

# Quantitative analysis of kerogen content and mineralogy in shale cuttings by Diffuse Reflectance Infrared Fourier Transform Spectroscopy

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## ABSTRACT

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been used for qualitative investigation of hydrocarbons, source rocks, core and cuttings. However, in the past, quantitative analysis has been unreliable. In the DRIFTS technique, an infrared laser shines onto the material and a detector measures the reflected light intensity as a function of frequency. The reflected light frequency spectrum is related to characteristic vibrational modes of elemental bonds in the material. In some cases these modes have been linked to compounds or minerals.

This paper demonstrates that quantitative analysis of kerogen, calcite, illite, kaolinite, quartz, dolomite and smectite is possible for cuttings obtained from a well drilled with oil-based mud in a formation in Texas. The cuttings mineral concentrations solved from DRIFTS spectra were compared with mineralogy determined by the highly accurate transmission dual-range Fourier transform infrared (DRFT-IR) technique developed in our laboratory and the concentrations are similar to within a few percent. The kerogen content from DRIFTS was compared to the organic carbon content determined by a LECO elemental analyzer and the agreement is better than  $\pm 1$  wt % kerogen.

Our procedure removed the oil-based mud from the cuttings sample and then reduced the particle size. The samples were analyzed with a Bruker Alpha-R DRIFTS unit over the range of  $375 - 4000 \text{ cm}^{-1}$ . After converting the reflectance data to Kubelka-Munk units, the spectra were analyzed by assuming that the Beer-Lambert law holds at every wavelength. In this analysis, the mineralogy was determined from over 2500 simultaneous least squares solutions of the unknown absorbance as a linear combination of the mineral standard spectra. Mineral concentrations were evaluated with artificial mixtures of minerals and by comparison with the DRFT-IR and LECO measurements on well cuttings.

## INTRODUCTION

The ability to better understand unconventional reservoirs in order to optimize the recovery of hydrocarbons continues to be of growing economic importance. Tight shale reservoirs especially are not well understood and formation evaluation and characterization of these reservoirs often require more comprehensive datasets in order to

understand their behavior [1-4]. As it is however, the horizontal drilling technique that often makes oil and gas shales economically viable also makes it difficult, if not impossible, to obtain important petrophysical data from logs and core. Even in many vertical wells, core and comprehensive log data are not always available. Two major properties which are often beneficial to understanding the behavior of the reservoir are mineralogical composition and total organic carbon content. Identifying the mineralogical composition may be important for understanding petrophysical properties such as permeability and geomechanical properties affecting the fracability of the reservoir [3]. Additionally, understanding the total organic carbon content and being able to accurately quantify these values is valuable as they relate to both porosity and gas saturation [3, 4].

Drill cuttings are readily available for measurement from almost all wells and thus provide an alternative method of obtaining these crucial mineralogy and organic carbon measurements. While more accurate analytical techniques are available, they are often expensive, slow, or difficult to implement in the field. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) provides an easy and rapid measurement of drill cuttings, which can be analyzed for the mineralogy and kerogen content of reservoir rocks. DRIFTS responds to the modes of molecular vibrations of the components of the sample. When infrared light is shone at a sample, the light is specularly reflected, diffusely reflected, or transmitted through part of the sample (Figure 1). A detector then measures the diffusely reflected light as a function of wavenumber. Because each fundamental molecular vibration corresponds to a specific absorbance band, the sample components can then be extracted by analyzing the DRIFTS spectrum.

DRIFTS has been used in the past mainly for qualitative characterization of both hydrocarbons and minerals in reservoir rocks [5-11]. Difficulties in the analysis of the DRIFTS spectra arising in non-linearity have been ascribed to particle size, particle orientation, and “camouflaging” when mineral grains stick to each other so that they are not all probed by the infrared light. Other studies have aimed to quantify individual constituents, mainly by using partial least squares (PLS) models. The limitations of PLS techniques include being limited by the quality and number of samples used in the training set [7] and generally, quantitative analysis has been unreliable [8-11]. This paper describes how DRIFTS spectra can be analyzed using a least squares regression and minimal sample preparation to more accurately quantify mineralogy and kerogen content of oil shale cuttings.

## **PROCEDURES**

### **Sample Preparation and Data Collection**

The DRIFTS spectrometer used in this study is a Bruker Optics Alpha-R spectrometer. 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 (Figure 2). All samples were scanned at  $4\text{ cm}^{-1}$  resolution over the range mid infrared range 375 – 4000

cm<sup>-1</sup>.

The cuttings analyzed in this study were drilled with oil base mud (OBM). Therefore, before being analyzed for mineralogy and kerogen by DRIFTS, the OBM had to be removed from the surface of the cuttings. The OBM contains organic base oil and both organic and inorganic mud additives, which will contribute to the DRIFTS spectrum and interfere with the accuracy of the mineralogy and kerogen measurement. After removal of the OBM, the cuttings were reduced in particle size to reduce spectra effects [12]. Figure 3 shows the cuttings before and after the cuttings cleaning and particle size reduction steps. The minimum required sample amount is approximately 1 g. For each sample, 24 scans were collected (approximately 20 seconds) and then averaged to give the resultant DRIFTS spectrum. Spectra were collected in Kubelka-Munk intensity. The Kubelka-Munk theory [13] has its origin in measurement of optical properties of paint. It relates the concentration of the absorbing species in Kubelka-Munk intensity, KM, to the reflectance, R in %, of the sample:

$$KM = (1 - R)^2 / 2R \quad (1)$$

By making this conversion to Kubelka-Munk intensity, rather than collecting the spectra in absorbance units, the spectra exhibit improved linearity as described by the Beer-Lambert law [14] relating concentration, c in mol/L, to absorbance, A:

$$A = \epsilon lc \quad (2)$$

Where  $\epsilon$  is the molar absorptivity of the sample in cm<sup>-1</sup> and l is the absorption path length in cm.

### **Mineral and Kerogen Standard Spectra and Spectral Processing**

By assuming DRIFTS spectra obey the Beer-Lambert Law when collected as Kubelka-Munk spectra at every wavelength, the mineralogy and kerogen content can be extracted from the spectrum by solving for the sample components as a linear combination of known standard minerals. A library of mineral standard spectra was built by collecting spectra of mineral species known to be chemically pure as measured by X-ray fluorescence. Current mineral standards in the library include calcite, quartz, illite, dolomite, smectite, and kaolinite (Figure 4). For the play analyzed in this study, these minerals accounts for over 98 wt% of the minerals present, although additional mineral standards such as feldspar and biotite can be used. Additionally, five kerogen spectra were collected from demineralized rocks [15], and added to the library as standard organic spectra (Figure 5). Although other organic components may be present in rocks, including bitumen, for the purpose of this study, all organic components of the sample which have an aliphatic C-H bond will be referred to as kerogen. In our processing, the kerogen standards are solved for individually and reported as a sum.

The standard library described above enables determination of constituents of a sample of

unknown composition by assuming the sample's spectrum is a linear combination of each standard spectrum times its concentration in the sample. This is accomplished by using a least-squares regression over the entire spectrum to solve for the mineral and kerogen concentrations. Even though over 2500 simultaneous regressions are made, the computation only takes milliseconds.

### **Experimental**

To evaluate the ability of the least squares regression to solve quantitatively for individual minerals from DRIFTS spectra, 70 artificial mineral mixtures were made consisting of two components each. For each two component combination of calcite, illite, quartz, dolomite and kaolinite, mixtures were made in the following proportions: 10:90, 20:80, 30:70, 50:50, 70:30, 80:20, and 90:10. The components of each mixture were weighed, added to a 25mL mixing vial and homogenized using a Retsch mm 400 mixer mill. A DRIFTS spectrum was then collected of the homogenized mixture. Figure 6 shows the spectra for the ten illite:quartz mixtures.

### **Cuttings Case Study**

A total of 95 cuttings samples obtained from a tight shale well drilled with OBM located in Texas were prepared for DRIFTS measurement as described above. A DRIFTS spectrum was collected for each cuttings depth interval and analyzed for mineralogy and kerogen. The mineralogy values acquired from the DRIFTS analysis were compared to mineralogy values as measured on a split of the sample by DRFT-IR analysis, which has been shown to accurately measure mineralogy to within an error of  $\pm 2$  wt% [16, 17]. Kerogen values obtained by DRIFTS were compared to total organic carbon (TOC) values independently measured by SGS laboratories in Canada by LECO.

## **RESULTS AND DISCUSSION**

### **Artificial Binary Mixtures**

The spectra of the ten artificial illite:quartz mixes shown in figure 6 demonstrate the linearity of the DRIFTS spectra. As the concentration of one component, e.g. illite, increases, its peak amplitude increases or decreases proportionally. Similar trends can be observed in all the laboratory mixtures. To quantitatively evaluate the accuracy and precision of the least squares regression, the calculated mineralogy values are compared to the known concentrations. Table 1 shows the average absolute difference (aad) of these values for each of the five mineral components. The low errors show that with the current sample preparation and spectra analysis procedure used in this study, non-linear spectra effects are largely overcome.

### **Case Study: Mineralogy and Kerogen Determination from Cuttings**

The results of the least squares regression used to analyze the DRIFTS cuttings spectra are plotted vertically against sample number in Figure 7. The values plotted are carbonate (calcite + dolomite), clay (illite + smectite + kaolinite), quartz, kaolinite and kerogen. Kaolinite also has been plotted separately because its spectrum has very distinct

absorbance bands between 3600 and 3700  $\text{cm}^{-1}$  which make it more easily solved for in the least squares regression. Plotting the data in this way allows one to see distinct changes in the formation lithology while traversing the well path. For example, at sample 17, a formation boundary is crossed, and the samples become more clay rich with a significant decrease in carbonate. In addition to changes in the mineralogy, changes in the amount of kerogen can be detected with DRIFTS. The fifth track in Figure 7 shows an increase in the amount of kerogen at sample 17, corresponding to the lithology change at this point.

The DRIFTS mineral values are compared to mineral values measured by transmission DRFT-IR in Figure 8. The results show good matches between the DRIFTS measured value and DRFT-IR measured value for carbonate, clay, quartz and kaolinite. Although each of the plots appear to show some scatter in the data, the aad values are all below 3 wt% (Table 2), and the general trends can still be seen in the DRIFTS mineralogy. Tracks one through four in Figure 9 show that the DRIFTS mineralogy analysis is able to quantitatively measure the same changes in the lithology as the highly accurate transmission DRFT-IR mineralogy technique.

To approximate kerogen from TOC, the TOC value is multiplied by the commonly used factor of 1.2 to account for the non-carbon portion of the kerogen by other elements such as hydrogen. For each new basin or geographic area analyzed, the DRIFTS kerogen standards are calibrated on a small number (approximately 20) to account for the fact that the intensity of the kerogen peak changes with the maturity of the kerogen. Track 5 in Figure 9 shows the kerogen values measured from DRIFTS compared to 1.2\*TOC from LECO. The DRIFTS kerogen values match very closely to 1.2\*TOC. This is better seen in the cross plot of the two measurements as shown in Figure 10 where a tight correlation between the two values can be seen.

## **SUMMARY AND CONCLUSIONS**

In the past DRIFTS has been hampered by non-linearity effects making mineral quantification difficult. However, through sample preparation and signal processing these effects are largely reduced and, as shown in Figure 8, mineral and kerogen quantification from DRIFTS are in good agreement with the DR-FTIR mineralogy and the TOC from LECO. Although minerals outside of the limited suite used in this study could be measured, quantification of additional minerals may be more difficult. Another challenge is dealing with the aliphatic C-H bonds in kerogen. As the composition of kerogen changes with maturity, the FT-IR response changes as well, and the standards must be then calibrated to match the maturity of the samples being analyzed; the recommended procedure is to validate or calibrate the kerogen standard on a small number of samples.

Through the use of the Kubelka-Munk conversion of spectra and a least squares regression analysis, DRIFTS spectra can be analyzed for mineralogy to an average error of  $\pm 2.1\%$  and kerogen to  $\pm 0.7 \text{ wt}\%$  for well cuttings. DRIFTS is sensitive to the

changes in lithology and kerogen content over the length of a well and therefore can be used to identify formation tops and organic rich zones. It must be kept in mind that DRIFTS is not intended as a method to identify biomarkers or replace full analysis on core. Its ability to accurately measure both mineralogy and kerogen content rapidly on cuttings samples, with little sample preparation, is an enormous benefit, particularly where there may otherwise be little well data. These data provide a quick way to measure some of the major parameters governing production in unconventional reservoirs.

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## REFERENCES

1. Ejofodomi, E., J. Baihly, R. Maipani, R. and R. Altman, "Integrating all available data to improve production in the Marcellus shale," paper 144321 presented at the 2011 Society of Petroleum Engineers North American Unconventional Gas Conference, June 14 – 18, 37p.
2. Strickland, R., D. Purvis, and T. Blasingame, "Practical aspects of reserve determinations for shale gas," paper 144357 presented at the 2011 Society of Petroleum Engineers North American Unconventional Gas Conference, June 14 – 18, 34p.
3. Passey, Q., K. Bohacs, W. Esch, R. Klimentidis, and S. Sinha, "From oil-prone source rock to gas-producing shale reservoir – geologic and petrophysical characterization of unconventional shale-gas reservoirs," paper 131350 presented at the 2010 CPS/SPE International Oil & Gas Conference and Exhibition June 8 – 10, 29p.
4. Bust, V., A. Majid, J. Oletu, and P. Worthington, "The petrophysics of shale gas reservoirs: technical challenges and pragmatic solutions," paper 14631 presented at the 2012 International Petroleum Technology Conference, February 7 – 9, 15p.
5. Machnikowska, H., A. Krzton, and J. Machnikowski, "The characterization of coal macerals by diffuse reflectance infrared spectroscopy," *Fuel* (2002) **81**, 245-252.
6. Zhang, Y., X. Xu, N. Song, Z., Wu, X. Zhou, J. Chen, X. Cao, and B. Wang, "The evaluation of hydrocarbon potential generation for source rocks by near-infrared diffuse reflectance spectra," *Guang Pu Xue Yu Guang Pu Fen Xi/Spectroscopy and Spectral Analysis*, (2011) **31**, 955-959.
7. Kramer, R. "Chemometric techniques for quantitative analysis", Marcel Dekker, Inc., New York (1998), 192p.
8. Rosén, P., H. Vogel, L. Cunningham, A. Hahn, S. Hausmann, R. Pienitz, B. Zonlitschka, B. Wagner, and P. Persson, "Universally applicable model for the quantitative determination of lake sediment composition using Fourier transform infrared spectroscopy," *Environmental Science and Technology*, (2011) **45**, 8858 –

- 8865.
9. Breen, C., F. Clegg, M. Herron, G. Hild, S. Hillier, T. Hughes, T. Jones, A. Matteson, and J. Yarwood, "Bulk mineralogical characterisation of oilfield reservoir rocks and sandstones using Diffuse Reflectance Infrared Fourier Transform Spectroscopy and Partial Least Squares analysis," *Journal of Science & Engineering*, (2008) **60**, 1 – 17.
  10. Awaja, F. and S. Bhargava, "The prediction of clay contents in oil shale using DRIFTS and TGA data facilitated by multivariate calibration," *Fuel*, (2006) **58**, 1396 – 1402.
  11. Vogel, H., P. Rosén, B. Wagner, M. Melles, and P. Persson, "Fourier transform infrared spectroscopy, a new cost-effective tool for quantitative analysis of biogeochemical properties in long sediment records," *Journal of Paleolimnology* (2008) **40**, 689 – 702.
  12. Mustard, J., and J. Hays, "Effects of hyperfine particles on reflectance spectra from 0.3 to 25  $\mu\text{m}$ ," (1997) **125**, 145-163.
  13. Kubelka, P., F. Munk, "An article on the optics of paint layers," *Technical Physics*, (1931).
  14. Miller, F., A. Vandome, and McBrewster, J., "Beer-Lambert Law," VDM Publishing House Ltd., Saarbrücken (2009), 154p.
  15. Durand, B., Ed, "Kerogen: Insoluble organic matter from sedimentary rocks," *Procedures for kerogen isolation*, Éditions Technip, Paris (1980), 35 – 53.
  16. Matteson, A. and M. Herron, "Quantitative mineral analysis by Fourier Transform Infrared Spectroscopy," paper 9308 presented at the 1993 Society of Core Analysts Annual Meeting, August 9 – 11, 15p.
  17. Herron M., A. Matteson, and G. Gustavson, "Dual-Range FT-IR Mineralogy and the Analysis of Sedimentary Formations," paper 9729 presented at the 1997 International Symposium of the Society of Core Analysts, September 7 – 10, 12p.

Table 1. Average absolute difference in weight percent between known concentration and measured by DRIFTS for the 70 binary artificial mixtures.

Mineral	Average Absolute Difference (wt %)
Calcite	1.9
Illite	3.5
Quartz	3.7
Dolomite	3.4
Kaolinite	4.1

Table 2. Average absolute difference between DRFT-IR mineralogy and DRIFTS mineralogy, and average absolute difference between 1.2 \* TOC and DRIFTS kerogen for the 95 cuttings samples.

Mineral	Average Absolute Difference (wt %)
Carbonate	2.2
Clay	2.7
Quartz	2.5
Kaolinite	1.0
Kerogen	0.7

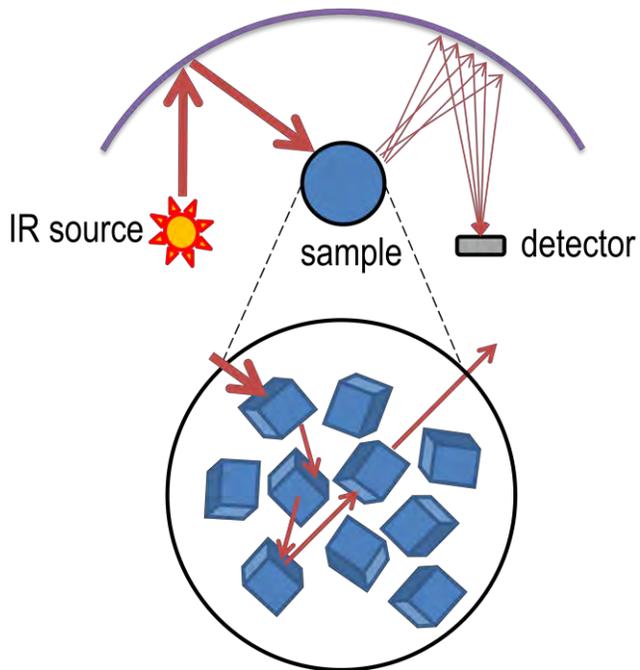


Figure 1. Diagram showing the general mechanisms of DRIFTS. A light from the IR source is focused on the sample where it interacts with particles. The diffusely reflected light is collected by a mirror and collated onto the detector.



Figure 2. Mounted spectrometer setup for ease of collecting measurements.

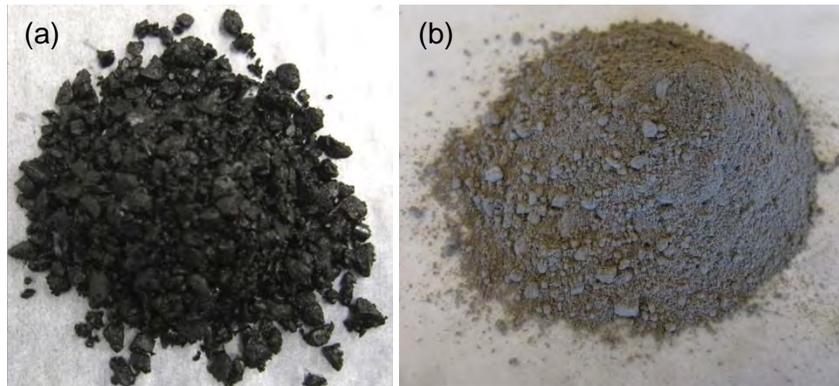


Figure 3. Cuttings sample as received from the well site (a), and after cleaning and particle size reduction (b).

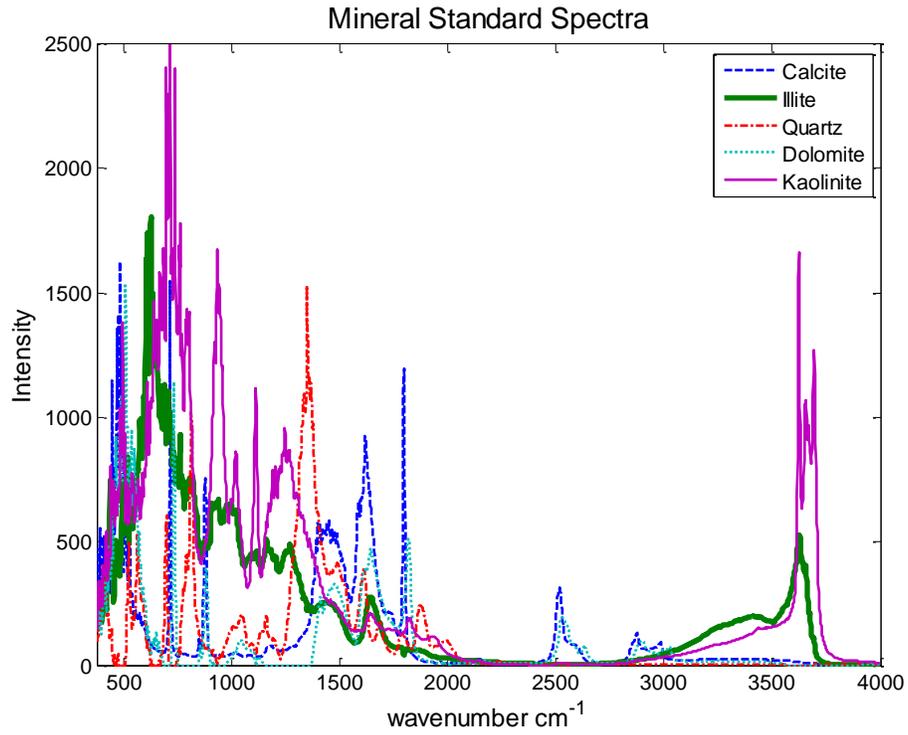


Figure 4. Standard mineral DRIFTS spectra.

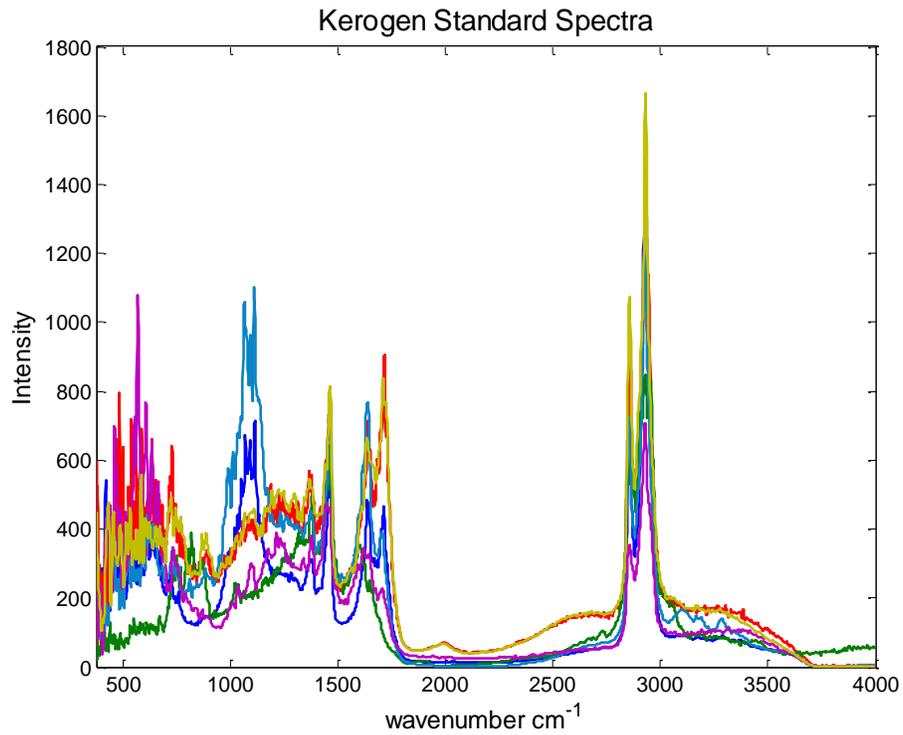


Figure 5. Isolated kerogen DRIFTS spectra.

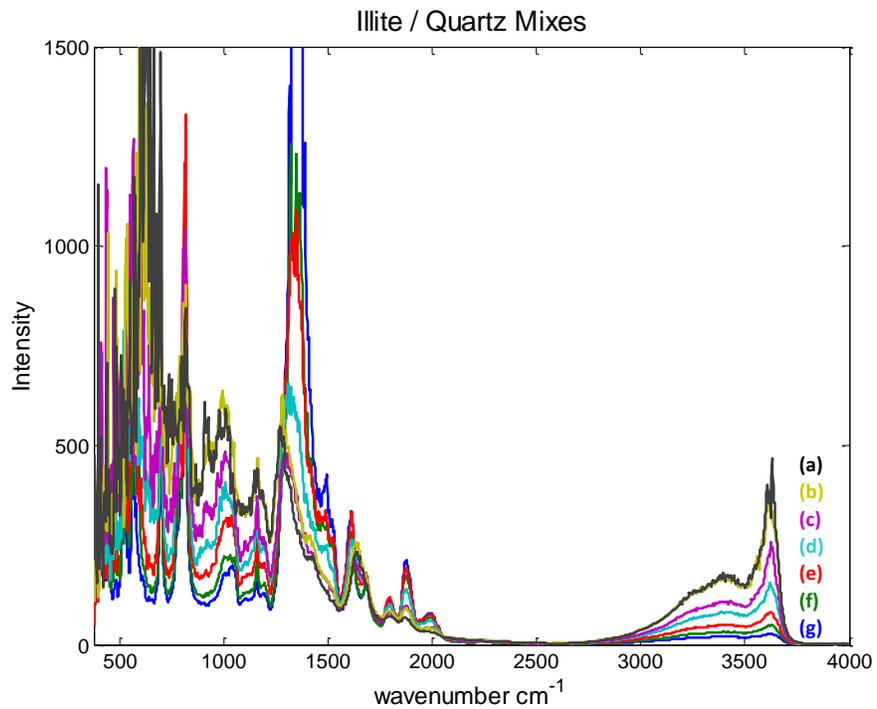


Figure 6. DRIFTS spectra of artificial mixtures containing varying known amounts of illite and quartz in the following proportions: (a) 90:10 (b) 80:20 (c) 70:30 (d) 50:50 (e) 30:70 (f) 20:80 (g) 10:90.

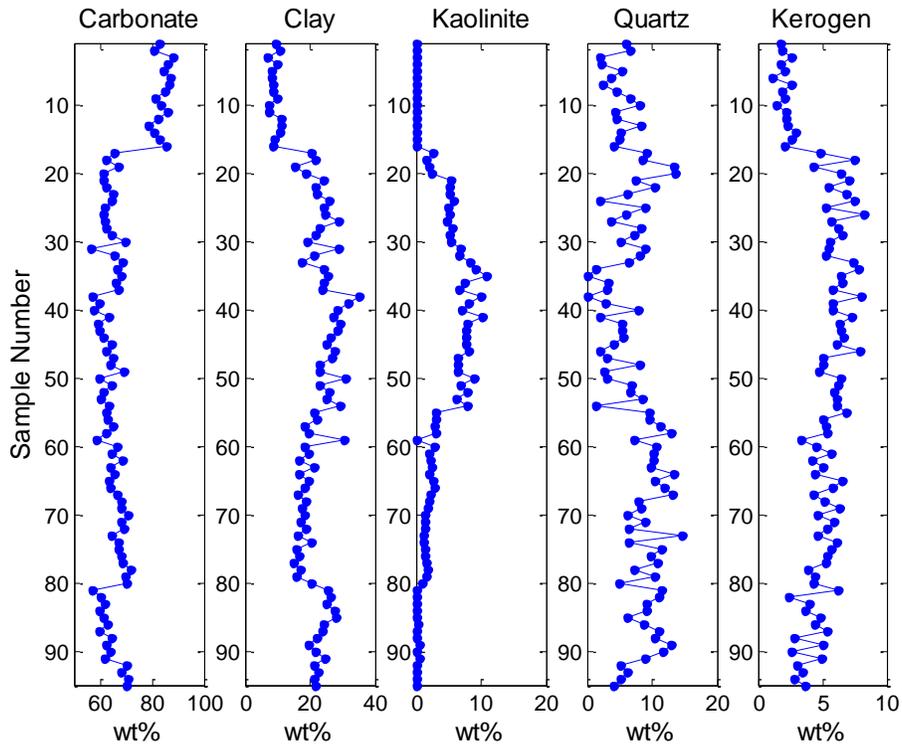


Figure 7. Mineral concentrations from DRIFTS measured on cuttings samples plotted vertically against sample number to show the formation changes.

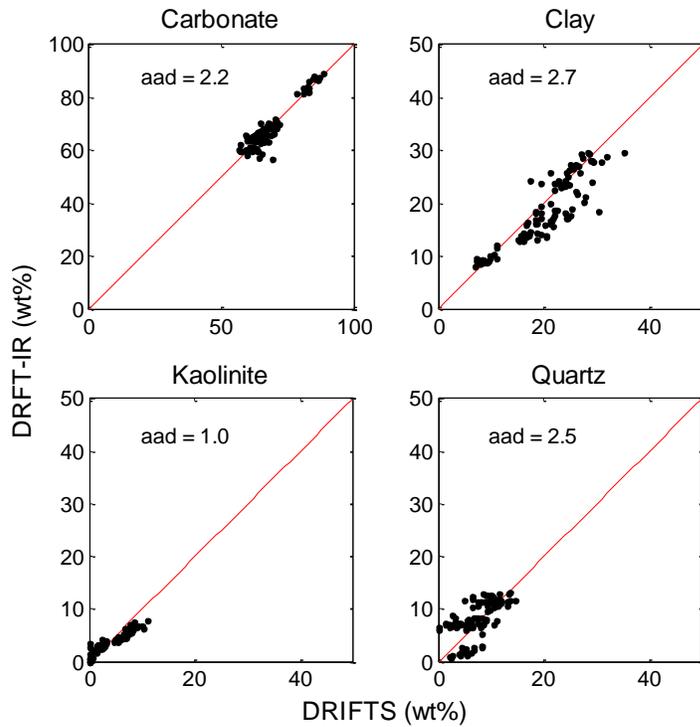


Figure 8. Comparison of DRIFTS mineralogy in weight percent and transmission DRFT-IR mineralogy in weight percent.

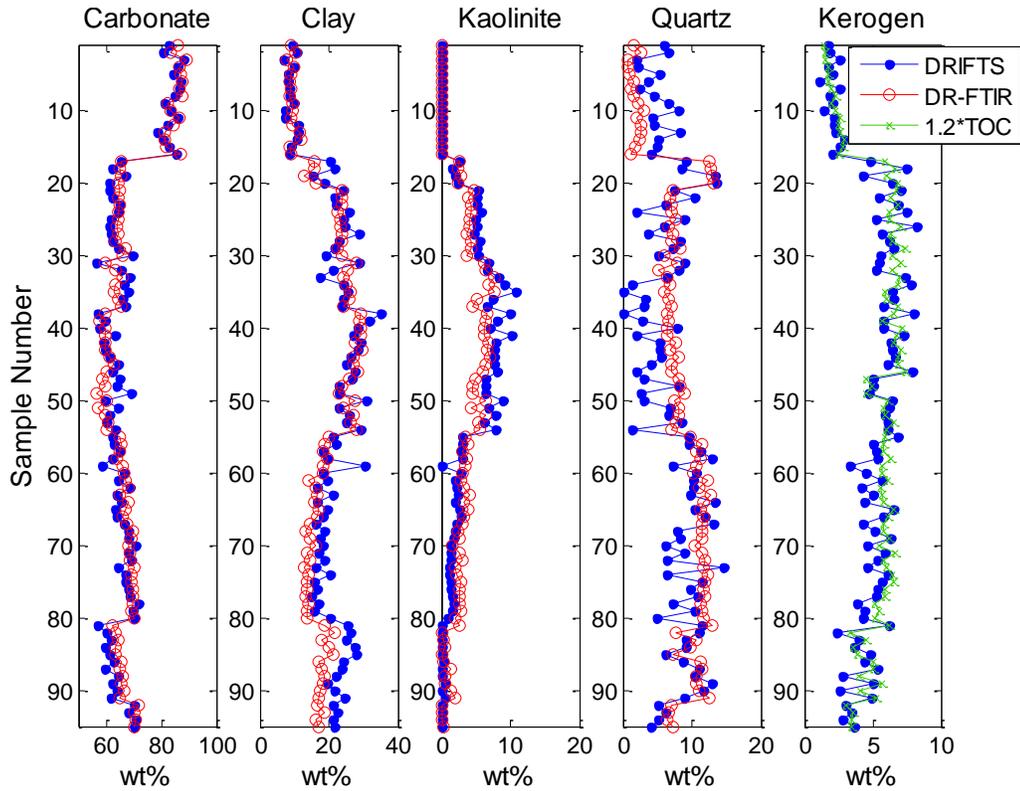


Figure 9. DRIFTS mineralogy and kerogen are plotted as closed circles and overlaid by transmission DRFT-IR mineralogy as open circles in tracks 1 through 4 and 1.2\*TOC is indicated by 'x's in track 5. DRIFTS results give very similar results to the highly accurate DRFT-IR and 1.2\*TOC values.

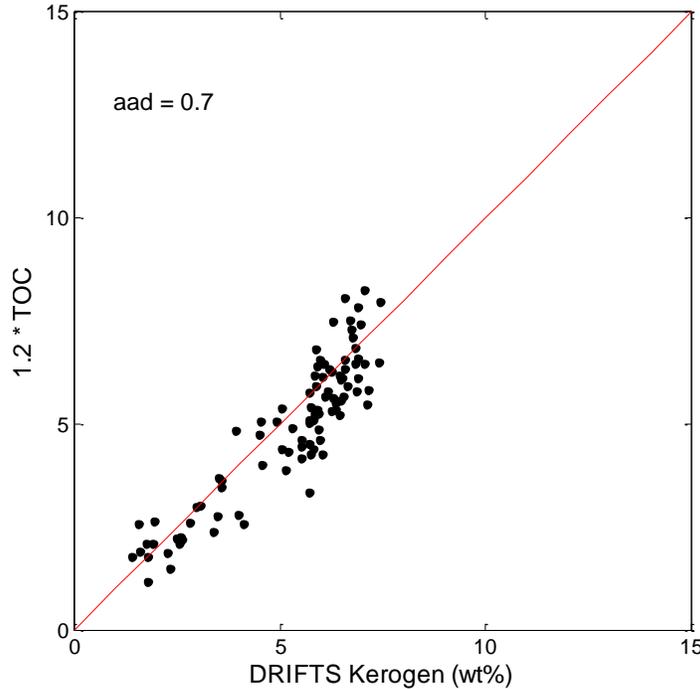


Figure 10. Comparison of DRIFTS kerogen in weight percent plotted and 1.2 \* TOC measured by LECO.