Clay Typing, Mineralogy, Kerogen Content and Kerogen Characterization from DRIFTS Analysis of Cuttings or Core

Michael M. Herron*, Mary Ellen Loan, Alyssa Charsky, Susan L. Herron, Andrew E. Pomerantz and Marina Polyakov, Schlumberger-Doll Research, Cambridge, MA USA

Copyright 2014, Unconventional Resources Technology Conference (URTeC) DOI 10.15530/urtec-2014-1922653

This paper was prepared for presentation at the Unconventional Resources Technology Conference held in Denver, Colorado, USA, 25-27 August 2014.

The URTeC Technical Program Committee accepted this presentation on the basis of information contained in an abstract submitted by the author(s). The contents of this paper have not been reviewed by URTeC and URTeC does not warrant the accuracy, reliability, or timeliness of any information herein. All information is the responsibility of, and, is subject to corrections by the author(s). Any person or entity that relies on any information obtained from this paper does so at their own risk. The information herein does not necessarily reflect any position of URTeC. Any reproduction, distribution, or storage of any part of this paper without the written consent of URTeC is prohibited.

Abstract

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has recently been introduced and is currently being evaluated as a rapid, robust, and efficient technique for simultaneously quantifying kerogen and mineralogy from core and cuttings samples in the laboratory or at the wellsite. The technique we have developed is based on DRIFTS and quantifies mineralogy and kerogen content by measuring the vibrational frequency of chemical bonds. These bonds produce characteristic infrared signatures in common sedimentary minerals as well as organic matter. Core and cuttings samples from wells in unconventional reservoirs in North and South America were analyzed using our standard processing technique and the new full clay processing that solves for kerogen, illite, smectite, kaolinite, and chlorite, in addition to non-clay mineral components. Samples were also analyzed for mineralogy by the more accurate transmission dual range Fourier-transform infrared spectroscopy technique and for total organic carbon (TOC) by LECO/coulometry, and results for both mineralogy and TOC compare very well. The DRIFTS hydrocarbon signal is due to the C-H bond vibrational modes of aliphatic hydrocarbons. For samples of a given maturity, the strength of this absorbance is simply proportional to the hydrocarbon concentration. This signal decreases in magnitude faster than the TOC decreases for samples of differing maturities. As a result, the ratio of TOC to the DRIFTS signal is a new estimate of organic maturity that is shown to agree well with estimates from vitrinite reflectance or T_{max}. This ratio is especially sensitive to kerogens that have entered the gas zone. Full DRIFTS analysis including sample preparation generally takes less than 30 minutes for any mud type allowing the technique to keep up with the drill bit at the wellsite.

Introduction

Quantitative mineral analysis is an important part of formation evaluation for all reservoirs. The mineralogy, particularly the clay mineralogy, exerts a significant influence on log responses and affects many aspects of economic hydrocarbon production. Two prominent mineral analysis techniques are X-ray Diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy, including the combined mid-IR and far-IR dual range FTIR version (Matteson and Herron, 1993; Herron et al.; 1997). Accurate analysis of clay mineralogy by XRD or FTIR commonly requires several hours of sample preparation. A separate XRD run of a sample exposed to ethylene glycol is usually required to identify swelling components such as smectite or mixed-layer illite smectite. The long times involved in accurate clay mineral identification and quantification have necessitated that these techniques are only performed in the laboratory.

Reservoir quality evaluation in unconventional reservoirs also involves assessing the kerogen content and the kerogen thermal maturity. The analysis of TOC by industry standard techniques such as LECO or coulometry and the thermal pyrolysis procedures such as RockEval, which gives the temperature of maximum organic emission that is a proxy for thermal maturity, are also time consuming. The measurement of mineralogy, TOC, and maturity are separate analyses. There is a need for a rapid technique that is capable of providing mineralogy, especially clay
mineralogy, plus TOC and information on kerogen maturity. DRIFTS can quickly measure mineralogy and provide estimates of organic matter in sediments with minor sample preparation.

**Analytical Procedures**

Samples for this study consisted of core and cuttings samples from numerous wells in North and South America. Samples were crushed and homogenized and then split for separate mineralogical and organic analyses.

Some of the cuttings analyzed in this study were drilled with oil based mud (OBM). Therefore, before being analyzed for mineralogy and kerogen, the OBM had to be removed from the surface of the cuttings. The OBM contains organic base oil and additives which can contribute to the DRIFTS spectrum and interfere with the accuracy of the mineralogy and kerogen measurement.

The cleaned cuttings and core samples were reduced in particle size to minimize non-linear effects (Mustard and Hays, 1997). The DRIFTS analyses were carried out on a Bruker Optics Alpha-R spectrometer (Charsky and Herron, 2012). The spectrometer has been mounted vertically on a movable arm so that the infrared light shines down onto the sample at an optimal distance from the source. All samples were scanned at 4 cm\(^{-1}\) resolution over the mid-infrared range 375 – 4000 cm\(^{-1}\). For each sample, 90 one-second scans were collected and then averaged to give the resultant DRIFTS spectrum. Spectra were collected in Kubelka-Munk intensity which treats all reflections as occurring in a single direction, and is better conditioned than absorbance units for reflection quantification (Kubelka and Munk, 1931). The minimum required sample amount is approximately 1 gram. Total analysis time per sample is less than three minutes.

Samples were also analyzed by transmission FTIR (Matteson and Herron, 1993; Herron et al., 1997). This procedure involves reducing the sample size to less than 2 microns through crushing and grinding in a McCrone micronizing mill. The sample powder is then diluted in KBr, pressed into a pellet, and scanned in a Bruker FTIR spectrometer.

Transmission FTIR and DRIFTS spectra of samples were solved as a weighted linear combination of mineral standard spectra. The standards have all been assured of purity by XRD and chemical analysis. Total organic carbon analyses for this study were performed by SGS using a coulometric technique. Maturity values were measured by GeoMark using \(T_{\text{max}}\) values.

**DRIFTS Mineralogy and FTIR**

The DRIFTS methodology of performing a weighted least squares regression of a sample spectrum on a library of pure mineral spectra was followed (Charsky and Herron, 2012) but expanded to include smectite, illite, chlorite, and muscovite standards. The model was applied uniformly to 1139 core and cuttings samples of oilfield samples primarily from North and South America. The DRIFTS mineralogy on a kerogen-free basis is compared with FTIR measurements on identical splits of the same samples in Fig. 1. The average absolute differences (aad) between DRIFTS and FTIR mineral concentrations are provided in Table 1.

Illite is the most abundant clay mineral in oilfield sediments analyzed in our laboratory over the last 20 years and that is the case in this set of samples. The aad of 6.6 wt.% for illite is higher than for the other clays, but that reflects the higher abundance. Quartz and calcite are major sedimentary minerals and the aad values of 4.4 and 3.2 wt.% demonstrate that DRIFTS can measure these components accurately. Smectite is important in the oilfield, as mentioned, for its impact on petrophysical analysis and completion and production operations due to its high surface area and cation exchange capacity and swelling nature. The aad of only 1.8 wt% is consequently quite satisfying.
Fig. 1. DRIFTS and FTIR mineralogy comparison for 1139 core and cuttings samples. The average absolute difference values between DRIFTS and FTIR are given in Table 1.

Table 1. Average absolute differences (aad) between DRIFTS mineralogy and FTIR mineralogy on 1139 cuttings and core samples.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>aad (DRIFTS and FTIR (wt.%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Clay</td>
<td>5.1</td>
</tr>
<tr>
<td>Illite</td>
<td>6.6</td>
</tr>
<tr>
<td>Smectite</td>
<td>1.8</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>0.7</td>
</tr>
<tr>
<td>Chlorite</td>
<td>2.0</td>
</tr>
<tr>
<td>Quartz</td>
<td>4.4</td>
</tr>
<tr>
<td>Calcite</td>
<td>3.2</td>
</tr>
<tr>
<td>Dolomite</td>
<td>2.1</td>
</tr>
<tr>
<td>Total Carbonate</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Dolomite is a major carbonate mineral with a different structure and a significantly higher grain density than calcite. In spite of the similarities in DRIFTS standard spectra (Herron et al., 2014), the DRIFTS signal processing is able to independently quantify both calcite and dolomite with aad values of 3.2 and 2.1 wt\%, respectively. Kaolinite has a very distinctive infrared spectrum, and so DRIFTS analysis is quite accurate with aad in these samples of only 0.7 wt\%. Chlorite is regularly overestimated compared to our FTIR, and this might reflect an error in the FTIR as much as in the DRIFTS.
In making such a comparison between DRIFTS and FTIR it should be noted that the FTIR error in artificial mixture experiments was ± 2 wt.%, and the DRIFTS errors shown in Table 1 are about ± 5 wt.%. The average differences between DRIFTS and FTIR for the oilfield samples are mostly similar to these uncertainty estimates. The aad levels given in Table 1 for such a wide variety of samples are probably within acceptable limits for most applications.

**Individual Wells**

Fig. 1 shows DRIFTS mineralogy computed on a large number of oilfield samples, all using exactly the same processing. It is useful to examine the comparison between DRIFTS and FTIR on samples from some individual wells.

Samples from a well in Canada were analyzed by DRIFTS and FTIR for mineralogy. These were core samples from the Montney Formation (Davies et al., 1997) which also contains organic matter. Thirty-nine core samples were crushed and split into different representative fractions. The DRIFTS results, expressed in weight percent including kerogen, are shown in Fig. 2. The cored interval is mostly a simple mixture of dolomite, quartz plus feldspars, and illite as the dominant clay. At occasional depths there are high concentrations of calcite. The DRIFTS mineralogy is confirmed by FTIR analyses as shown in Figs. 3 and 4.

![Fig. 2. DRIFTS mineralogy and kerogen content for a vertical well in Canada. Depths are in meters. Discrete core sample points are connected to make this log display.](image-url)
Fig. 3. DRIFTS and FTIR mineralogy comparison for samples from the well shown in Fig. 2. The aad values are a) illite 4.0 wt.%; b) quartz 4.4 wt.%; c) dolomite 2.0 wt.%; d) kaolinite 0.1 wt.%; e) smectite 3.4 wt%; f) calcite 2.9 wt.%; g) chlorite 1.8 wt%; h) muscovite 0.8 wt%.

Figure 4 presents DRIFTS mineralogy and kerogen analysis for core samples from a vertical well in the Wolfcamp formation. The mineralogy shows intriguing alternating facies with one set of illite, muscovite, quartz, and occasional smectite, alternating with a second set of calcite, dolomite, and lower concentrations of quartz and illite. The kerogen content shows similar variability with lower concentrations in the high calcite-dolomite intervals.

Fig. 4. Mineralogy and kerogen concentrations for the Wolfcamp well. This is a vertical well and the samples are core samples analyzed by DRIFTS and by FTIR.
For the same well, Fig. 5 compare the DRIFTS mineralogy with FTIR mineralogy on splits of the same samples. Again, both sets are compared on a kerogen-free basis. Interestingly, there is a slight underestimation of the illite concentration computed by DRIFTS. This might reflect the effects of shadowing of smaller clay particles by larger quartz particles. Because the computed mineralogy is normalized to unity in the end, as is done for all mineralogy procedures, a low bias in one mineral is necessarily seen as a high bias in one or more other minerals. In this case, the high bias in quartz almost exactly matches the low bias in illite. Note that the distinctive variations of mineralogy described above are discernible even if the absolute values of the illite and quartz concentrations are slightly off.

Fig. 6 presents the DRIFTS mineralogy profile of cuttings from a horizontal well in the Marcellus formation. The formation is composed almost exclusively of quartz, illite, muscovite, and occasional intervals of calcite. It has been our experience that high intervals of calcite in horizontal wells in siliciclastics may be due to calcite filling vertical fractures in highly fractured intervals. Such fractured intervals can have different production characteristics than less fractured intervals. Abundant kerogen is detected in the samples, but it is far from constant across the profile.
Figure 6. DRIFTS mineralogy and kerogen content for cuttings from a horizontal well in the Marcellus formation. Depths are in feet. Discrete cuttings sample points are connected to make this log display.

Fig. 7. DRIFTS mineralogy compared to FTIR mineralogy for the Marcellus cuttings samples. The aad values are a) illite 8.7 wt.%; b) quartz 9.5 wt.%; c) dolomite 1.5 wt.%; d) kaolinite 0.8 wt.%; e) smectite 0.5 wt%; f) calcite 2.1 wt%; g) chlorite 3.2 wt.%; h) muscovite 5.2 wt%.

The comparisons between DRIFTS mineralogy and FTIR mineralogy on splits of the same cuttings are shown in Fig. 7. The mineralogy across the profile has a fairly constant clay concentration and this is observed in both the DRIFTS and FTIR data. The DRIFTS illite is slightly lower than the FTIR, and the quartz is slightly higher, as was also seen in the Wolfcamp well samples. Again, the calcite comparisons are good. The DRIFTS data in Fig. 7 show a strong agreement with FTIR in the analysis of kaolinite. It is somewhat surprising that the agreement with muscovite is as good as it is, given the similarity in DRIFTS spectral shape with illite and smectite.
DRIFTS and Kerogen Thermal Maturity

While the preceding section has focused on estimating mineralogy from DRIFTS spectra, one of the useful features of DRIFTS is that it can simultaneously measure absorbance related to organic matter. In the cleaning procedure used in the samples in this study, oil and bitumen have been removed, so organic matter here refers to kerogen. Kerogen is not crystalline, so XRD cannot detect it. DRIFTS can detect the organics, and the challenge is the calibration of the signal to total organic carbon (TOC) because the infrared signal strength in the 2800-3000 cm⁻¹ region is known to decrease as kerogen matures (Lis et al., 2005).

By accurately accounting for the mineral DRIFTS signature, we are uniquely able to compute the organic matter signal by subtracting the mineral signal from the total spectrum. This has significant advantages over techniques that require the kerogen to be isolated or the minerals to be dissolved in order to get a kerogen signal because these techniques are time consuming and require the use of concentrated acids (Robl and Davis, 1993; Barth et al., 1995; Lis et al., 2005). In previous work, Schenk et al. (1986) used a calcite standard to partially remove the mineral signal. As an advancement beyond that concept, the current multi-mineral spectral reconstruction permits complete removal of the mineral signals, thus producing an accurate organic signal. This also eliminates the need to use multivariate statistics such as partial least squares on a test data set to establish trends with maturity (Barth et al., 1995; Washburn and Birdwell, 2013).

Fig. 8 shows a plot of the standard mineral-stripped DRIFTS organic signal against the measured TOC in four different wells of varying thermal maturity. While it has long been known that the strength of the aliphatic hydrocarbon signal decreases with increasing maturity, such relationships have been generally discussed in a qualitative fashion. Lis et al. (2005) discussed many ratios of FTIR absorbance of kerogen isolates as a function of maturity, but not the magnitude of the aliphatic absorbance per weight of TOC.

Fig. 8 shows that for a given maturity, the magnitude of the DRIFTS organic signal varies linearly with TOC and that the slope, or coefficient of proportionality, is a simple function of the kerogen thermal maturity (R₀) as determined from vitrinite reflectance or T_max measurements. Therefore, if organic maturity is known, as is often the case for a given field, the ability to derive a clean organic signal provides a means of calibration, thus eliminating the need for local core analysis.

Fig. 8. DRIFTS mineral-stripped organic signal and TOC for four sets of samples of varying maturity. a) Core samples of maturity R₀ 0.5; b) cuttings samples from Marcellus at R₀ 1.35; c) core samples from the Wolfcamp formation at R₀ 0.79; d) core samples with R₀ 1.0. In each case, the ratio of the true TOC to the DRIFTS standard signal is about equal to the R₀ value.
For example, in Fig. 8a, a very immature kerogen with a $R_o$ of approximately 0.5, has a low TOC/DRIFTS signal, and the data plot along a ratio of 0.5. In Fig. 8b, the Marcellus data are mostly from a region with a maturity of 1.35 and the ratio of TOC/DRIFTS signal is also about 1.35. In other words, the DRIFTS signal decreases per mass of organic carbon in the more mature sediments. Further, the ratio of TOC/DRIFTS signal mirrors the maturity values and this provides a means of determining the DRIFTS-to-TOC calibration factor and quantifying TOC without local calibration in areas of known maturity.

![Graph showing DRIFTS TOC compared with TOC in the Wolfcamp well.](image)

**Fig. 9.** DRIFTS TOC compared with TOC in the Wolfcamp well. The calibration factor for DRIFTS kerogen for all samples was determined from the maturity value shown in Fig. 8c.

To demonstrate this capability, Fig. 8c shows the DRIFTS signal compared to TOC on the Wolfcamp well. The measured maturity in this well is 0.79. The ratio of the TOC/DRIFTS organic signal averages 0.7, close to the maturity. The ratio can then be used to convert the DRIFTS signal directly into TOC. Fig. 9 shows the DRIFTS signal multiplied by the 0.7 ratio to produce DRIFTS TOC and compares that value with the measured TOC over the entire well. Since the calibration ratio is numerically equivalent to the maturity, which is usually known, this is an easy means of calibrating DRIFTS TOC.

**Conclusions**

In summary, the quantitatively developed DRIFTS processing has been expanded to include smectite, illite, kaolinite, and chlorite, in addition to non-clay minerals. The comparison on over 1100 samples with FTIR results establishes that DRIFTS is reasonably accurate for estimating mineralogy. The level of agreement, quantified as average absolute deviation, is generally better than a few weight percent. The clay mineralogy was further validated by comparison with independently measured CEC.

Smectite is an important mineral in conventional as well as unconventional reservoir analysis because of its swelling nature as well as its high cation exchange capacity which impacts electrical log response. The capability of DRIFTS to quantify smectite shown here, is a significant advance in reservoir description.

The mineral quantification permits stripping of the mineral contributions to the measured DRIFTS spectrum leaving the organic or kerogen spectrum. The kerogen spectrum can be interpreted in terms of kerogen maturity and there are many absorbance ratios that might be taken directly from the spectrum for interpretation of maturity (Lis et al., 2005). In addition, the ratio of the TOC of the sample to the mineral-stripped kerogen spectrum magnitude is an independent maturity indicator whose value is close to $R_o$ determined by $T_{\text{max}}$. The $R_o$ values give a means of calibrating DRIFTS to provide the TOC value from the mineral-stripped kerogen spectrum. Additional means of estimating kerogen thermal maturity from kerogen infrared spectra exist (e.g. Lis et al., 2005) and are applicable.

DRIFTS can be measured on core and cuttings with minimal sample preparation and with a total sample preparation and analysis time of less than 15 minutes in the laboratory. Initial wellsite measurements were done within 30 minutes. The speed and accuracy of the clay mineralogy and kerogen analyses makes DRIFTS suitable for wellsite as well as laboratory analyses. At present, we have run DRIFTS as a wellsite service on five wells.
Acknowledgements

The authors would like to thank A. Sibbit for manuscript review and A. Matteson and R. Akkurt for continued support.

References


