

Log Interpretation Parameters Determined by Analysis of Green River Oil Shale Samples: Initial Steps

Michael M. Herron, Malka Machlus, Susan L. Herron

Schlumberger-Doll Research, Cambridge, Mass.

Abstract

Determination of those parameters which are suitable for converting Green River well log data into useful variables is a challenging task because the formation components are very different from those encountered in conventional oil reservoirs. Among the differences are the solid nature of the hydrocarbon and the presence in significant abundance of unusual minerals such as dawsonite and nahcolite. We have found that a useful approach in such a case is to develop a data table of measurements made on core and outcrop samples comprising quantitative mineral abundances, chemical concentrations, and computed properties from nuclear forward modeling. As a prelude to mineral analysis of Green River samples, we have upgraded our analysis system. In 1993 and 1997, we showed that assemblages of common sedimentary minerals could be quantitatively analyzed using Dual Range (combined mid- and far-IR) Fourier Transform Infrared (DRFT-IR) spectroscopy. The technique relied on rigorous sample preparation procedures which produced spectra that honored the linear portion of Beer-Lambert law. We analyzed known artificial mixtures as a function of the spectra of standard minerals and in each case, the standard errors on minerals identified by our technique were 1- 2 weight percent. Mineral standards now include quartz, feldspars, calcite, dolomite, ankerite, siderite, illite, smectite, kaolinite, chlorite, glauconite, muscovite, biotite, pyrite, dawsonite, nahcolite, trona, buddingtonite, and halite. We have collected over 110 outcrop samples and 160 core samples from the Green River formation. Analysis of chemistry and mineralogy of these samples is underway and preliminary results will be presented.

Introduction

The Green River formation is notoriously heterogeneous both vertically and horizontally. And yet, some features can be correlated horizontally over hundreds of kilometers. In many of the papers presented at this symposium, the formation was treated as a homogeneous body with singular values of thermal conductivity, etc. But the Green River formation is quite heterogeneous as can be seen in outcrop or core photos. It is also mineralogically very complex.

Optimal development of Green River strata will benefit from a detailed continuous profiling of the formation mineralogy, porosity, kerogen content, and water saturation. This type of information is most readily obtained for conventional oil and gas reservoirs from interpretation of wireline geophysical and geochemical log data. In many cases, a

standard inversion of such data yields meaningful results because the mineralogy of many oil reservoirs is similar (Herron et al., real time).

An accurate inversion of geophysical and geochemical log data for mineral and fluid volumes requires that the response parameters for the constituents be known, and that there is sufficient contrast in signature to enable distinction of one component from another. For some minerals, response parameters for many geophysical measurements can be determined from the matrix density and chemical formula (McKeon and Scott, 1988). However, many common sedimentary minerals have chemical compositions that are more complex than the simple chemical formula and a more complete chemical characterization is required to determine the log response

parameters (Herron and Herron, 1997). In such minerals, chemical elements such as boron and transition elements influence a variety of nuclear log responses due to their large thermal neutron capture cross sections.

Methodology

We approach the problem of characterization of Green River minerals in two ways. The first is end-member characterization, where pure end-member minerals are retrieved from select locations and analyzed for multi-element composition. These pure end-member minerals are from collection locales that may be thousands of miles from the Green River formation. The second approach is to use Green River samples with varying, though not pure, concentrations of minerals. These are also subjected to detailed chemical analysis and the end-member concentrations are determined by statistical analysis of the data.

The mineralogy of these samples is determined by Dual Range Fourier Transform Infrared (DRFT-IR) analysis (Herron et al., 1997). X-ray diffraction is the customary methodology for mineral assessment in the industry. Although XRD is the preferred method for mineral identification, it is usually only semi-quantitative at best (Srodon et al., 2003). In contrast, DRFT-IR has been shown to provide quantitative analysis of minerals when the sample spectrum is solved as a linear combination of standard mineral spectra. This requires that the minerals in a sample also be in the standard library.

For dawsonite, we found sources of the pure mineral from Francon Quarry in Quebec and Terlano, Italy. In each case, the dawsonite consisted of tiny crystals attached to a rock matrix (Figure 1). The crystals were manually isolated under a microscope and collected for DRFT-IR analysis. We did not recover enough material for complete chemical analysis. We received nahcolite from Searles Lake in California. We received trona from Green River, Wyoming and from Wamsutter, Wyoming. We received a sample of buddingtonite from

Menlo Park, California. These and other mineral standards were added to the standards library described in Herron et al. (1997).

Both the end member characterization and the statistical analysis of samples with varying mineralogy involve multi-element chemical analysis. We used SGS Laboratories in Don Mills, Ontario, Canada to analyze for major elements Al, Ca, Cr, Fe, K, Mg, Mn, Na, P, Si, Ti, S, H (as H₂O⁺) and C (as organic carbon and CO₂) plus Loss on Ignition, Gd, Th, U, Ag, As, B, Ba, Be, Bi, Cd, Ce, Co, Cs, Cu, Dy, Er, Eu, Ga, Ge, Hf, Ho, In, La, Li, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sc, Sm, Sn, Sr, Ta, Tb, Tl, Tm, V, W, Y, Yb, Zn, Zr. Analytical techniques include Induction Coupled Plasma (ICP) Atomic Emission Spectroscopy, ICP Spectrometry, X-Ray Fluorescence, and LECO.

The chemical concentrations are used to compute the nuclear logging parameters on the formation basis, *i.e.* defining the formation as the sum of the minerals and the kerogen, and also on a kerogen-free basis. Ellis (1987, pp. 187-190) described the value of matrix gamma ray, GR_{mat} for rock as a linear combination of the ²³⁸U, ²³²Th, and 40K concentrations.

$$GR_{mat} = 4 \text{ Th} + 8 \text{ U} + 16 \text{ K},$$

where Th is the thorium concentration in ppm, U is the uranium concentration in ppm, and K is the potassium concentration in weight percent. The remaining nuclear parameters were calculated using the SNUPAR program (McKeon and Scott, 1988; Herron and Herron, 1997). The pa-



Figure 1: Dawsonite crystals emanating from rock matrix

rameters calculated include the thermal neutron capture cross section, the photoelectric factor in barns per electron, the apparent thermal and epithermal neutron porosities, and the hydrogen index.

For the statistical analysis of samples, we have collected over 100 outcrop samples from most of the Green River basins covering each of the major rich and lean zones and exploring some geographic variance within a basin and between basins. For the existing cores, we have collected over 160 core samples, again from each of the R- and L-zones and with significant geographic variability.

Minerals in the collected samples include quartz, sodium feldspar, potassium feldspar, calcium feldspar, muscovite, biotite, pyrite, calcite, dolomite, high magnesium calcite, aragonite, ankerite, siderite, magnesite, illite, kaolinite, smectite, chlorite, glauconite, opal-A, opal-CT, chert, anhydrite, gypsum, barite, hematite, fluorite, celestite, analcime, apatite, dawsonite, nahcolite, trona, buddingtonite and halite.

Results

The results of this study focus first on the DR-FTIR spectra of some of the mineral added to our library to address the special

needs of the Green River formation. Figure 2 shows the absorbance spectrum of a sample of dawsonite from Monticolo, Italy. This is a terrific spectrum because it shows absorbance not simply in the $<1800\text{ cm}^{-1}$ range where most minerals absorb, but it also has a very significant peak at 3300 cm^{-1} , which is absent in most other minerals and is therefore diagnostic of dawsonite.

One of the interesting facets of the development of our DRFT-IR library has been the appreciation that, for a given mineral, there may exist slight variations in the spectrum due to many possible factors including degree of crystallization, temperature of solidification, and stress history. To accommodate these factors, we have sought to include multiple mineral standards that sample the inherent diversity of spectra.

Figure 3 shows a dawsonite DRFT-IT spectrum for a sample of dawsonite from Francon Quarry, Quebec. As with the Monticolo sample, the dawsonite crystals had to be painstakingly removed from the host material before a KBr pellet could be made. The spectrum of the Quebec dawsonite is very similar to that of the Monticolo dawsonite, but the peak heights are typically only 70% as high. Using only one dawsonite would yield a significant uncertainty in the quanti-

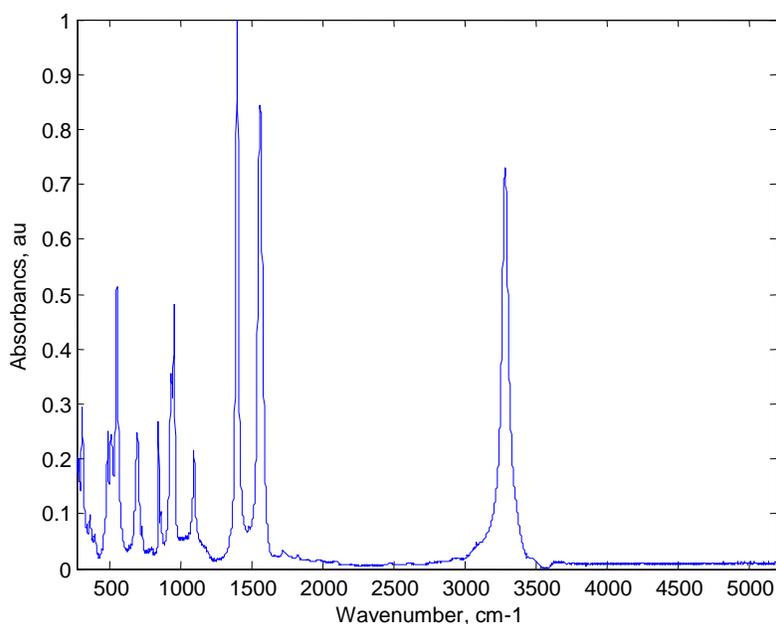


Figure 2. DRFT-IR spectrum for dawsonite from Monticolo, Italy

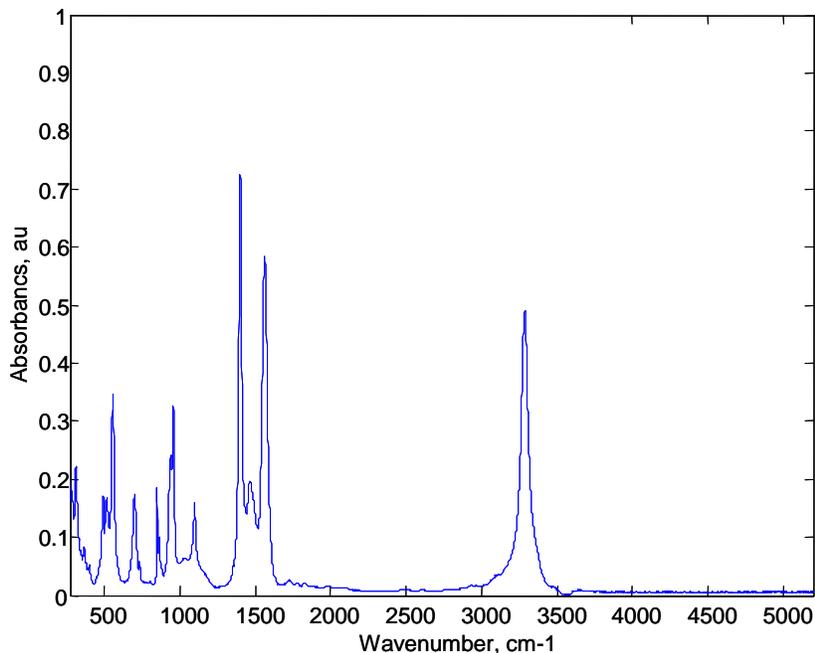


Figure 3: DRFT-IR spectrum for dawsonite from Francon Quarry, Quebec

fication because of this difference.

Nahcolite and trona, two minerals that have been found in the Green River formation, have DRFT-IR spectra that are very similar. Figure 4 shows the spectra of these two sodium bicarbonate minerals. The spectra are so similar that accurate distinction will be difficult and results will probably have to

be reported as the sum of the two minerals.

Buddingtonite has been suggested by Burnham (personal communication, 2008) to be a possible mineral constituent in the Green River formation carrying the non-kerogen nitrogen in the formation. Buddingtonite is a mineral formed by ammonia alteration of a feldspar. The DRFT-IR spectrum of two

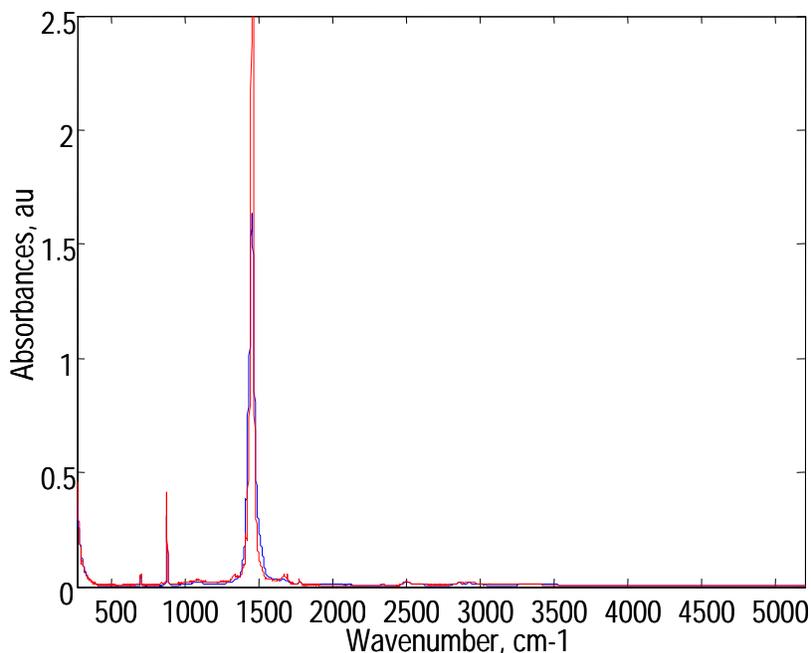


Figure 4: Nahcolite (blue) and trona (red) have very similar DRFT DRFT-IR spectra.

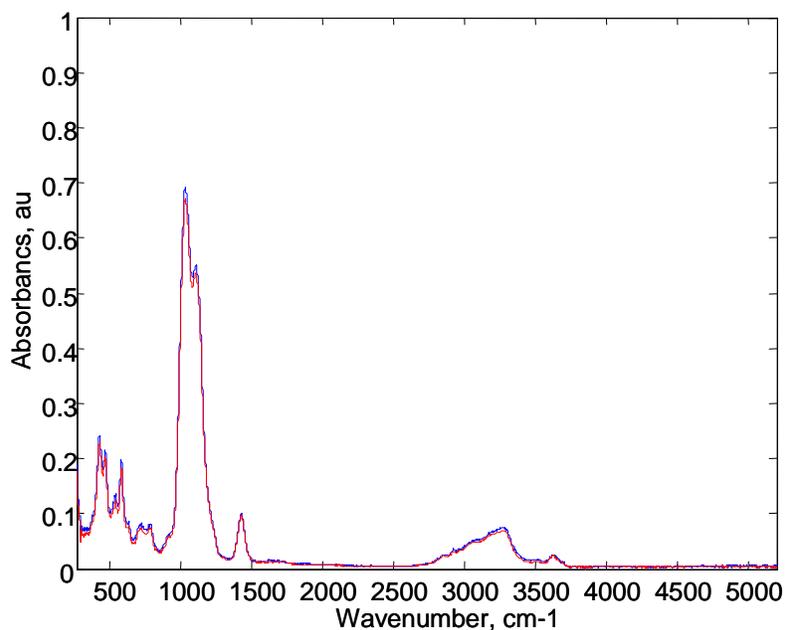


Figure 5: DRFT-IR spectra of two samples of buddingtonite, an ammonia alteration of feldspar.

buddingtonite samples is shown in Figure 5. The ramp between 2800 cm⁻¹ and 3300 cm⁻¹ appears to be diagnostic. When we included buddingtonite in analysis of some of Burnham's samples, we recorded several weight percent in a few samples.

Two samples of kerogen, mechanically removed from a Green River oil shale sample, were analyzed for their DRFT-IR spectrum

(Figure 6). These samples were processed as though they were mineral samples. The major feature of the spectrum is the doublet at around 2900 cm⁻¹. These peaks have been seen to change as kerogen type and thermal history change. We do not yet have the array of kerogen standards to address such variability.

One other standard of interest is halite.

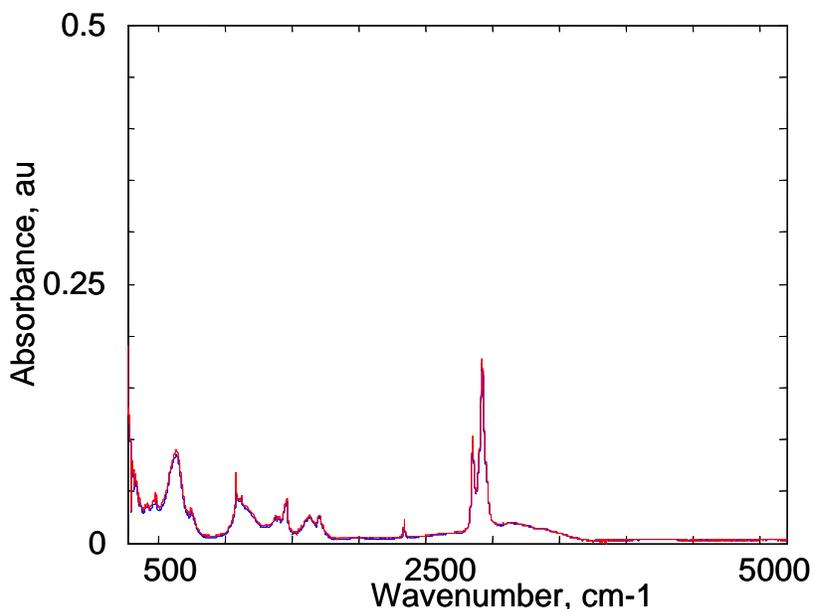


Figure 6: DRFT-IR spectra for two kerogen samples.

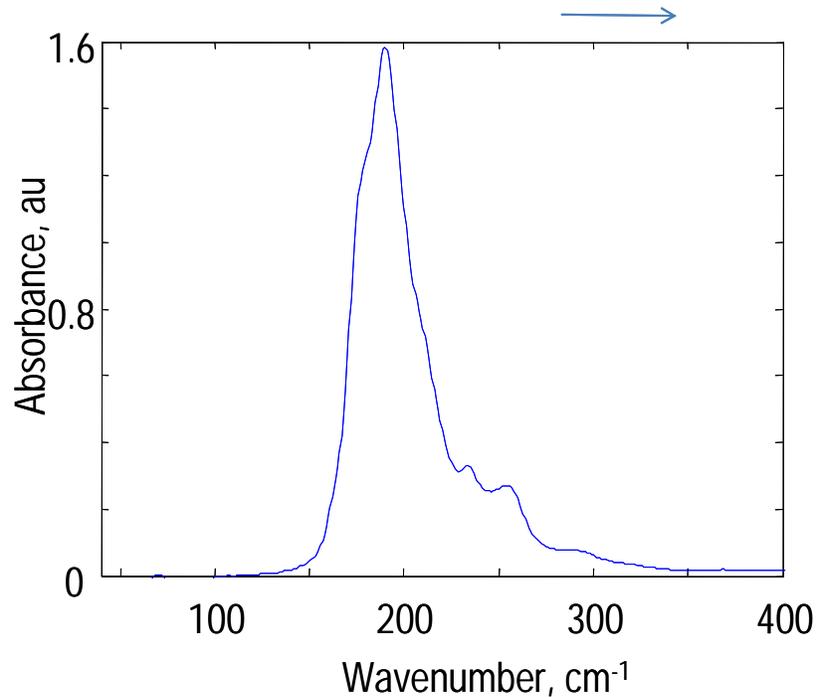


Figure 7. Far-IR spectrum of halite with polyethylene medium. The vertical line represents the normal lower cutoff of KBr medium pellets.

Halite is present below the saline zone in much of the Green River Formation where fresh waters have not dissolved it. In normal DRFT-IR, a tiny amount of rock sample is mixed with KBr and pressed into a pellet for transmission. Halite is however transparent in the region we usually examine. It has absorbance bands in the same far-IR region as does KBr. A different medium than KBr, one that is transparent in the far-IR is required for halite quantification. We chose polyethylene to produce the far-IR spectrum of halite shown in Figure 7.

While we have only begun to analyze kerogen types, we were interested in examining how sensitive the DRFT-IR spectrum for kerogen is as a proxy for the total organic carbon content. Figure 8 compares the absorbance at a single frequency in the 2900 cm^{-1} band that is characteristic of organic matter to the total organic carbon content of a dozen Green River oil shale samples. This simple comparison suggests that it may be possible to simultaneously estimate the kerogen content and the mineralogy.

Finally, we examine the practice of associating gamma ray activity with clay content.

Total gamma ray content in wells has been measured for a long time and it is true that in many shales the gamma ray activity is higher than in sandstones or carbonates. So qualitatively, the higher gamma ray activity has been used for decades. One of the benefits of the study we are beginning is that we can collect hard data on core and outcrop samples of the true clay content as determined by DRFT-IR as well as the chemical concentrations of thorium, uranium, and potassium on the same sample.

Figure 9 shows the comparison of total gamma ray computed from the Th, U and K concentrations, and total clay content measured on the first seven Green River samples. It is clear from these few data that there is not a simple relationship between the gamma ray content and the clay content.

Summary and Conclusions

To develop relationships between parameters which can be measured in geophysical and geochemical well logging, we have begun to apply two approaches.

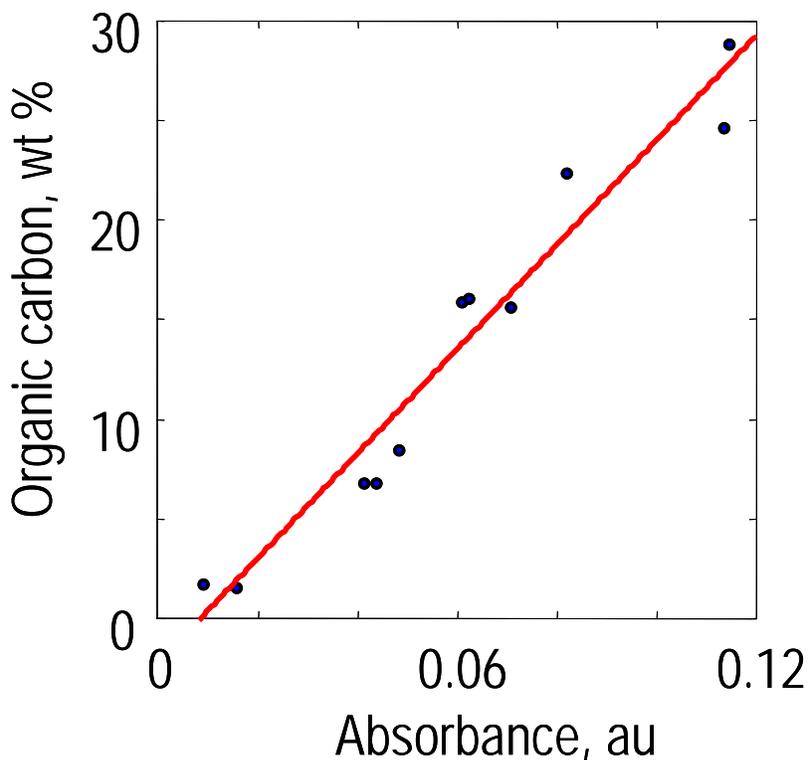


Figure 8. Relationship between absorbance at a single frequency in the kerogen peak to the organic carbon content. Significant linearity is apparent, but best practices for estimating kerogen content from multi frequency IR data are not yet solved.

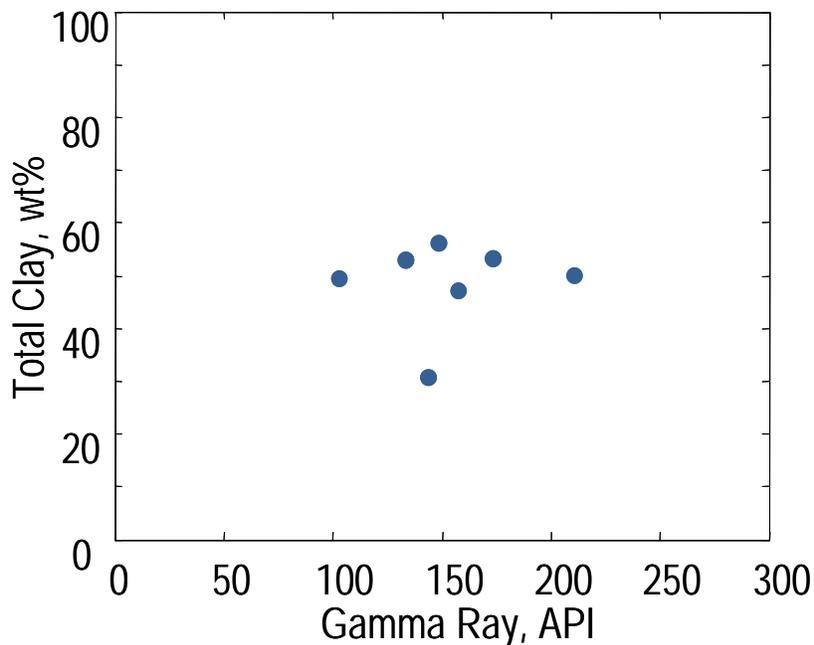


Figure 9: Relationship between the Gamma Ray, computed from Th, U and K concentrations, and the total clay content determined from DRFT-IR spectroscopy. N

In the first, we acquire pure mineral standards to address the unique mineralogy in the Green River formation. Then we analyze these pure minerals for their geophysical and chemical properties. In addition, we compute nuclear logging properties using published relationships and the SNUPAR program. This gives end-point properties for use in programs such as ELAN and Flame which solve for formation volumes from geophysical and geochemical log data.

The second approach is the statistical analysis of samples with varying concentrations of each constituent to determine relationships that might not be intuitive or readily apparent. This approach has permitted short cut estimations of formation mineralogy or petrophysical properties in many oilfields.

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