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Visible–Near-Infrared Spectroscopy by Downhole Fluid Analysis Coupled with Comprehensive Two-Dimensional Gas Chromatography To Address Oil Reservoir Complexity

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One of the largest problems facing the oil industry today is to characterize fluid and architectural complexities of oil reservoirs. This applies particularly in the development of offshore fields where reservoir reconnaissance is impeded by the high costs of wells, often exceeding $100 million. As such, new methods are being developed to address these complexities. Downhole fluid analysis (DFA) is a new method of in-situ fluid characterization used to understand the heterogeneous distributions of hydrocarbon fluids in the reservoir and to identify which crude oils merit subsequent analysis in the laboratory. Comprehensive two-dimensional gas chromatography (GC×GC) is a powerful new method to analyze complex hydrocarbon mixtures such as crude oils and, especially when combined with mass spectroscopy, to elucidate explicit chemical structures. Here, we explore the protocol of DFA coupled with GC×GC to address reservoir complexities.

Introduction

Reservoir and Downhole Fluid Analysis. The characterization of oil reservoirs is exceedingly difficult and represents one of the largest uncertainties faced by the oil industry today.[1] The problem is that the physics methods used to interrogate oil reservoirs are incommensurate with important reservoir properties. The structure of hydraulic units or compartments, which must be penetrated by a well to drain, determines to a large extent the economics of oil field development. Large-scale structural features of oil reservoirs are obtained from seismic surveys. However, hydraulically sealing barriers can be quite thin and are often invisible to seismic response. High-resolution, in-situ borehole measurements are useful for delineating lithology and petrophysical parameters. These measurements are often made immediately after drilling is completed by lowering an instrument package on a cable or "wireline" that is capable of measuring electrical, nuclear, sonic, nuclear magnetic resonance, and optical properties.[2] However, high-resolution, petrophysical measurements only provide limited depth of investigation[2] and thus are of limited utility for resolving compartment structure. Furthermore, sealing barriers can be invisible to conventional wireline logging yet can hold off 2000 psi pressure differential resulting from production.[3]

Because of the difficulties confronting reservoir characterization, the best method of predicting a well's oil and gas production is to perform such measurements in nearby wells over long periods of time.[1] Indeed, "history matching" production vs prediction is the best way to constrain reservoir models.[1] This method is only employed when the oil well and facilities costs are low. History matching becomes problematic for fields located under deep water. The oil well and facilities that must be in place before the first oil is achieved can cost billions of dollars. If history matching predicts a massive shortfall in production (which is routine[1]), it may be too late to alter the multibillion dollar investment. Furthermore, according to the best estimates of the United States Geologic Survey (USGS), one half of the world's undiscovered oil is offshore.[4] Much of this oil is found outside the Middle East, and the exploitation of these resources, which are distributed globally, might help ease geopolitical tensions. Subsequently, new methods must be developed to exploit this oil in an efficient manner.

The difficulties of elucidating reservoir complexities led to two heuristics, both of which have outlived their utility. It had been commonly assumed that oil fields consist of giant compartments and, second, that the reservoir hydrocarbons in these compartments were to a large degree in equilibrium. Moreover, it had been presumed that equilibrium would normally produce a homogeneous hydrocarbon composition throughout the reservoir. It is now understood that oil fields are often comprised of smaller compartments filled with heterogeneous hydrocarbons.[3,5] These former heuristics resulted in large measure from technological limitations associated with efficient reservoir characterization. Methods used to distinguish compositional differences between fluid hydrocarbons were inadequate thereby resulting in very limited sample acquisition from oil wells for subsequent laboratory analysis. This limitation

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coupled with the high cost of sample acquisition led to gross undersampling of crude oils in the oil column. Without proof of fluid complexities, assumptions of simple fluid distributions prevailed.

Even in equilibrium situations, large hydrocarbon concentration gradients can exist.[6] In particular, large equilibrium gradients can be produced when there is a small difference between the reservoir pressure and the fluid saturation pressure (at reservoir temperature) and, furthermore, when there is a small difference between the saturation pressure and the critical pressure.[6] For example, field and laboratory studies indicate that compressible fluids can yield large gradients.[7] In addition, a recent reservoir study showed that large asphaltene[8] concentration gradients can exist by virtue of asphaltene negative buoyancy coupled with the colloidal dispersion of asphaltenes in crude oil.[9] The colloidal nature of asphaltenes in crude oil[9] was shown to match the colloidal nature of asphaltenes in toluene.[10–13] Additionally, reservoir fluids are often not in equilibrium. For example, biodegradation can cause a steady state condition to exist in the oil column. Microbes living in the formation pore water can preferentially consume n-alkanes at the oil–water interface, resulting in an amplification of higher molecular weight compounds.[14,15] The resulting large-scale variations in viscosity significantly impact production.[14] Current reservoir charging can give rise to huge, nonequilibrium gradients and even change the nature of the reservoir fluid.[16] For example, a massive influx of biogenic methane into a reservoir filled with medium-weight oil has created a highly variable, nonequilibrium supercritical fluid in the reservoir.[16] Other sources of disequilibrium include multiple charges, water washing, and leaky seals. Even though hydrocarbons have been present in reservoirs for geologic time, diffusional mixing is very slow, and other dynamic processes that affect fluid disequilibrium can dominate.[17] It is well known that the chemistry of the fluid hydrocarbons produced in kerogen catagenesis changes considerably as a function of time and temperature.[18] The most common expression of this is the generation of much lighter hydrocarbons during late stages of catagenesis.[18] It is only now being understood that these different stages of kerogen cracking release hydrocarbons into a reservoir *without* mixing and that large variations in hydrocarbon composition can remain throughout long stretches of geologic time.[19] Although hydrocarbon disequilibrium complicates reservoir characterization, understanding the chemical and physical controls that produce, maintain, and transform fluid disequilibrium in the reservoir will enable development of novel, improved strategies for modeling reservoir architecture.

Technological limitations that lead to undersampling of oil wells have changed dramatically. Downhole fluid analysis (DFA) enables characterization of fluid complexities in a column at small marginal charge.[3,5,9,16,20–22] Consequently, the oil column can now be analyzed at many points, and compositional grading can be identified. In addition, discontinuous changes in fluid properties and, in many cases, the existence of higher density fluids higher in the column identify flow barriers and thus compartments.[3,5] In particular, DFA as currently configured analyzes the light ends of the oil, methane, other hydrocarbon gases, and hydrocarbon liquids via NIR spectroscopy.[23,24] In addition, asphaltene content of a crude oil is roughly correlated with crude oil coloration, particularly for crude oils in a single oil column. Measurement of crude oil color in the visible and near-infrared[25] is an important DFA measurement that characterizes asphaltene concentration variations.[9]

With this much improved reconnaissance of the variation of hydrocarbon properties in the reservoir, it is now an opportune time to revisit chemical analysis methods utilized by laboratories. Recently, a study was performed to relate DFA with ultrahigh-resolution mass spectroscopy.[26] This study showed that oils from closely spaced but noncommunicating oil compartments were very similar in heavy end chemistry even though the concentration of the heavy ends varied by up to a factor of 3 for these oils. Nevertheless, there were subtle differences indicated particularly with regard to organic acids, which might be associated with differing biodegradation.[27] In mass spectroscopy, the ionization method electrospray ionization (ESI) is very soft and can place large molecules in the vapor phase. However, ESI cannot ionize alkanes which are obviously a very

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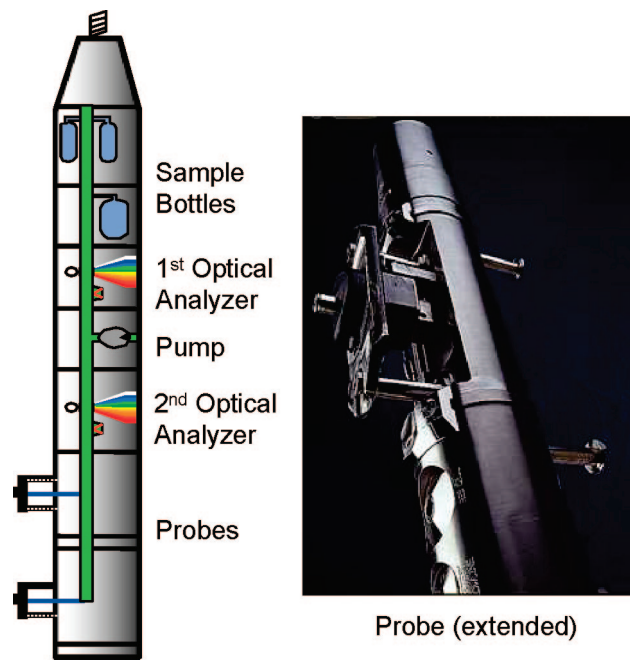
Figure 1. Schematic diagram of a sampling tool which acquires crude oil samples and performs spectral analysis on these samples for chemical analysis in situ in the oil well. This tool is used in so-called "open hole" just after the well is drilled and prior to placement of steel casing in the well. A photograph of the "probe" or stout tube is shown which is pressed firmly against the borehole wall to make hydraulic communication with permeable zones in the oil well to extract formation fluids.

important class of compounds in crude oils. It is necessary to link DFA with advanced methods of analysis of alkanes.

Comprehensive Two-Dimensional Gas Chromatography (GC×GC). Gas chromatography (GC) is a powerful tool that facilitates the separation of complex molecular mixtures for compound identification and quantitation. GC uses a single capillary column packed with a stationary phase that differentially adsorb compounds based on the specific volatility a compound has to the stationary phase. GC has been particularly useful for analyzing the molecular composition of crude oils. The addition of a second dimension column to the GC vastly enhances the number of compounds that can be observed and identified. The second dimension column is typically configured to separate compounds eluting from the first column by the polarity of the compounds. The GC×GC system links the first- and second-dimension columns by temporally freezing the effluent as it is leaving the first dimension column and then reinjects the effluent into the second dimension column using a modulator. The modulator separates the mixture into small packets of analyte that are sequentially injected into the second dimension column. A fast elution through the second dimension column sharpens peaks and increases the signal-to-noise ratio by a factor of 10–100 compared to traditional gas chromatography. Coupling the GC×GC to a flame ionization detector
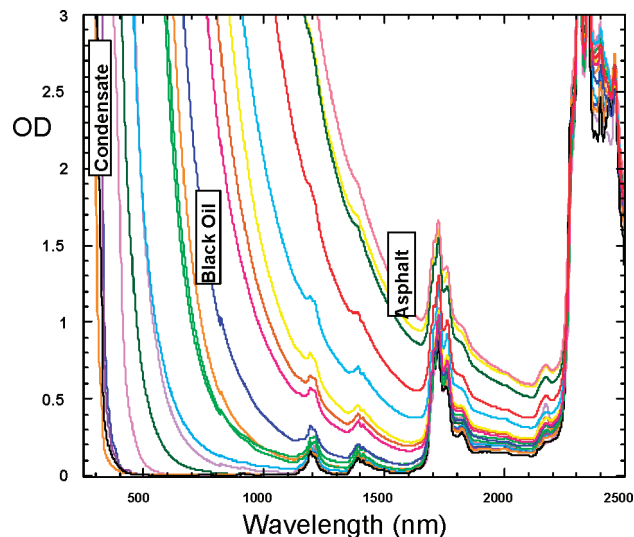
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Figure 2. Visible–near-infrared absorption spectra for crude oils under laboratory conditions. The "coloration" is due to electronic absorption of aromatic molecules while the NIR overtones are dominated by saturated compounds.
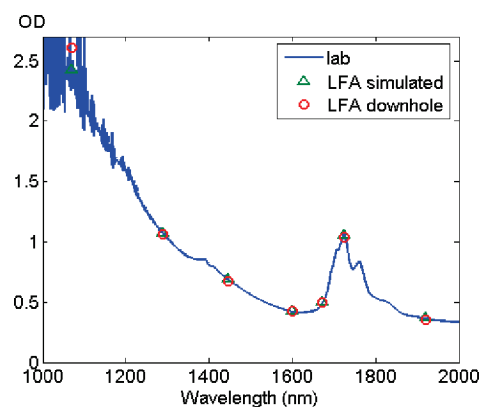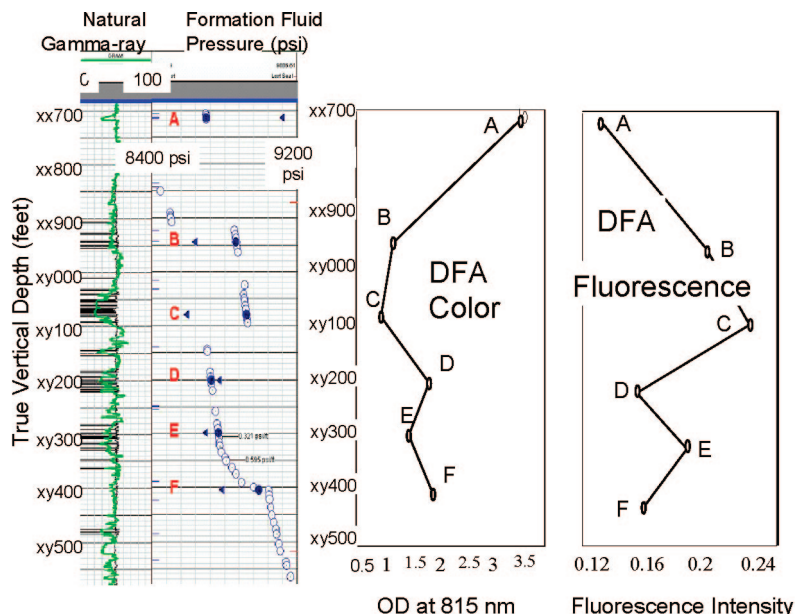

Figure 3. Chain of custody for oil field samples. The comparison of the filter spectrometer results obtained in situ in the oil well compares favorably with the corresponding continuous NIR spectrum of the same sample in the laboratory. This comparison establishes that the laboratory sample is valid and with known provenance.

(GC×GC-FID), one can assume that all hydrocarbons have the same response factor. Hence, estimating the content of each hydrocarbon (or groups of hydrocarbons) in an oil sample is straightforward and does not require elaborate calibration curves. When using GC×GC-TOFMS (time-of-flight mass spectroscopy), the increased chromatographic resolution allows for little or no background and much cleaner mass spectra of unknown compounds, which, in turn, can be used to identify specific chemical structures.

Within the second dimension of a GC×GC chromatogram, saturated hydrocarbons elute earliest and multi-ring aromatic hydrocarbons elute the latest. The added separation capacity provides three powerful tools for (geo)chemical analysis of petroleum hydrocarbons. First, saturated and aromatic compounds can be simultaneously analyzed without an additional liquid chromatographic separation that traditionally marks a necessary protocol. This simplification not only reduces processing time and cost but also ensures more accurate analysis of hydrocarbon mixtures by ensuring identical GC conditions. Second, such separations allow the calculation of the saturate to aromatic ratio for the whole sample or as a function of an n-alkane window (such as C_{16} to C_{17}, etc.). Third, compounds in the same class will have a similar elution pattern which results

Figure 4. Left: a log from an oil well in which six oil samples were collected. True vertical depth is plotted on the *y*-axis (with an offset to prevent identification of the well). The natural *γ*-ray plot shows high signal levels in shales (which are not permeable) and a decrease is signal level in zones with higher levels of sandstone. The six sandstones are labeled A through F. Whether the shale barriers are or are not sealing is of major concern to establish the size of the compartments holding crude oil. Formation pressure is plotted. Large pressure changes, for instance between zones C and D, clearly show lack of flow connectivity. Pressure analysis for some other zones is less compelling.

in a predictable elution order of a compound class. This provides a very powerful predictive tool for the identification of new compounds and for the determination of whether multiple compounds belong to one or more compound classes.

In this study, we analyze a series of crude oils which are of known provenance. In particular, these derive from a stacked shale/sand sequence, deepwater Gulf of Mexico. DFA and in-situ pressure measurements show that the corresponding sand bodies are not in flow communication. Furthermore, DFA shows that these crude oils possess gross compositional differences; the concentrations of heavy ends differ by up to a factor of 3. GC×GC-FID and GC×GC-TOFMS are performed on these crude oils. The laboratory and downhole chemical analyses are placed into the reservoir perspective, and the potential of this methodology to reveal reservoir and fluid complexities is discussed. We note that large-scale variations in gross compositional differences which are reflected by only subtle chemical distinctions are often the norm in reservoir fluids.[28] Consequently, general chemical analysis methods of DFA need to be linked with exquisite chemical analysis methods in the laboratory.

Experimental Section

Downhole fluid analysis (DFA) measurements are performed on the MDT (module formation dynamics tester) platform.[29] Shortly after a well (or section of a well) is drilled, but prior to completing the well with steel casing, it is often desirable to perform a series of "open hole" measurements to delineate completion parameters and production strategies. At this stage the well is filled with drilling "mud" to maintain pressure among other purposes. Formation fluid

samples obtained in open hole are acquired with the MDT. The MDT is a complex instrument package that is lowered into the well on a cable or "wireline". The MDT consists of many components or modules such as pumps, fluid analyzers, and sample bottles. The MDT has one or more probe modules which establish hydraulic communication with permeable formations using a stout, steel tube (cf. Figure 1). This tube is pressed against the formation wall with great force creating a seal. The MDT has onboard pumps which can lower the pressure in the flowline enabling extraction of fluids from the (permeable) formation.

These samples are analyzed using various downhole analyzers. A common analyzer, the LFA (live fluid analyzer), utilizes visible–near-infrared spectroscopy to analyze the crude oils providing the gas–oil ratio and crude oil coloration which is related to the concentration of asphaltenes.[9] Figure 2 shows a series of visible–NIR spectra for various dead crude oils. A dead crude oil is at laboratory conditions so its gas has been lost. In contrast, live crude oils have the same composition as in the reservoir; thus, they have their (dissolved) gas fraction. The spectra in Figure 2 consist of a broad sloping absorption which increases at shorter wavelength. This absorption is due to electronic transitions of large polycyclic aromatic hydrocarbons (PAHs).[30,31] These large PAHs are mostly found in the asphaltene fraction.[8] In addition, the spectra possess vibrational overtones and combination bands which are useful for analyzing live crude oils.[20–24] In addition, these spectra also provide a basis to determine that the sample which is analyzed in the laboratory is indeed the fluid sample acquired by the MDT. This spectral comparison is referred to as "chain of custody" similar to the forensic concept.[32] Figure 3 shows an example of the chain of custody measurements comparing downhole and laboratory spectra on a live crude oil. In this case the laboratory sample is valid (or at least as valid as the downhole sample).

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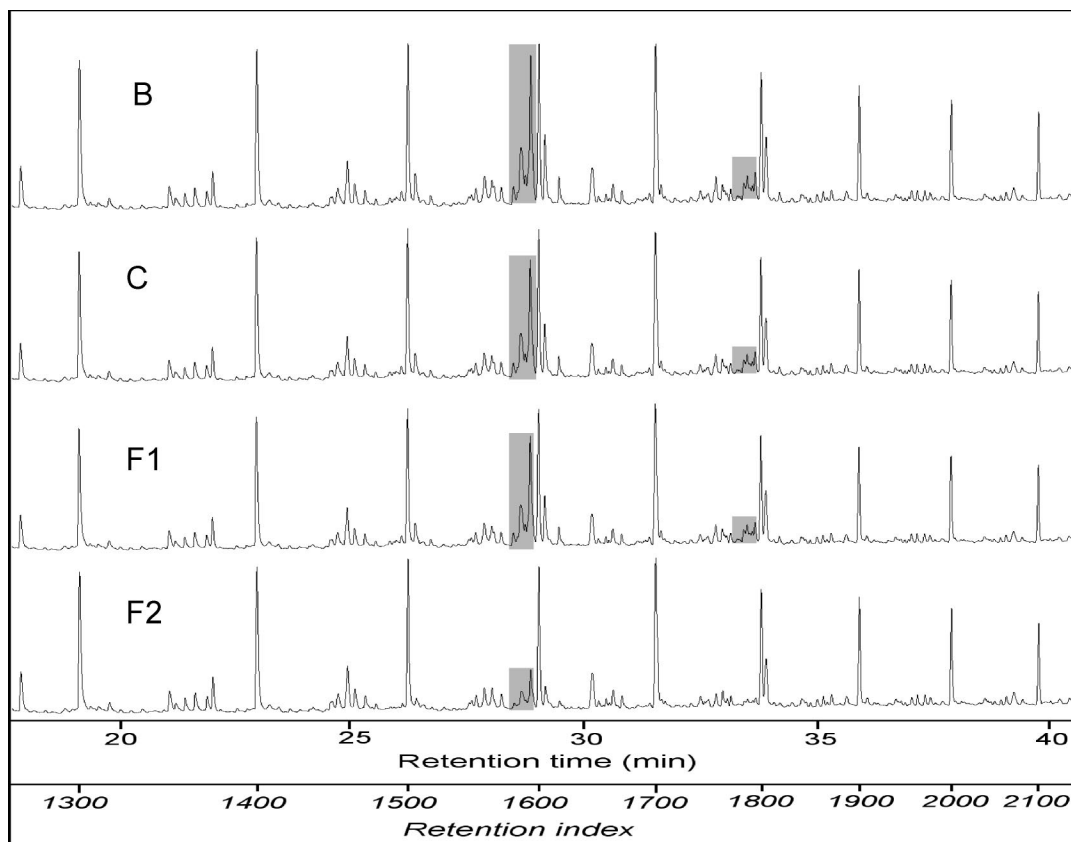
Figure 5. One-dimensional GC-FID chromatograms for (top to bottom) samples B, C, F1, and F2. The shaded areas in each chromatogram are alkenes from the drilling fluids and are not native to the crude oils. The alkene content relative to the total signal in the chromatogram can be used to determine the contamination from the drilling fluid base oil.
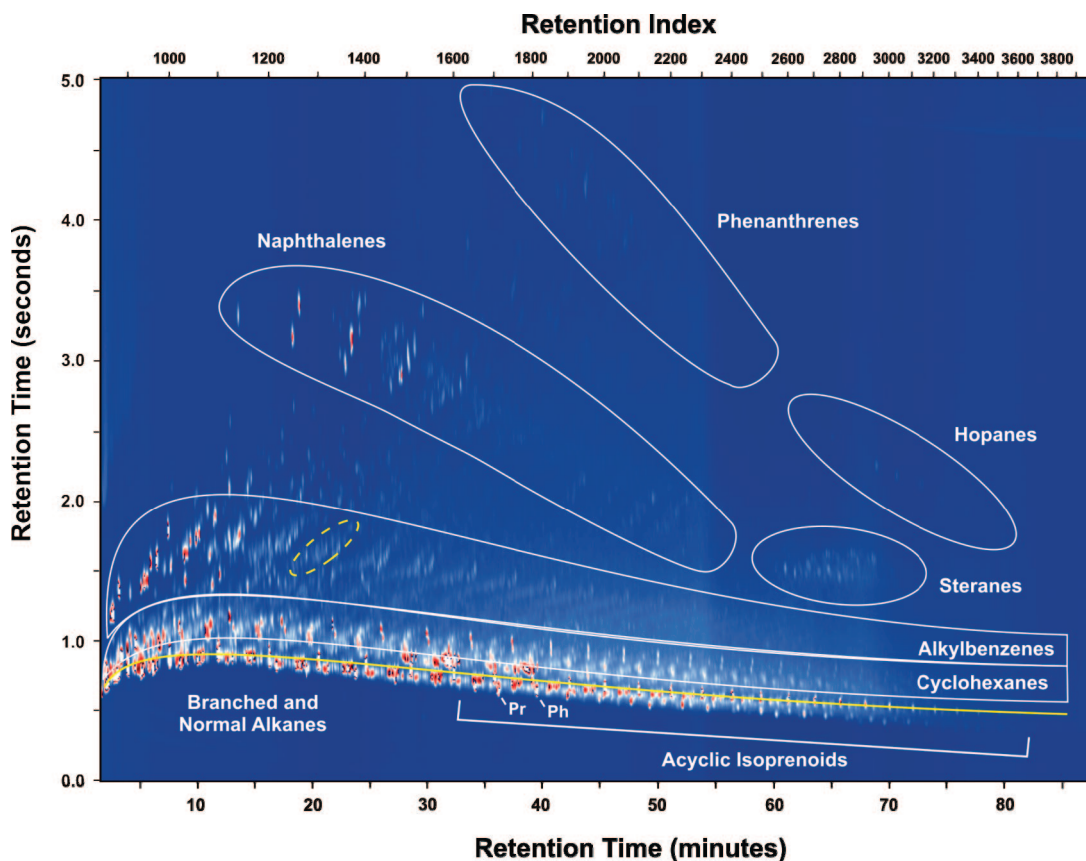

Figure 6. GC×GC-FID chromatogram of the F1 oil sample. Enscribed areas represent peaks of specific compound classes. The yellow line marks the elution of *n*-alkanes and branched alkanes. Pr and Ph are respectively the compounds pristane and phytane. The yellow circle enscribes the area analyzed by GC×GC-TOFMS.
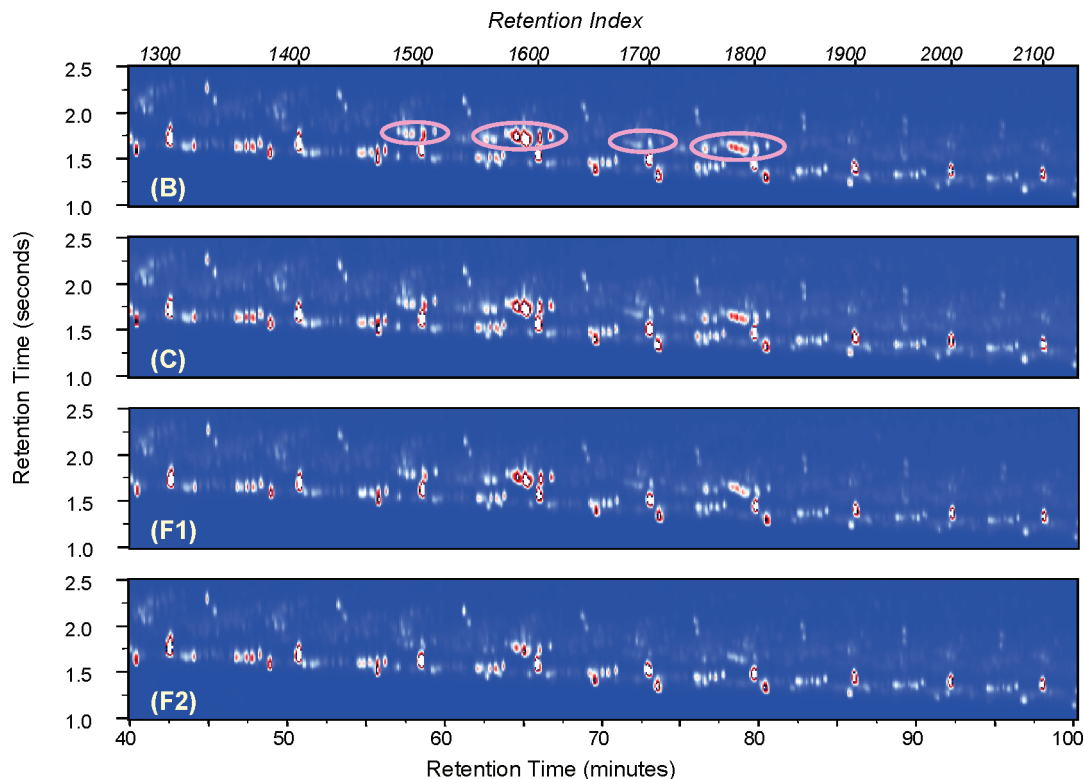
Figure 7. GC×GC-FID color-contour chromatograms for samples B, C, F1, and F2 showing the alkene separation (from the drilling fluid) compared with native components of the crude oil. Note the enhancement separation provided by GC×GC in comparison to single dimension GC (Figure 5).
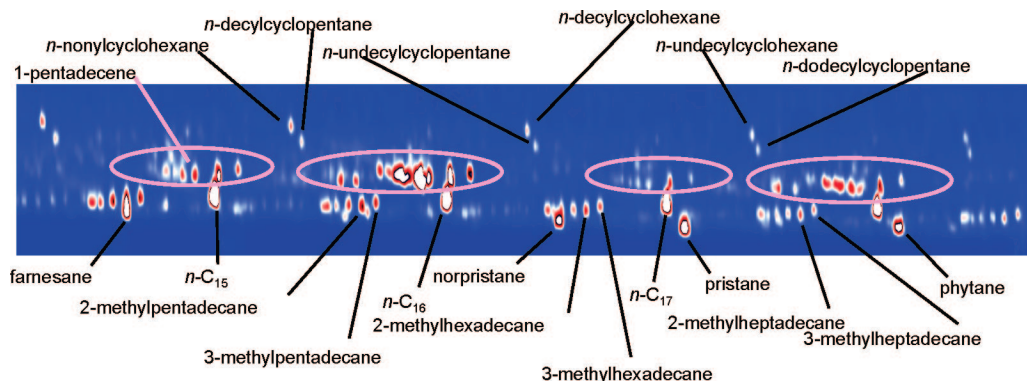

Figure 8. GC×GC-FID color-contour chromatogram for sample C with petroleum compounds and alkenes annotated. The ovals indicate the alkenes. Excellent chemical resolution is possible with GC×GC.

In these experiments, six live crude oil samples from four sands were acquired from a closely spaced, stacked, shale, and sandstone sequence from a reservoir under deepwater Gulf of Mexico. As reported elsewhere,[26] the spectral measurements acquired downhole were compared to the corresponding laboratory spectra to assure the samples were valid. Figure 4 depicts a vertical section of this well. True vertical depth (as opposed to well trajectory length) is shown on the extreme left. A natural γ-ray log is shown; shales are enriched in heavy nuclides which undergo radioactive decay. Formation fluid pressures are shown for the six sandstones. The pressures show that the fluids in these six sandstones are not in hydraulic communication; thus, they are not in flow communication.[26] The optical absorption at 815 nm of the six crude oils is shown. Crude oil A has much higher color and thus much more asphaltene than crude oil B. However, asphaltenes are more dense than the bulk crude oil and would tend to sink not float if these two sand bodies were in flow communication.[9] That is, these two fluids represent a density inversion, thus indicating that these two sands are not in flow communication, a conclusion in concert with the pressure data. Crude oils B and C exhibit another density inversion in color again showing compartmentalization. The same applies for crude oils D and E. Four of these crude oil samples

are analyzed by GC×GC: samples of crude oils B, C, F1, and F2. The samples F1 and F2 represent two samples collected from the sand F; they should be identical provided the sampling operation was performed without incident except for potentially differing amounts of mud filtrate. The extent of mud filtrate contamination is always of major concern and varies as a function of pumping time for sample acquisition with the tool in the well bore.[20,21] Laboratory fluorescence measurements were made on six crude oils, one from each zone, and show that the optical absorption measurements performed downhole match expectations for fluorescence;[26] higher chromophore concentrations in crude oils yield smaller fluorescence intensities due to quenching.[33]

GC×GC-FID Analysis. The asphaltene fractions of the four samples were removed prior to sample analysis by filtering after addition of 30 mL heptane/g oil through a vacuum filter containing a 0.5 μm Milipore GF/F fiberglass filter. Each extract was analyzed on a GC×GC-FID that employed a loop-jet modulator, which was purchased from the Zoex Corp., Lincoln, NE. The complete system

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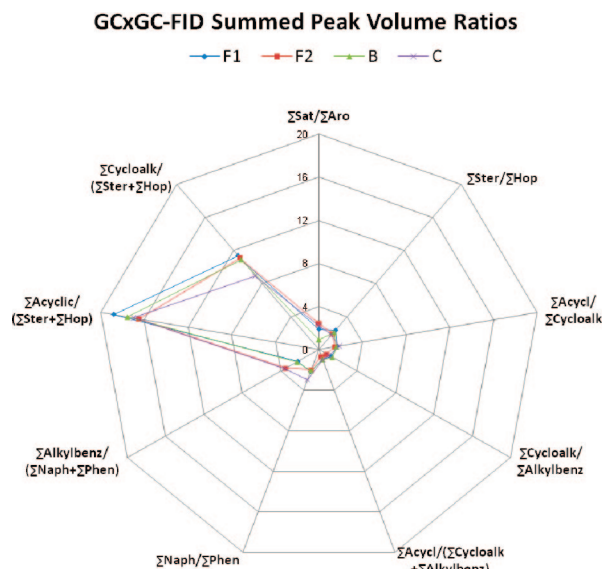
GCxGC-FID Summed Peak Volume Ratios

→ F1 → F2 → B → C

Figure 9. Spider diagram of compound class ratios computed from the summed peak volumes of of four oils (F1, F2, B, and C) analyzed by GC×GC-FID. Ster, Hop, Acycl, Cycloalk, Alkylbenz, Naph, and Phen refer to the respective compound classes steranes, hopanes, normal and branch alkanes, linear and substituted alkylbenzens, and substituted naphthalenes and phenanthrenes, respectively.

included an Agilent 6890 gas chromatograph configured with a 7683 series split/splitless autoinjector, two capillary gas chromatography columns, and a flame ionization detector. Each extract was injected in splitless mode, and the purge vent was opened at 0.5 min. The inlet temperature was 295 °C. The first-dimension column and the loop jet modulator reside in the main oven of the Agilent 6890 gas chromatograph (Agilent, Wilmington, DE). The second-dimension column is housed in a separate oven installed within the main GC oven. With this configuration, the temperature profiles of the first-dimension column, thermal modulator, and the second-dimension column can be independently programmed. The FID signal was sampled at 100 Hz. The carrier gas was H_2 at a constant flow rate of 0.7 mL min^{-1}. Peaks were identified with commercially available standards from Aldrich, U.S. National Institute of Standards and Technology (NIST), and Chiron (Chiron, Trondheim, Norway).

We used the following GC×GC setup. The first-dimension column was a nonpolar 100% dimethylpolysiloxane phase (Restek Rtx-1 Crossbond, 7.5 m length, 0.10 mm i.d., 0.1 μm film thickness) that was programmed to remain isothermal at 33 °C for 5 min and then ramped from 33 to 285 °C at 1.5 °C min^{-1}. The modulation loop was deactivated fused silica (1.5 m length, 0.10 mm i.d.). The modulator cold jet gas was dry N_2 chilled with liquid Ar, with a constant flow rate of 2.2 L min^{-1}. The modulator hot jet air was heated to 105 °C above the temperature of the first oven. The hot jet was pulsed for 350 ms every 10 s (0.10 Hz). The modulation period, therefore, was 10 s. Second-dimension separations were performed on a 50% phenylpolysilphenylene–siloxane column (SGE BPX50, 2.0 m length, 0.10 mm i.d., 0.1 μm film thickness) that was programmed to remain isothermal at 46 °C for 5 min and then ramped from 46 to 298 °C at 1.5 °C min^{-1}. GC×GC-FID peak volume measurements were calculated using GC-Image software.

GC×GC-TOFMS Analysis. Each sample was injected into a Leco Pegasus IVD GC×GC-TOFMS that consists of a Hewlett-Packard 6890 gas chromatograph configured with a split/splitless injector, two chromatography columns, and a two-stage liquid nitrogen cooled modulator coupled to a time-of-flight mass spectrometer. 1 mg of sample was dissolved in 1 mL of hexane, of which 1.0 μL was injected into a 300 °C splitless injector (2 min purge time). The first-dimension separation was performed on a 10 m, 5% phenyl-substituted polydimethylsiloxane phase capillary column (Restek, Rtx-5, 180 μm i.d., 0.2 μm film thickness) and temperature programmed from 50 °C (5 min) to 300 °C at 3 °C/min, followed by a 10 °C/min temperature increase to 335 °C. Second-dimension separation was performed on a

0.7 m capillary column using a 50% phenyl-substituted polysiloxane phase (BPX-50, SGE, 100 μm i.d., 0.1 μm film thickness) housed in a secondary oven programmed to offset the first-dimension oven temperature program by an additional 20 °C. Analytes were modulated on a deactivated fused silica column (0.5 m × 0.22 mm i.d.), which was programmed to offset the second-dimension oven by 60 °C. The GC×GC modulation period was 8 s. Helium was used as the carrier gas in constant flow mode (1.0 mL/min). A 1.0 m × 0.10 mm i.d. deactivated transfer line column connecting the second-dimension column to the TOF MS was heated to 270 °C. After a 5.83 min solvent delay, the TOF MS collected 50 spectra/s from m/z 50 to 776 u with a detector voltage of 1575 V and a 230 °C ion source temperature. The mass defect was set to 110 mu/100 u. Sample data acquisition and data processing were performed using ChromaToF software.

Results and Discussion

Figure 5 shows conventional high-resolution GC traces for four of the crude oil samples B, C, F1, and F2. These traces are very similar, showing that in spite of the large coloration differences of the different crude oils their alkane populations are seen to be quite similar, especially when plotted on a relative scale. In addition, gray bands appear in the figure at 29 and 33.5 min retention time. The components in these bands are largely, not entirely, the oil-based mud drilling fluids that are used during drilling the well. That is, these components, present in variable amounts, are contamination.

Figure 6 shows the GC×GC-FID chromatogram for one of the F1 crude oil sample. The exquisite ability to resolve the hydrocarbon components into various families of compounds enables a much more detailed look at the chemistry of these reservoir fluids. The analysis of these samples by GC×GC with emphasis on mud filtrate has been discussed elsewhere.[34] These chemical families are determined by characterizing the GC×GC response to many model compounds. In addition to the dominating population of alkanes and alicyclic alkanes, one also finds aromatics such as naphthalenes and phenanthrenes and various biomarker classes of compounds. The data of Figure 6 are displayed as a color-contour plot, with blue representing low signal, white representing medium signal, and red representing a high signal. In order to visualize the minor peaks, the dynamic range that is plotted is less than the total dynamic range of the sample, with the tops of the tallest peaks "chopped off". This produces a larger red area near the center of large peaks. The nonpolar polydimethylsiloxane column produced essentially a boiling point separation along the x-axis. A polarity-based separation with a 50% phenyl-substituted polydimethylsiloxane column produced chemical class-type separation along the y-axis. In the second dimension, the least polar and least polarizable petroleum classes observed in this sample, the branched and n-alkanes have the least retention on the second column and are located at the bottom of the chromatogram. The most polar and most polarizable classes, multi-ring aromatics, have the greatest retention on the second column and are located near the top of the chromatogram. The cycloalkanes appear in bands just above the branched alkanes because the ring structure makes them have a slightly higher polarizibility. Other petroleum components of interest in Figure 6 are the sterane and hopane biomarkers. This type of carbon range as well as distribution and abundance of petroleum components is typical of other GC×GC-FID images published for crude oils or other heavy refined oils.[35,36]

It is clear from Figure 6 that it is relatively easy to see all of the compounds "spread out" across the two-dimensional plane.

(34) Reddy, C. M.; Nelson, R. K.; Sylva, S. P.; Xu, L.; Peacock, E. A.; Raghuraman, B.; Mullins, O. C. Identification and quantification of alkene-based drilling fluids in crude oils by comprehensive two-dimensional gas chromatography with flame ionization detection. *J. Chromatogr. A* **2007**, *1148*, 100.
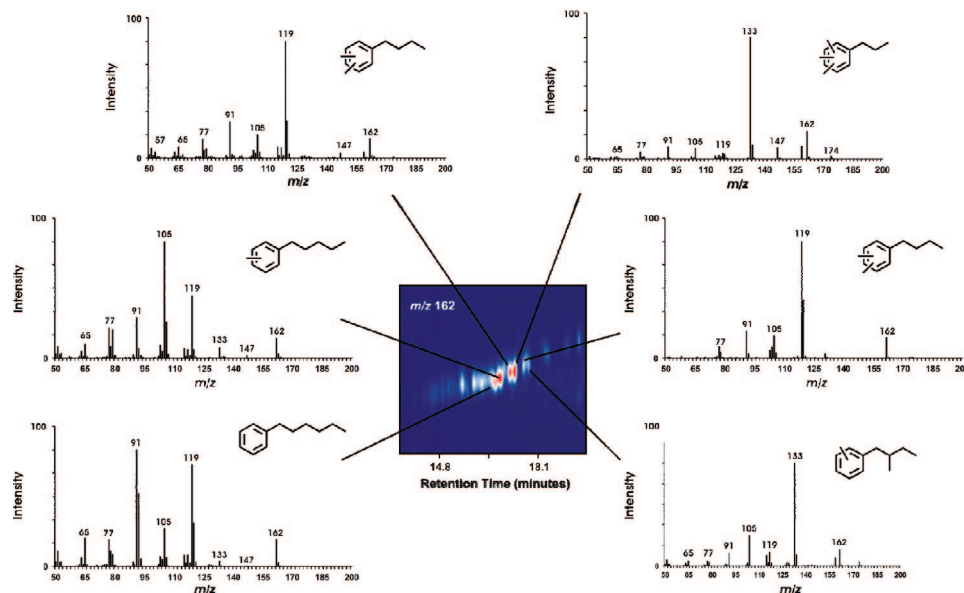
Figure 10. Tentitive identification of compounds within the F1 oil using GC×GC-TOFMS. Mass spectra of C_5-substituted alkylbenzene isomers surround the section of the *m/z* 162 ion chromatogram (the molecular ion) denoted by the dotted yellow circle in Figure 6.

Moreover, calculating the saturate to aromatic ratio is relatively straightforward. In fact, as demonstrated in Figure 6, numerous groups can be used to compare different oils.

Figure 7 expands the chromatographic space encompassing C_{13} to C_{21} *n*-alkanes for several of these crude oils. The oil-based mud contamination is circled in pink on the topmost GC trace showing the excellent resolution of this contamination.[34] The separation power of GC×GC enables contaminants to be easily identified and their contributions to a fluid quantitatively assessed; this has been shown elsewhere in great detail.[34] Other than the significant difference of contamination, these GC×GC traces are very similar in this region for these crude oils. A more detailed break down of the chemical components for the GC×GC traces in Figure 7 is provided in Figure 8. In particular, the contamination is seen to be alkene, a chemical group absent in crude oils. Several biomarkers of note are indicated in this figure. Chemometric techniques such as the comparison of specific sterane and hopane biomarker ratios are frequently used to assess differences in fluid composition. However, more sophisticated calculations include difference chromatograms and principal component analysis of quantitated compounds. These methods can not only elucidate compounds which are contaminants but can also provide quantitative metrics for assessing compositional differences of fluids.

For example, referring back to Figure 6, the circled region at 20 min retention time (first column) is discussed. We used data to create a spider plot (Figure 9) for the four oils that we analyzed. Spider plots of this type are routinely used to analyze differences among different crude oils. The different spider plots are somewhat similar, which is consistent with their provenance. Nevertheless, some differences are noted. F1 and F2, two samples from the same sand, are both plotted, enabling an error to be determined. Sample C is seen to be different in two of the spider plot metrics. For example, sample C is distinct in the ratio of alicyclics to the sum of steranes and hopanes. Even more elaborate spider plots are capable with the amount of compounds or compound groups that are available with this technology.

To highlight the power of GC×GC-TOFMS, we analyzed F1 with the goal of identifying the trace amounts of compounds, encircled in yellow, that we observed in the GC×GC-FID chromatogram (Figure 6). Because of the "clean" mass spectra afforded by GC×GC-TOFMS, we were able to determine that these compounds were mostly C_6-substituted alkylbenzenes. Their tentative structures are shown in Figure 10. This extraordinary chemical specificity is enabling a detailed look at the reservoir crude oils. This chemical identification can be used particularly if one has an understanding of expected differences among reservoir oils in a particular column (e.g., biodegradation, water washing, current charging, etc.).

Conclusions

This introductory paper highlights new methods for the chemical analysis of crude oils and their distribution in oil reservoirs. DFA is demonstrated to be an effective approach for in-situ analysis of reservoir fluid and architecture properties in oil wells. We demonstrate how DFA can be used to elucidate important reservoir complexities. We also explore how GC×GC-FID and GC×GC-TOFMS can be used to elucidate the molecular composition of such fluids. These analytical methods are shown to effectively differentiate crude oils in closely spaced vertically stacked sands. In particular, the chemical specificity of GC×GC-FID can be used to target explicit chemical differences in crude oils expected for a particular column in order to validate the corresponding geologic and fluid models of a reservoir. The task that lies ahead is to identify those signatures in current and future DFA measurements which point to potentially important samples and then to identify specific laboratory methods. We are continuing along these lines which we expect will enhance the efficiency of all aspects of fluid analysis in the upstream oil business.

(35) Arey, J. S. R.; Nelson, K. C.; Reddy, M. Disentangling Oil Weathering Using GCxGC. 1.Chromatogram Analysis. *Environ. Sci. Technol.* **2007**, *41*, 5738.

(36) Arey, J. S. R.; Nelson, K.; Plata, D. L.; Reddy, C. M. Disentangling Oil Weathering Using GCxGC. 2. Mass Transfer Calculations. *Environ. Sci. Technol.* **2007**, *41*, 25641.