions ranged from 0 to 0.58%, within the expected uncertainties. The $\delta^{13}C$ values of Pr and Ph determined directly from the whole oil and/or the saturated fraction were consistent with those from the branched/cyclic alkane fraction, with an RSD of less than 0.43%. The accuracy and precision were acceptable [10, 12].

3.3 | Compound-specific hydrogen isotopic compositions

The SD of compound-specific δD values in different fractions was generally within ±5.0‰ (Table S3) and within instrumental error, indicating the stability of the developed method. For each crude oil sample, the compound-specific δD values of *n*-alkanes and acyclic isoprenoids were similar among the different fractions (Figure 3). The RSD of the δD values of Pr and Ph was less than 7.8%. The δD values from the different fractions closely matched those of the individual compounds in the four different crude

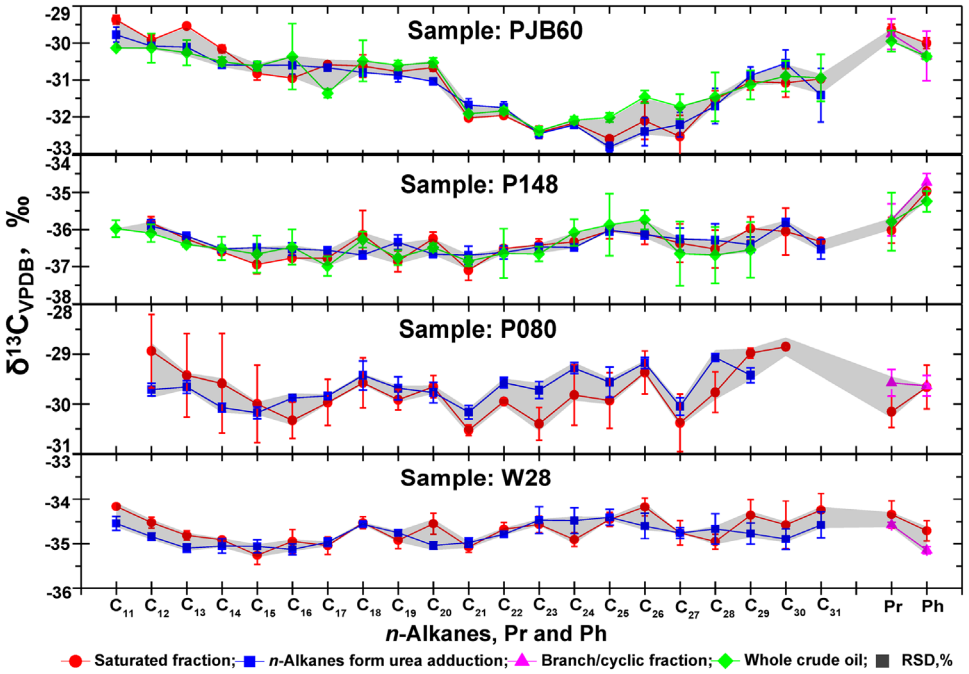

FIGURE 2 Comparison of the measured carbon isotope values obtained for *n*-alkanes, Pr, and Ph in whole crude oils (condensate and light oils) and the corresponding saturated, *n*-alkanes, and branched/cyclic fractions after treatment with urea adduction of the four oil samples. Error bars show the standard deviation for three injections. The shadow shows the RSD for individual compounds between different fractions

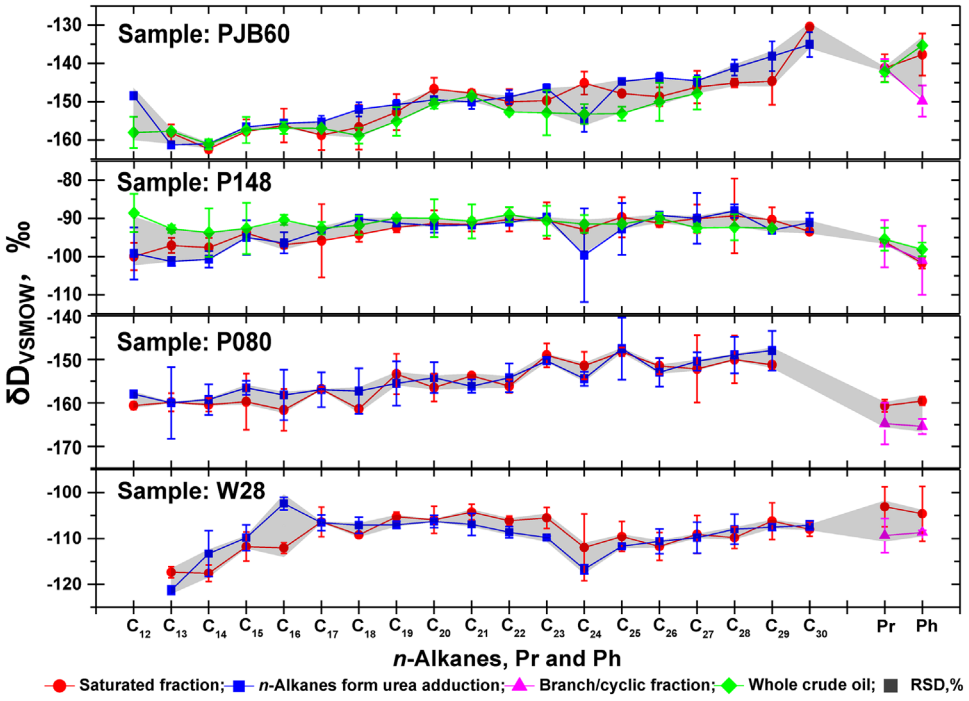

FIGURE 3 Comparison of measured hydrogen isotope values obtained for *n*-alkanes, Pr, and Ph in two whole crude oils (condensate and light oils) and the corresponding saturated, *n*-alkanes, and branched/cyclic fractions after treatment with urea adduction of the four oil samples

oil samples, with an RSD of approximately 0.6%. Most of *n*-alkanes, Pr, and Ph were within 0.3% RSD. The measured δD values of the direct hydrogen isotope analyses of whole crude oils and the saturated fractions agreed well with the corresponding *n*-alkane and branched/cyclic fractions after urea adduction treatment. Therefore, this method can also be adopted for the simultaneous determination of the compound-specific δD values of *n*-alkanes and acyclic isoprenoids in crude oil by a single GC-IRMS run of the whole crude oil (for condensate and light oil) or the saturated fraction.

3.4 | Methodology considerations

Direct injection of different types of untreated whole crude oils (including heavy oil) has been used for CSIA of $\delta^{13}C$ values [12]. However, in the method developed in this study, the normal and heavy oil samples are not directly injected. Black crude oil (including heavy and normal oils) contains a higher content of the resin and/or asphaltene fractions and higher boiling point compounds (e.g., NOS heteroatom compounds), which are generally difficult to vaporise completely at an injection temperature of approximately 300°C. Heteroatom compounds entering the GC column may not easily flow out during the sample analysis time, thus contaminating the inlet, column, or entire GC-IRMS system; reducing service life; and interfering with subsequent sample analysis. In addition, injecting a heavy crude oil sample using an injection needle is difficult. Therefore, we recommend that direct injection of untreated whole crude oil for CSIA be primarily applied to the condensate and light oil, which are not ideal for black oil. However, direct injection of the saturated fraction of CSIA is suitable for all types of crude oils.

4 | CONCLUDING REMARKS

In this study, we optimized the GC conditions by introducing a polar column (DB-17ms) to measure the compound-specific carbon and hydrogen isotope compositions of *n*-alkanes and acyclic isoprenoids in crude oils. For the condensate and light oil samples, the untreated whole crude oil injection simultaneously determined the $\delta^{13}C$ or δD values of *n*-alkanes, Pr, and Ph by GC-IRMS. The saturated fractions of different types of crude oils (including heavy oil) were used for direct injection to achieve this goal. The simultaneously measured compound-specific carbon and hydrogen isotopic ratios of *n*-alkanes, Pr, and Ph using this method were equivalent to those from traditional methods using purified *n*-alkane and isoprenoid fractions and were within instrument error. This method simplified the pre-treatment for carbon and hydrogen isotopic analyses and saved human resources and material resources, such as the fraction separation of silica/alumina chromatography or the use of complex and time-consuming molecular sieves or urea adduction techniques.

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CONFLICT OF INTEREST

The authors have declared no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that supports the finding of this study are available in the supplementary material of this article.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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