

Characterization of High-Molecular-Weight Paraffin in Ordovician Simpson Group Reservoirs (Oklahoma and Texas)—Implications for Advanced Recovery Technologies

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ABSTRACT.—Crude oils with high pour points and undesired flow properties have been documented in a variety of geologic provinces, representing a condition that is frequently attributed to paraffin or wax. Recent advances in analytical technologies allow this material to be separated into individual compounds by high-temperature gas chromatography (HTGC). Although the oil type that is indigenous to the Simpson Group petroleum system is characterized by a diminutive C_{20+} fraction, HTGC indicates the presence of compounds exceeding nC_{60} . As tradition dictates that the high-molecular-weight compounds are derived from higher plants (cuticular material), their presence in crude oils generated from marine sequences in the lower Paleozoic (Ordovician Simpson Group) requires an alternative origin (e.g., algae). Thus, paraffin from the alternative organic-matter sources (higher plant vs. algal) may respond to specific production chemicals.

INTRODUCTION

The chemical composition of crude oil is known to be highly complex, the main groups being aliphatic (saturate) and aromatic hydrocarbons plus resins and asphaltenes (Tissot and Welte, 1984). The aliphatic hydrocarbon fraction contains the normal (straight) and branched alkanes along with the cycloalkanes (naphthenes), whereas the aromatic hydrocarbon fraction contains pure aromatic compounds, cycloalkanoaromatic (naphthenoaromatic) molecules, and the simple cyclic sulfur compounds. The resin and asphaltene fractions have a similar composition, with their distinction based on solubility. Asphaltenes are generally precipitated from a crude oil in excess solvent, whereas the resins are separated from the saturate and aromatic fractions by liquid chromatography. Each compound class coexists in an equilibrium state within the crude-oil reservoir, although the production of petroleum can induce changes (e.g., decreased temperature and/or pressure) that may lead to the precipitation of solid components. Indeed, the component known as paraffin or paraffin wax is well known for its deleterious behavior. In strict chemical terms the paraffin fraction should be composed of straight chain aliphatic hydrocarbons (i.e., alkanes), although the industry practice usually includes a complex mixture of aliphatic compounds (normal, branched, and naphthenic alkanes). Information on the high-molecular-weight (HMW)

paraffin has been limited to bulk methods of characterization (e.g., direct-insertion-probe mass spectrometry), as the requirements for separating the individual compounds exceeded the limits of analytical technology. However, advances in capillary-column technology (Lipsky and Duffy, 1986a,b) and supercritical fluid chromatography (Hawthorne and Miller, 1987; Stadler and others, 1993) have enabled investigators to study this fraction directly. This paper provides a report of our progress in developing instrumentation to study the compounds present in the high-molecular-weight fraction by high-temperature gas chromatography (HTGC).

Gas chromatography (GC; Fig. 1) is commonly used to separate individual components in a complex mixture. The technique relies on the ability of the components to be separated within an elongated tube (column) by differential partitioning between two phases: a stationary liquid phase and a mobile gas phase. Several types of columns are available for use in GC analysis, but the one used in this study has a capillary design (<0.35 mm diameter). The stationary phase in this type of column is a thin coating on the inner surface of the tube. The column is mounted in an oven with one end of the column attached to an inlet while the other end is connected to a detector. The column is continuously swept with the mobile gas phase. The mixture is introduced to the column via the inlet, and separation occurs

Dahdah, N. F.; and Wavrek, D. A., 1997, Characterization of high-molecular-weight paraffin in Ordovician Simpson Group reservoirs (Oklahoma and Texas)—implications for advanced recovery technologies, in Johnson, K. S. (ed.), Simpson and Viola Groups in the southern Midcontinent, 1994 symposium: Oklahoma Geological Survey Circular 99, p. 203–208.

as individual molecules of each solute are swept toward the detector as they enter the moving stream of carrier gas after desorption from the stationary phase. Thus, the time that a solute spends in the column is dependent on the ratio of time spent in the mobile phase versus the stationary phase, a property that is a function of the vapor pressure exerted by the individual component at a given temperature. The column is mounted in an oven, where the temperature can be isothermal or programmed to aid in the separation of the less volatile components. The abundance of each component is recorded with a detector (e.g., flame ionization detection or FID) and presented as a function of time (Fig. 2). The basic system can be modified for specific applications (Freeman, 1981; Jennings, 1987; Jennings and Rapp, 1983).

Conventional GC analysis of crude oils provides data on components containing up to 35 carbons (C_{35}). This type of analysis is widely used to screen and correlate samples, because it provides information on biogenic

source input, diagenetic environment, and secondary alteration processes. The former items are useful to differentiate individual petroleum systems in the region (Wavrek, 1992; Wavrek and others, 1997), and the latter is essential for evaluating secondary alteration mechanisms that can have an adverse affect on the quality of petroleum (e.g., biodegradation). This type of analysis provides a significant amount of information, but it does not provide information on the fraction that is believed to be responsible for paraffin wax deposits in reservoirs, oil-well equipment, and pipeline facilities. This is attributed to the fact that the temperature required to elute this fraction from the column has been greater than the stability range for a conventional stationary phase (325°C). Fortunately, recent advances in capillary-column technology (Lipsky and Duffy, 1986a,b; Dawes and Cumber, 1989) provided stationary phases that are stable at significantly higher temperatures (450°C), which allows compounds greater than C_{100} to elute from the column. Utilization of these phases has allowed novel applications in the emerging field of HTGC. In the course of developing this technology, it became apparent that the operating parameters needed to be refined. The results of this research are reported in this paper, along with practical examples from Simpson Group reservoirs in southern Oklahoma.

DEVELOPMENT OF TECHNIQUE

For an analytical method to gain acceptance in an industrial application, a reasonable level of accuracy and precision must be attained at a reasonable cost with readily available instrumentation. Proponents of the supercritical fluid chromatography (SFC) technology (Hawthorne and Miller, 1987; Smith and others, 1987; Stadler and others, 1993) cite advantages of this technique for analysis of samples containing organic components that lack sufficient thermal stability and/or volatility to be separated by conventional GC methods. Additional benefits of the SFC technology include the direct analysis of nonvolatile polar components (i.e., avoids derivatization) and a low carrier flow volume that allows direct coupling to a mass spectrometer (SFC-MS). However, we decided to pursue the HTGC technology on the basis of instrument availability, low operating cost, reliability, ease of operation, and chromatographic resolution. The latter is particularly important, as the focus of this research is investigation of the compositional variability of compounds in the HMW range. Specifically, it can be demonstrated that the composition of the paraffin fraction is dependent on the origin of the organic matter in the correlative source-rock facies (Carlson and others, 1993; Wavrek and Dahdah, 1995). An additional benefit of the HTGC technology is the

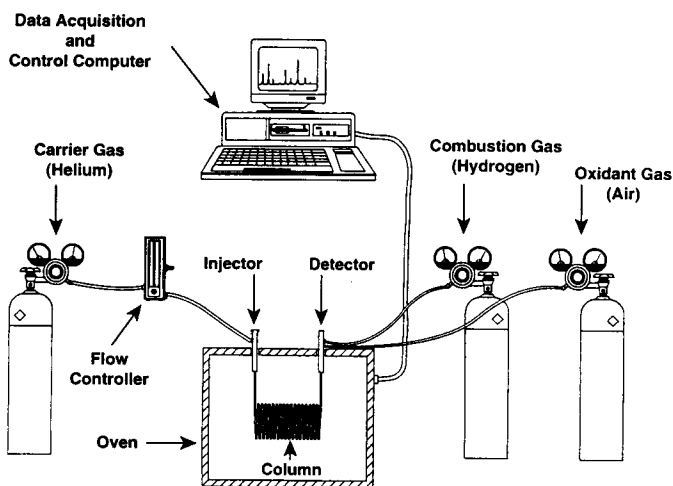


Figure 1. Basic components of gas-chromatograph (GC) instrumentation (from Tashiro and Clement, 1990).

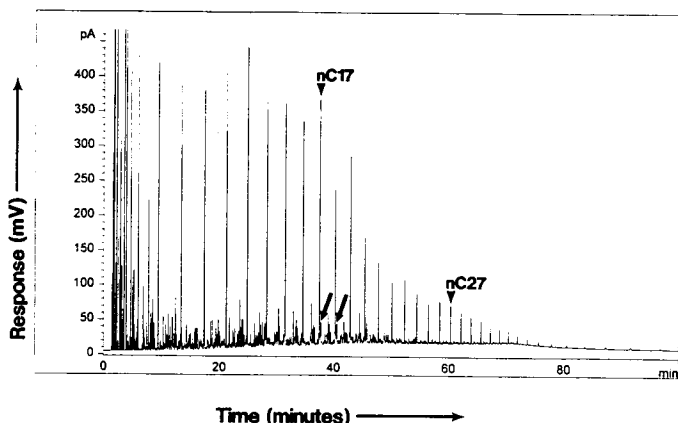


Figure 2. Conventional GC analysis of crude oil from Simpson Group petroleum system (TX060C) in the southern Midcontinent. Arrows identify pristane and phytane, respectively.

direct application to high-temperature gas chromatography-mass spectrometry (HTGC-MS; Fig. 3), which can be used in ion monitoring or in SCAN mode to provide critical data for the identification of individual peaks (Fig. 4). However, preliminary research indicated that potential problems with the type of inlet, the solvent system, and the oven program needed to be investigated. It was also established that the ability to provide quantitative results would be a necessary enhancement for the technique to be successfully applied to wax-related production problems.

The purpose of the inlet (Fig. 1) is to introduce the sample to the analytical column. With capillary columns, a split injection with flash vaporization is generally utilized, owing to the limited capacity of the system. This inlet is favored in many applications, but it is responsible for introducing analytical artifacts when HMW material is present (Fig. 5). In fact, the problem of introducing high boiling and thermally-labile substances to the gas chromatograph has been studied by a number of chemists (Desty, 1965; Grob and Grob, 1978; Hinshaw, 1985). This work determined that successful transfer could be

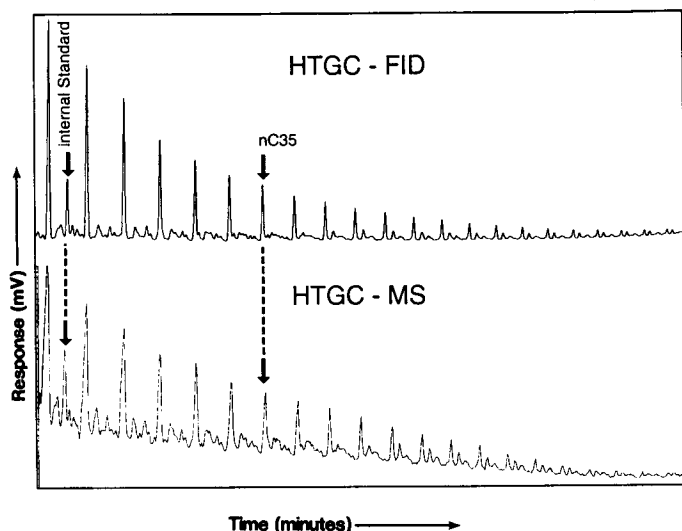


Figure 3. Illustration of the response from different HTGC detectors. The flame ionization detector (FID) is routinely used for monitoring the response of hydrocarbons eluting from the column, although the results can be directly compared to data obtained with a mass spectrometer (MS). The HTGC-MS data in this illustration are displayed as a total ion count (TIC).

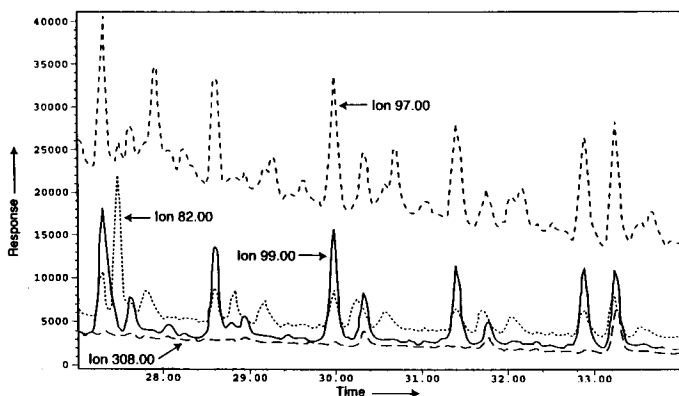


Figure 4. Illustration of the HTGC-MS data displayed as single ion monitoring (SIM) analysis to aid in the identification of individual peaks. The signal obtained from different mass-to-charge (m/z) ratios will show enhanced response from particular compounds: n -alkanes (m/z 99), n -alkylcyclohexanes (m/z 82), and methyl- n -alkylcyclohexanes (m/z 97). The m/z 308 trace is used to monitor for a parent mass (molecular weight of entire compound).

achieved with either the cool on-column or the temperature-programmed injection methods. The primary problem with the on-column technique is that residue from the whole oil or bitumen (resin or asphaltene) restricts the orifice and contributes to the rapid deterioration of column performance (Sinninghe Damste and de Leeuw, 1990). This problem was not encountered in this research, possibly because of the solvent system and maintenance program used. The solvent system developed for this HTGC application was an aliphatic:aromatic mixture consisting of nonane:toluene. The solvent system has the dual purpose of providing the samples with similar viscosity for consistent syringe ejection. The solvent system also introduces the internal standard at a concentration of 2,500 ppm. The aliphatic:aromatic solvent system was selected to provide solvating activity to a wide variety of crude-oil and bitumen samples. Perdeuterated triacontane ($nC_{30}D_{62}$) was selected as the internal standard on the basis of routine criteria (Lee and others, 1984). Additional hints for successful sample introduction include mild heating prior to injection ($40^{\circ}C$), along with a slight agitation. Finally, it was concluded that the use of a guard column was not necessary, as problems associated with the apparatus outweigh the potential benefits. The frequency for column maintenance was determined by monitoring chromatographic resolution; approximately one-half turn from the head of the column was generally removed at intervals commensurate with 30 injections. With this routine, it is established that excellent to good chromatographic resolution can be achieved for 100 samples oven programmed to $410^{\circ}C$, although this number decreases to 30 for samples analyzed at $450^{\circ}C$ (discussed below).

A variety of oven programs were evaluated for the HTGC application. The purpose of the oven program is to provide adequate thermal energy to volatilize (required for elution) the HMW compounds. Studies of paraffin from a worldwide sample bank indicate that an empirical relationship exists between paraffin-related production prob-

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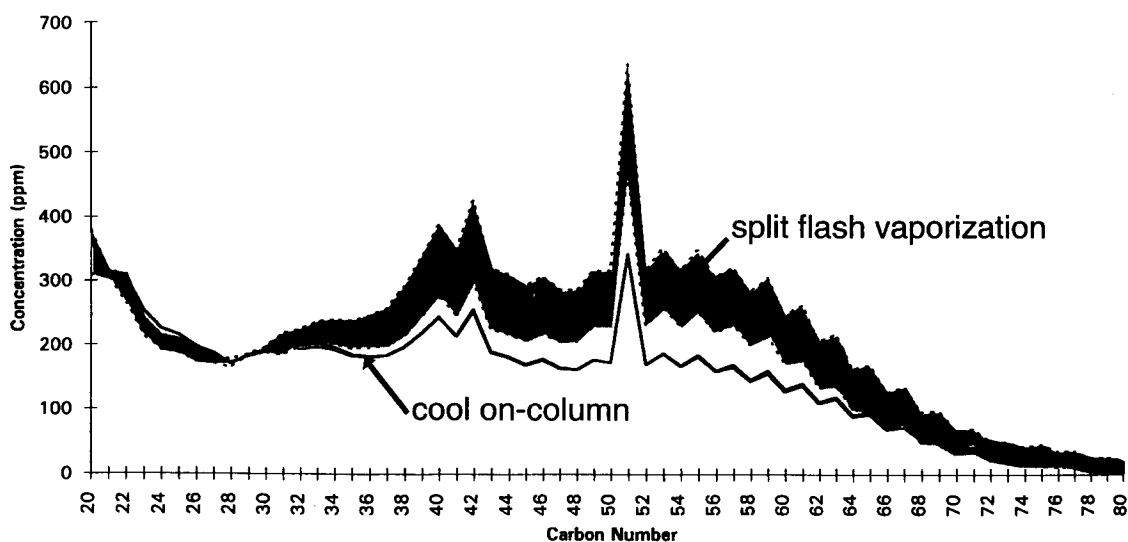


Figure 5. Comparison of the analytical precision obtained for two different injection methods. Quantitative results obtained from replicate analysis indicate significant variance with the split-mode injection, in comparison to the on-column technique.

lems and compounds in the range of C_{40} to C_{80} . Thus, an oven program was established to analyze this carbon-number range in less than 60 min (Fig. 6). This program provides excellent chromatographic resolution at minimal cost. In practice, the oven is programmed to 410°C , an analytical compromise that minimizes other potential problems with residual materials in the column. Byproducts formed from thermal decomposition have not been observed in analyses performed at 410°C , although research continues on this subject.

EXPERIMENTAL PROCEDURES

The instrument used in this HTGC study is a Hewlett-Packard 5890A gas chromatograph equipped with a flame ionization detector (GC-FID) and outfitted with a nonpolar Restek MXT-1 ($30\text{ m} \times 0.28\text{ mm} \times 0.1\text{ }\mu\text{m}$) capillary column. A cool on-column injection technique was used. The oven was programmed from 70°C to 410°C (11 min isothermal) at a ramp rate of $10^{\circ}\text{C}/\text{min}$. The total run time of 45 min allowed the elution of nC_{84} . Quantification of the HMW fraction was accomplished with perdeuterated triacontane ($nC_{30}D_{62}$ at 2,500 ppm) that was introduced as part of the solvent sample preparation.

RESULTS AND DISCUSSIONS

Crude oils with high pour points and undesired flow properties have been documented in a variety of geologic provinces, conditions that are frequently attributed to "paraffin or wax." Hedberg (1968) recog-

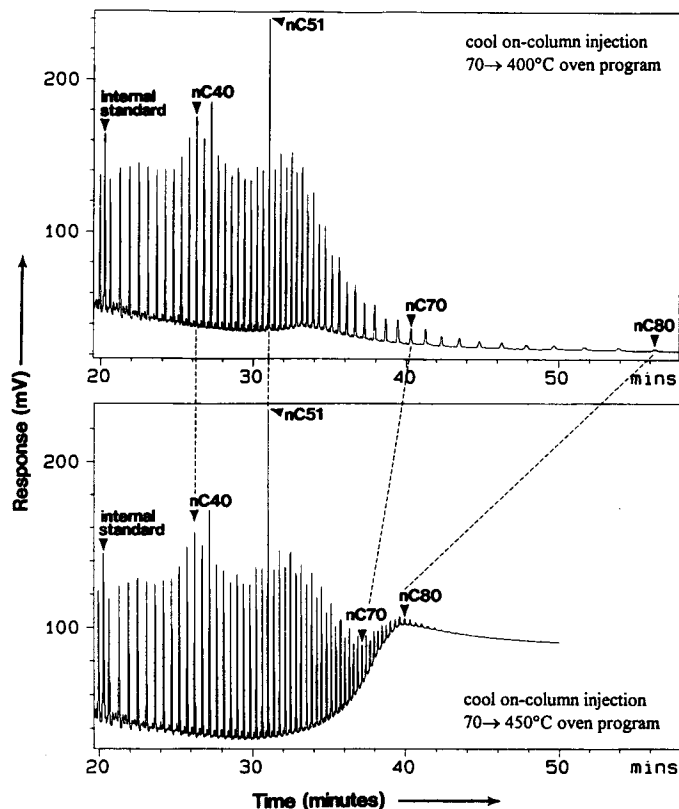


Figure 6. Comparison of chromatograms (HTGC) obtained with different oven programs. The $70^{\circ}\text{C} \rightarrow 400^{\circ}\text{C}$ program allows compounds responsible for paraffin-related production problems to be analyzed in less than 60 min. The $70^{\circ}\text{C} \rightarrow 450^{\circ}\text{C}$ program accomplishes this task in 40 min, but the higher temperature contributes to column degradation; the "hump" at the end of the trace is due to column bleed. This sample was collected as a stock-tank paraffin deposit.

TABLE 1.—OIL WELLS THAT PRODUCE FROM THE SIMPSON PETROLEUM SYSTEM

Code	Field	Operator	Well	Location	API well no.	Reservoir	Perf. (ft)	API gravity	Total sulfur	Nickel (ppm)	Vanadium (ppm)
OK097C	Ardmore SW	Triple Dee	SW Ardmore Unit	26-5S-1E		Tulip Creek	2100	37°	0.27%	6	10
OK208C	Sho-Vel-Tum	L. E. Jones	No. 1 Harley	24-2S-4W	35-137-22431	Oil Creek	7426-7454	42°	0.51%	1	2
OK286C	Ardmore SW	Mack	Marris Tank	36-5S-1E		McLish	2700	30°	0.27%	4	5
TX060C	Walnut Bend	ARCO	No. 1 McGeorge		42-097-00753	Oil Creek	8156-8160	46°	0.21%	3	5

nized a number of common features within the global occurrence of high-paraffin oils that led him to suggest a relationship with the organic matter from which the oil was derived, namely, an association with source-rock facies containing a significant component of terrigenous organic matter and/or organic matter derived from organisms indigenous to brackish-water columns. These observations remain valid, as the origin of the paraffin associated with oils derived from terrigenous source rocks is generally attributed to the cuticular coating of higher plants and/or the reworking of this material by microbial activity (Tissot and Welte, 1984; Tegelaar and others, 1989). However, the origin of paraffin in petroleum systems of lower Paleozoic marine sequences requires an alternative explanation.

The Middle Ordovician Simpson Group of the southern Midcontinent commonly contains oils with distinctive GC traits (Wavrek, 1992). These oils (Fig. 2) are dominated by *n*-alkanes with a strong odd-carbon preference in the C_{11} to C_{20} range and contain relatively minor amounts of nC_{20+} hydrocarbons. These oils display minor to trace amounts of isoprenoids and anomalously light carbon-isotope values. The *n*-alkylcyclohexanes and *n*-alkylbenzenes display a distinctive carbon-number preference, along with the methyl-*n*-alkylcyclohexanes (Burgess and Wavrek, 1993). These molecular traits have been correlated to source-rock facies in the Simpson Group and correspond to organic-matter input from the Ordovician alga *Gloeocapsomorpha prisca*. This organism has been studied in numerous Ordovician-age petroleum systems (Martin and others, 1963; Fowler and Douglas, 1984; Reed and others, 1986; Hoffmann and others, 1987; Longman and Palmer, 1987; Fowler, 1992; Burgess and Wavrek, 1993; Wavrek and others, 1997). Despite the diminutive C_{20+} fraction of this oil type, HTGC analysis indicates the presence of compounds exceeding nC_{60} (Fig. 7). Features identified in the HTGC that appear to be indigenous to this group of oils (Table 1) include enhanced nC_{41} , nC_{42} , and nC_{51} alkanes. The documentation of HMW *n*-alkanes in these oils is significant, since an origin from higher plant debris and/or nonmarine algae can be ruled out, which is in contrast to the routine sources of these compounds (Tissot and Welte, 1984; Tegelaar and others, 1989). Thus, an origin of these compounds from marine algae, possibly reworked by microbes, is likely. The application is that different organic-matter sources may create waxes that respond to

different production chemicals (e.g., flow and crystal modifiers, viscosity improvers, pour-point depressants).

CONCLUSIONS

Significant advances in the control of paraffin deposition can be anticipated when HTGC is used to quantitatively determine the distribution of the HMW components (C_{40+}) in crude oils. The results suggest that a universal solution to the problem is unlikely, since these compounds can originate from a variety of sources. In particular, tradition dictates that the HMW compounds are associated with higher plants (cuticular material); thus, their presence in crude oils generated from the lower Paleozoic (Ordovician Simpson Group) requires an alternative origin (e.g., marine algae). Indeed, this suggests that production chemicals may be developed for specific types of paraffin-related production problems. The versatility of the analytical technique is increased by adapting the technology to readily available instruments.

ACKNOWLEDGMENTS

We wish to thank W. H. Kanes of the Earth Sciences and Resources Institute at the University of Utah and the University of South Carolina for providing the opportunity of pursuing this fundamental research. The authors are indebted to the operators who shared their expertise and samples (ARCO, Mack, L. E. Jones, K. Walker, Triple Dee) that make these studies possible. J. B. Fisher at Amoco Production Research is thanked for the elemental analyses. David Curtiss (USC-ESRI) is also thanked for his assistance in completing this research.

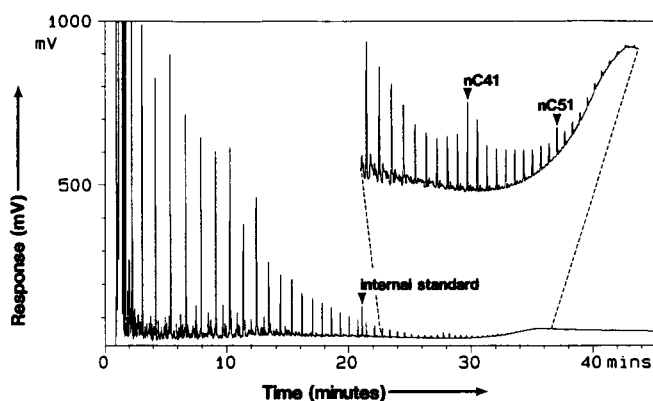


Figure 7. HTGC analysis of crude oil (TX060C) from Simpson Group petroleum system in the southern Midcontinent. Note that the high-molecular-weight (HMW) alkanes extend beyond nC_{60} and that nC_{41} , nC_{42} , and nC_{51} display an enhanced abundance.

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