

Fourier Transform Infrared Spectroscopic Determination of Shale Minerals in Reservoir Rocks

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ABSTRACT: Attenuated Total Reflectance Fourier transform infrared spectroscopy together with multivariate statistical regression was used to produce calibrations between spectra of standard mineral mixtures and gas shale reservoir rocks. A Classical Least Square (CLS) model was developed from the attenuated spectra of mixtures of five mineral standards chosen to represent the most frequently encountered minerals in shale-type reservoir rocks namely: quartz, illite/smectite (30:70), kaolinite, calcite and dolomite. The CLS model developed was able to quantify the mineral components of independent mixtures with an absolute error between 1 to 3wt% for all the pure minerals in the mixtures. Samples from a suite of shale reservoir rocks were analysed using standard Quantitative X-Ray Diffraction (QXRD) and with FTIR. Unknown mineral concentrations in the samples were then predicted using spectra and the calibration equations. Good correlations were achieved between the QXRD and ATR-CLS predicted concentrations ($r^2 > 0.8$), with average absolute error of between 1 to 6wt%. This provides evidence that attenuated FTIR is a promising method for rapid and accurate determination of minerals in reservoir rocks for building higher resolution data without additional time consuming and expensive traditional analyses.

Keywords: Attenuated Total Reflectance Infrared Fourier Transform Spectroscopy; Classical Least Square analysis; Mineralogy; Reservoir rocks; Shales

INTRODUCTION

The depletion of conventional petroleum sources and the increase in oil prices urge the search for alternative energy sources. The production of shale gas from gas shale is one of the energy generation alternatives available. Gas shale is one of the most promising sources of energy, with large deposits situated in many parts of the world. The term shale gas refers to unconventional, continuous-type, self-sourced resources contained in fine grained (ranging from clay to very fine sandstone), organic-rich, low permeability reservoirs in which thermogenic or biogenic methane is stored as free gas in the matrix or fracture porosity, or as adsorbed/dissolved gas on the organics and/or clays (Faraj *et al.*, 2004; Montgomery *et al.*, 2005; Ross and Bustin, 2007; Bustin *et al.*, 2008; Ross and Bustin, 2008).

The composition and origin of produced natural gas is fundamental for assessing reservoirs and guiding exploration strategies and has an impact on the overall economics of a gas shale play. Shale gases are primarily methane with minor amounts of other gases,

including ethane, carbon dioxide and nitrogen. The key elements for successful development of shale gas are the presence of adequate gas in place and either the existence of adequate permeability or a rock of suitable mechanical properties for efficient completion and fracture stimulation. The presence of gas in place requires adequate gas generative organic matter to generate either biogenic or thermogenic gas, and to retain significant gas. The shale gas petroleum system is self-contained. Shales act as the critical lithological units for most or all the key components of the shale gas petroleum system. Definition and prediction of the geochemical, fluid flow and geomechanical properties of shale-rich sequences must therefore be placed at the heart of any risking methodologies for shale gas exploration and production.

The inorganic constituent of the shales affects the reactions of the organic matter both physically and chemically (Karabakan and Yürüm, 2000). Previous researches acknowledged the fact that the minerals in the shale influence the conversion of kerogen and the release of gas during shale processing

(Bhargava et al., 2005). (Karabakan and Yürüm, 1998) studied the effects of mineral matrix in the reactions of oil shales using pyrolysis and oxidation reactions of Turkish Goynuk and US Green River oil shales. They reported the inhibition effects of silicate minerals and catalytic effects of the carbonate minerals on the pyrolysis reactions of the samples they studied. The specific mineralogical compositions can be very important in understanding fluid/rock interactions, acidizing challenges and kerogen adsorption and desorption. Accordingly, the quantitative determination of mineral matter in gas shale is an important analytical problem and one this work seeks to address. Such mineralogical data is useful in: the initial exploration phase; the construction of geological models and ensuing plans for the development and production; as well as the planning and execution of improved/enhanced oil recovery treatments (Breen et al., 2008).

The development of non-destructive, rapid logging techniques such as X-ray fluorescence (XRF) for major elements, reflected light for bulk carbonate, and, magnetic susceptibility for continental supply, have radically changed the potential for generating continuous high quality, and high resolution reservoir data (Deaton and Balsam, 1991). Despite progress in scanning technologies (i.e., the use of Nuclear Magnetic Resonance, 3-D Sonic Scanning and micro-resistivity logs), one of the most fundamental parameters in reservoir evaluation; mineralogy, is still not routinely determined using scanning techniques with high accuracy. Furthermore, the paucity of mineralogical quantification cannot be overemphasised giving the continuous decline in production from conventional sandstone reservoirs and the paradigm shifting towards shale gas exploration.

This study demonstrates that the method of Fourier transform infrared spectroscopy (FTIR) can be applied to reservoir rocks for the rapid determination of minerals. Spectroscopic methods have been used for almost 40 years in marine science (Deaton and Balsam, 1991; Mitchell, 1993; A.C. et al., 1995). Mid-infrared spectroscopy has been used for the determination of relative abundances of

quartz, clay and calcite in a range of deep sea sediments (Herbert et al., 1992). Few studies have used Near-infrared spectroscopy (Basalm and Deaton, 1996); (Chang et al., 2005) and its full potential is yet to be fully realised. Spectra give a graphical representation of how infrared light acts with inter atomic bonds in inorganic rock materials (particularly SiO_2 , Al_2O_3 , and Fe_2O_3) and it is the excitation of these bonds which gives rise to different spectra with the absorption being directly related to the mineral concentration in these rocks (A.C. et al., 1995).

Several studies have demonstrated the feasibility of combining infrared Fourier-transform spectra and multivariate statistical analyses to provide a simple, rapid chemometric technique for the simultaneous qualitative and quantitative analysis of soil properties. For example a methodology for obtaining quantitative mineral concentrations from transmission FTIR spectroscopy was presented by Abigail and Michael (1993). The study of Holman et al. (1994) highlight the fact that ATR-FTIR spectroscopy can provide accurate quantitative results when applied to analyse complex mixtures. Janik et al. (1995) demonstrated how experimentally derived soil mineralogical and organic components may be correlated with the infrared spectra of some of these components based on the theory that Mid-infrared diffuse reflectance Fourier transform (DRIFT) spectra of powdered soils present the major components, relative to their concentrations. They used PLS to model the properties of some 298 eastern and southern Australian soils and their spectra and then used the model to classify the soil spectra and their associated major oxides including SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , MgO and CaO . The PLS predicted values for SiO_2 , Al_2O_3 and Fe_2O_3 versus X-Ray Fluorescence (XRF) resulted with linear regression R^2 values of 0.973 - 0.917. Regressions for the other oxides, e.g. TiO_2 , MgO and CaO , were generally curved with a linear calibration giving severe underestimations at high concentrations. Transmission FTIR measurements however, require sample preparation in order to record a good quality spectrum; samples are studied

in the form of self-supporting thin and porous discs. The samples have to be diluted in KBr pellet due to the high absorptivities associated with mineral (Karakassides et al., 1997). The pressing of KBr pellet with clay is often associated with alteration in spectrum through absorption or exchange of the K into the clay structure (Ray and Ursula, 1998).

The DRIFTS method is applicable to powder and over comes the need to prepare the KBr pellet therefore, provide the advantage of rapid analyses time without having to go through rigorous sample preparations (Madejová and Komadel, 2001). Although, the samples still need to be mixed with KBr to minimise interference effect created by particle size and the incident IR wavelengths (towards the low frequency region, normally below 1000cm^{-1}) known as the Restrahlen effects

ATR technique combats the most challenging aspects of sample preparation and spectral reproducibility encountered in Transmission and DRIFT analyses. An attenuated total reflection accessory operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample. Unlike DRIFTS measurements, ATR sampling does not produce totally absorbing spectral bands because the effective path-length is controlled by the crystal properties thereby minimizing sample preparation time. A much smaller area of contact is required; as a result spectra can be obtained from a wide variety of solid materials including minerals. Other key advantages of the ATR include: improve sample-to-sample reproducibility; minimal user-to-user spectral variation and most importantly, the improved spectral acquisition and reproducibility associated with this technique leads to better quality database building for more precise material verification and identification.

(Clegg, 1998) highlights the principles and advantages involved in the technique while focussing on the distinction between bulk and surface mineralogy of sandstone-type rocks. Herein the feasibility of applying multivariate statistical models based on Classical Least Squares (CLS) to mid-infrared spectra

obtained via Attenuated Total Reflectance Fourier Transform Spectroscopy is investigated.

CLS is a multivariate statistical technique (Geladi and Kowalski, 1986); (Beebe and Kowalski, 1987) that can be used to quantify analyte in infrared spectra that are expressed using the Beer-Lambert law for absorbance or the Kubelka Munk equivalent for spectra obtained using DRIFTS. This technique is particularly appropriate when analysing complex multiple spectra, which contain broad and overlapping bands. In essence the CLS algorithm examines regions of the spectra to determine which areas vary as a function of component concentration (Martens and Naes, 1989.). (Hughes and Jones, 1992; Hughes et al., 1991) initially applied several multivariate calibration techniques to infrared spectra of drilled cuttings/solids, to quantify the mineralogical content. They demonstrated how FTIR spectroscopy can be combined with PLS spectral fitting to quantify the mineralogy of a complex mixture. They were able to estimate the types and amounts of clays, carbonates and the silicates. However, the technique gives poor estimation when extrapolated in order to distinguish between mineral species where only slight difference in structure or chemistry exists. (Hughes et al., 1995) applied Partial Least Squares (PLS) algorithms to DRIFT spectra to Portland cement and were able to describe up to 14 components with adequate accuracy. In another study, (Janik and Skjemstand, 1995) combined PLS and DRIFTS for the successful analysis of tubular halloysite in kaoline samples, whilst (Peussa et al., 2000) were able to determine, with sufficient accuracy, the hydroxyl group content in calcined silica thus removing that dependence on time consuming thermo-gravimetric analysis.

In CLS computation, the complex relationship between a very large number of X independent variables and dependent Y variables is compressed into a small number of linear combinations of the original X variables, and only those components are used in the calibration (Naes et al., 2004). In addition, the dependent Y variables are used explicitly in how each factor (component) is

computed from spectra (Bjorsvik and Martens, 2000). Possibly the most important advantage of CLS regression in comparison to more simple regression methods is that many collinear, independent **X** variables can be handled which is essential in FTIR analysis because of the large number of spectral data points which correlate with each other (Martens and Naes, 1989.).

CLS regression model is established between matrix **X**, containing absorbance at *m* wave - numbers for *n* samples; a **Y** matrix containing the concentration-path length product of *p* components in the *n* samples and a **K** which is a *p* by *m* matrix. Each row of **K** corresponds to the spectrum of one of the *p* analytes at unit concentration and unit path length. Each row of **X** is the spectrum of one of the *n* samples, containing the absorbance values at different wave numbers. The matrix formulation of Beers Law is:

$$\mathbf{X} = \mathbf{YK} \quad (1)$$

Where:

X is the *n* by *m* matrix of absorbance of the samples

Y is the *n* by *p* matrix containing the concentration-pathlength product of the *p* components in the *n* samples

K is a *p* by *m* matrix.

Any sample's spectrum is assumed to be the sum of the spectra of *p* components in the sample. Prior to modelling, the mixtures are divided into calibration and validation sets. The composition of new samples (*i.e.*, unknowns) can be determined immediately from their spectra and **K**. Designating the spectrum of a single new sample as **X_{new}**, equation (1) can be rearranged to give a vector of estimated concentrations for this sample:

$$\mathbf{Y}_{new} = \mathbf{X}_{new} \boldsymbol{\beta} = \mathbf{X}_{new} \mathbf{K}^T (\mathbf{K} \mathbf{K}^T)^{-1} \quad (2)$$

Where $\boldsymbol{\beta}$ is a **matrix** containing *p* column vectors, one for each component.

The individual regression vectors are thus the columns of the pseudo-inverse of **K**, symbolized by \mathbf{K}^\dagger :

$$\boldsymbol{\beta} = \mathbf{K}^T (\mathbf{K} \mathbf{K}^T)^{-1} = \mathbf{K}^\dagger \quad (3)$$

The aim of this study was to develop a CLS calibration model based on the Attenuated spectra of mixtures of mineral standards (ATR-CLS MODEL) for prediction of the mineralogy for shale gas reservoir.

MATERIALS AND METHODS

A suit of clastic and carbonates mineral mixtures were prepared from five mineral standards based on mineral combinations commonly found in shale reservoir rocks. The five minerals chosen to make up the mineral mixtures are: quartz, Illite-smectite (70:30), kaolinite, calcite and dolomite and were obtained from the British Mineralogical group standards with all standards having a percentage purity of 99.7%. All the minerals were used as received without further treatment. Each mineral in the mixture set was distributed within concentration ranges typical of sedimentary rock. A total of 23 mixtures were used to develop and validate the ATR-CLS model. Fourteen of the twenty-three mixtures were used to develop the model, and the remaining nine were used in the validation process. The weight percent ranges (concentrations) of the pure mineral components used in developing the model are given in Table 1. Furthermore, the mineral content of seven reservoir shale core samples from the Nile Delta and the Western Canada Sedimentary Basin were analysed using QXRD and the ATR-CLS model. This was done in order to assess the prediction capability of the model.

Table 1. The relative compositions of mineral standards used to develop the calibration model

| Mineral | Typical structural formula | Weight % ranges |
|---------------------------|--|-----------------|
| Illite | (K,H ₃ O)(Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ [(OH) ₂ ,(H ₂ O)] | 10-60 |
| Smectite(Montmorillonite) | (Na,Ca) _{0.33} (Al,Mg) ₂ (Si ₄ O ₁₀)(OH) ₂ .nH ₂ O | 10-60 |
| Kaolinite | Al ₄ Si ₄ O ₁₀ (OH) ₈ | 0-60 |
| Quartz | SiO ₂ | 0-60 |
| Calcite | CaCO ₃ | 0-80 |
| Dolomites | CaCO ₃ .MgCO ₃ | 0-10 |

Sample Preparation: The pure standard minerals and the reservoir shale samples were pulverised to less than 10 μm using Tema mill. 100mg of each mixture were prepared by weighing the material to within ± 0.1 mg of the preordained amounts. The mixture was then mixed with a pestle and mortar to a consistent homogeneity of less than 2 μm . The powdered mixtures were then oven dried at 110°C for 24 hours and kept in a dessicator for the FTIR analysis.

Absorption FTIR spectra were collected with a Varian 700 Scimitar series spectrometer equipped with an ambient DTGS detector. The samples were analysed over the 4000 cm^{-1} to 600 cm^{-1} wave-number range collecting 32 scans at a resolution of 4 cm^{-1} and background scan was performed for every sample. FTIR spectra were also obtained in transmission mode in the mid-infrared range (400 to 4000 cm^{-1}) using KBr pellets (1-2 mg mineral in ~ 200 mg KBr) with a resolution of 4 cm^{-1} and 100 scans on an AVATAR 360 FTIR ESP spectrometer with OMNIC software.

The CLS model was developed on Pirouette software platform. The optimum number for factors to be used in the model development was determined from the predicted error sum of squares (PRESS). Validation correlation coefficients are used to indicate the ability of the model to predict the concentration of the components; an excellent value is 0.990 and values less than 0.975 are considered to be poor (Naes et al., 2004). Because the weight percent of the mixtures in the external validation set and data for the unknown reservoir samples were, in fact known, the calibration model could be tested for accuracy by statistically comparing the ATR-CLS predicted values for the known mixtures and in the shale samples against their known values. This provides an indication of the likely performance of the calibration model in predicting the mineral composition of unknown samples in the future.

It should be noted that, occasionally, when composition of unknown samples are predicted using the calibration model, negative mineral predictions may be obtained when the concentrations are low. This is a problem encountered in all multivariate

models, and can either be ignored or assigned as containing none of the specified components (Beebe and Kowalski, 1987).

Independent bulk quantitative mineralogical analysis of the reservoir rocks was performed using the well documented quantitative X-ray powder diffraction technique in accordance with procedures of (Hillier, 2003). The bulk samples were dried at 105°C, wet ground in a McCrone mill and spray dried to produce a random powder. X-ray powder diffraction (XRPD) patterns were recorded from 2 to 75° 2 θ using Cobalt Ka radiation range. Samples were analysed in θ -2 θ coupled mode with 0.01° step size and 2s/step sampling time. Quantitative analysis was done by a normalised full pattern reference intensity ratio (RIR) method. Clay fractions of <2 μm were obtained by timed sedimentation, prepared as oriented mounts using the filter peel transfer technique and scanned from 2 to 45° 2 θ in the air-dried state, after glycolation, and after heating to 300°C for one hour. Clay minerals identified were quantified using a mineral intensity factor approach based on the calculated XRPD patterns

Theory of data processing: The analytical procedures followed in this study ensure that absorbance bands are in the linear region of Beer's law. Standard full spectrum processing program, normalisation to optimum of 1.0 absorption, linear baseline corrections and spectra smoothing using the SavGoley polynomial functions with 2 points was run to solve for the mineralogy of the mixtures. Therefore, each mixture spectrum is a linear combination of the mineral standard spectra multiplied by the concentration of each mineral standard in the mixture. This reduced variance between FTIR spectra of the same mixture. The concentrations are determined from minimising the difference between the measured FTIR spectrum and the product of the spectra and the concentrations of mineral standards over the mid-infra red region.

RESULTS AND DISCUSSION

Mineral Standard Spectra: The absorbance FTIR spectra of the mineral standards are shown in Fig 1. The mineral standards in this set of mixtures can be divided into three major

groups: the tectosilicates (framework silicates, e.g., quartz), phyllosilicates (layer silicates, e.g., clays), and the carbonates. The mineral groups have FTIR absorbance band features that make them clearly different from one another. However, within the carbonate group the spectra are similar. Both the calcite and dolomite are characterised by the strong absorption bands due to the asymmetric

stretching vibrations of the CO₃ which occur between 1540 and 1400 cm⁻¹ (Fig. 1) (Hughes et al., 1995). The silicates spectra are characterised by Si-O stretching and bending vibrations between 1200 and 800 cm⁻¹. The phyllosilicates can be separated from the tectosilicates based on the occurrence of the O-H stretch vibrations at 3750 to 3400cm⁻¹ (Peussa et al., 2000; Hughes et al., 1995).

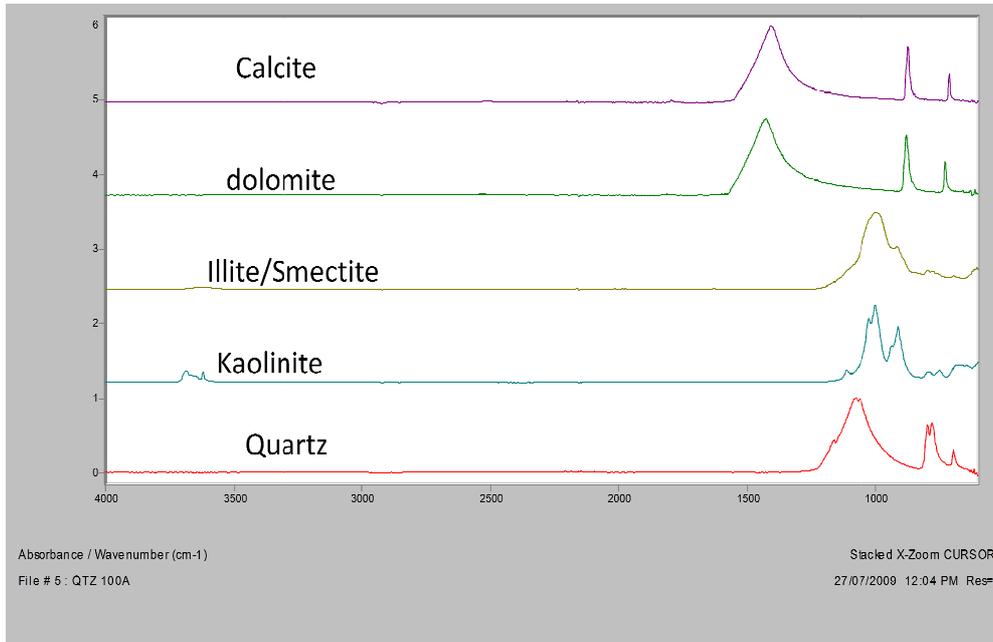


Fig.1. The FTIR spectra of the five standard minerals used to develop the calibration model showing differences and similarities in their infrared absorption characteristics.

The ability of the model to successfully predict the concentration of each mineral standard in the validation set and rock samples is represented in Fig 2. The figure shows the model output obtained from Pirouette software showing the correlation coefficients (rCal) and includes the number of factors used (at the right end of

the measured Y). For example, four factors were used to obtain a correlation coefficient of 0.994. In general, the least successful predictions were for calcite and dolomite as reflected in the scatter of data and the relatively low correlation coefficients of 0.955 and 0.946, respectively.

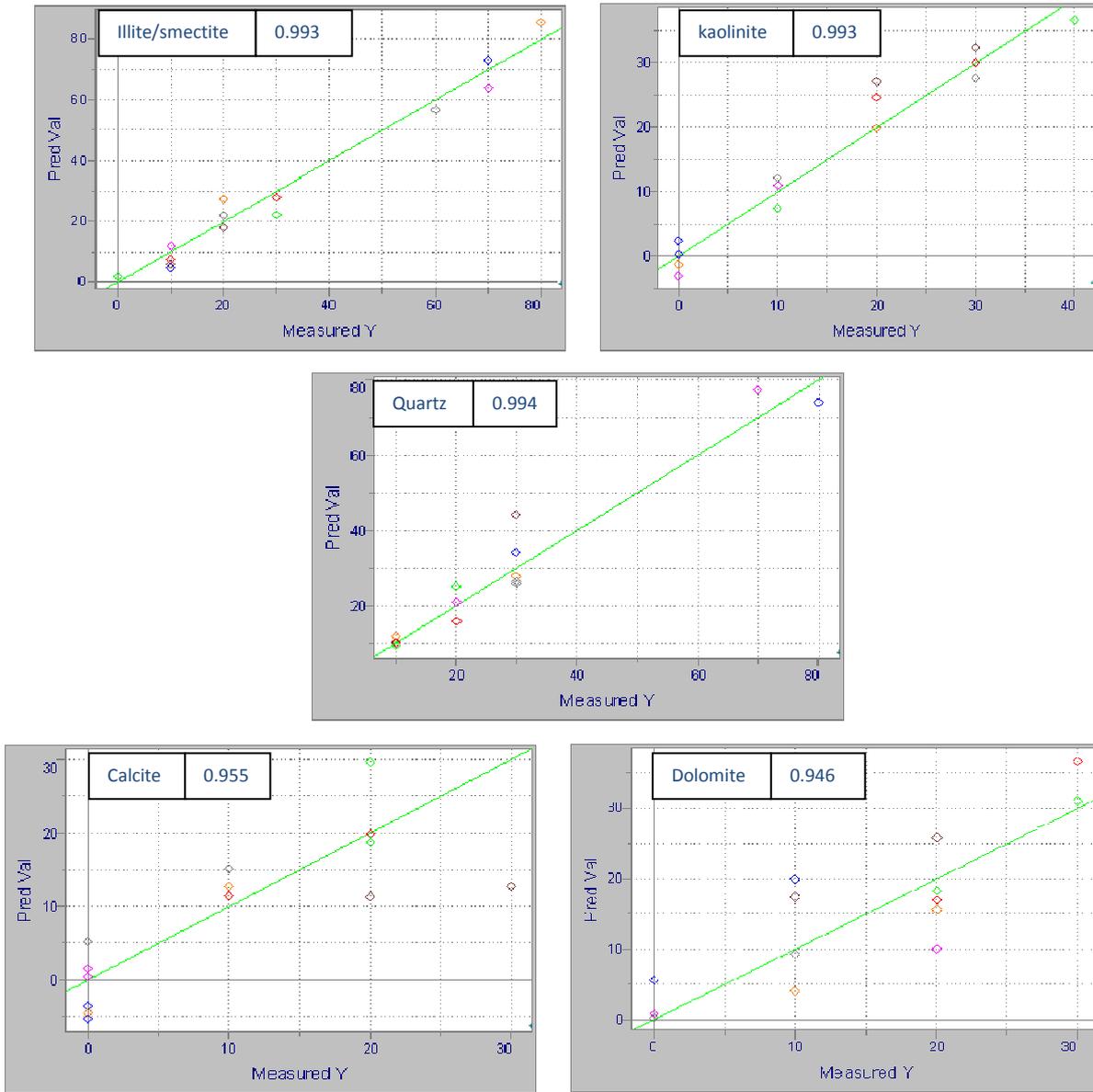


Fig.2. Plots of measured minerals concentration against the CLS-predicted concentration for the calibration sets showing calibration correlation coefficients and optimum number of factors used at the far left of Measured Y axis. Four factors were used to give the correlation coefficients.

The FTIR-CLS calibration results for each mineral in the internal validation set are plotted in Fig 3 as plots of actual against predicted concentrations. The average absolute difference (including zeros) between measured and predicted concentrations is calculated for each mineral. There is a very good agreement between the FTIR-derived and the known concentrations of the illite/smectite, kaolinite and quartz with an average absolute difference of 2.7wt%, 2.4wt%

and 1.7wt% respectively. However, the average absolute difference and the correlation coefficient for the calcites and dolomites suggest that it might be difficult to differentiate these minerals from one another as shown by significant scatter in the plots (Fig 3). A plot of the combined calcite and dolomite concentrations is presented because the method produced relatively poor predictions for the two minerals. This was anticipated as the attenuated spectra of

calcite and dolomite are very similar (Fig.1), which might be because of their similar intra-atomic bonds in the carbonate radicals (CO_3^{2-}), structure and properties (A.C. et al., 1995). These results are consistent with the findings of (Abigail and Michael, 1993) and comparable to the study of (Hughes and Jones, 1992). This demonstrates that the ATR spectra exhibit similar quantitative characteristics as spectra obtained from Transmission and DRIFT techniques.

Ideally, the spectral information in each mineral spectrum should be unique.

Consequently, if the spectra of two or more components are similar then correlations between spectra and concentration information will be difficult to distinguish and quantitative results will be inaccurate. Despite these limitations for the carbonates minerals, ATR-CLS model produced robust determination coefficients of more than 0.90 for illite/smectite, kaolinite, quartz and combined calcite and dolomite with measured QXRD values.

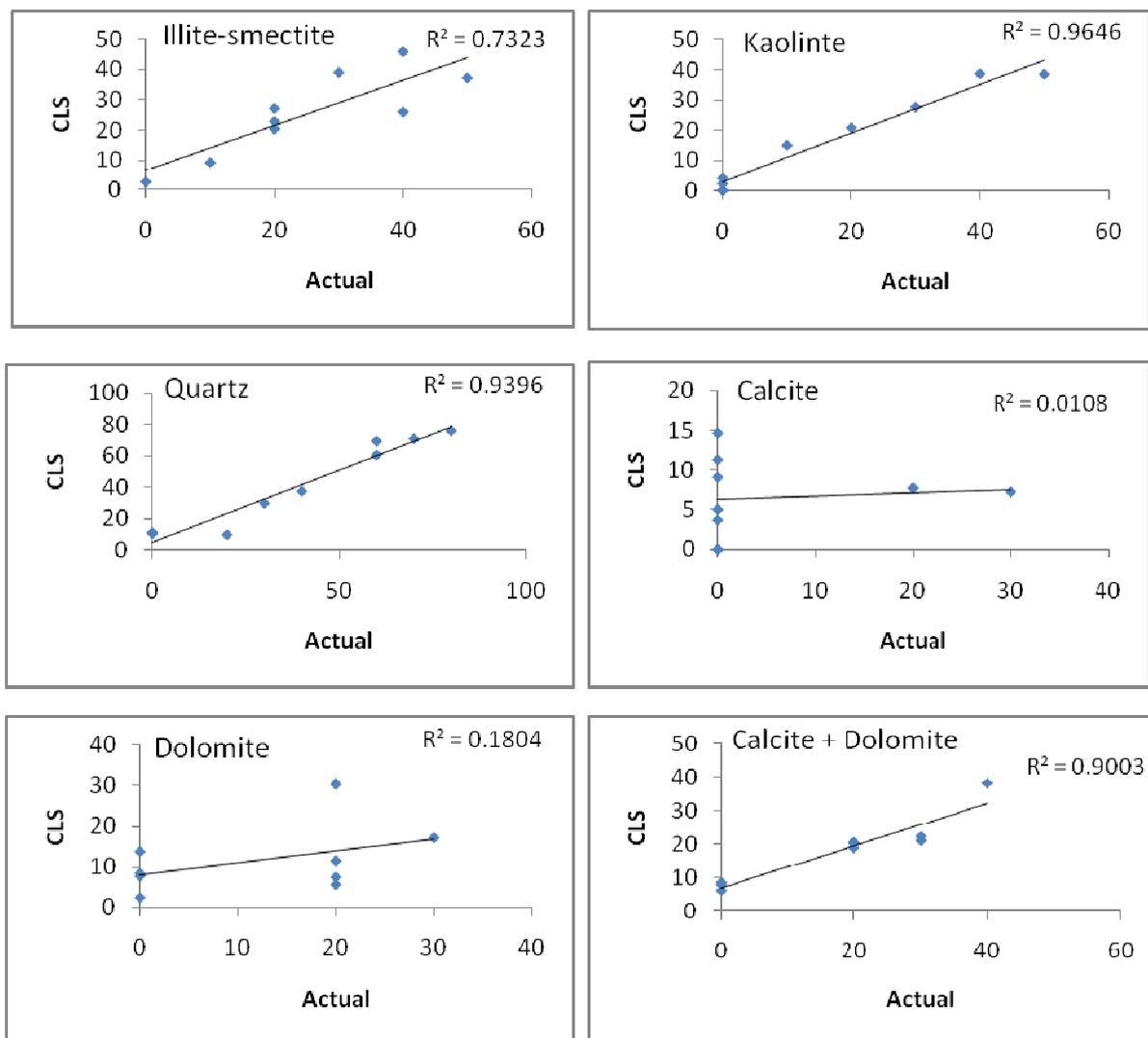


Fig.3. Regression plots showing comparison of known concentrations of mineral mixtures (validation set) and FTIR-CLS model predicted mineral concentrations.

Fig. 4 shows scatter plots of mineral concentrations measured by XRD versus ATR-CLS predicted concentrations for all the shale. The averages absolute difference (including zeros) between measured (XRD) and predicted (ATR-CLS) concentrations for each mineral are shown in Table 2. The two measurements match each other closely (Fig 4). The correlation between the two measurements for the carbonates is poor however; and agrees with the model predicted values for mixtures used in the internal validation set. The concentrations of the mixed layer clays (Illite-Smectite) calcite predicted by the ATR-CLS model were generally higher than those obtained by the QXRD. This may be because the shale rocks contain small amounts of other clays (chlorite possibly) and carbonates (possibly siderite and/or, magnesite). These clay minerals exhibit infrared bands in similar spectral regions to those of the

mixed layer in the OH stretching region as well as the Si-O bands. Similarly, siderite and magnesite exhibit infrared bands in similar spectral regions to those of dolomite and even though they were not included in the model, they might have contributed to the results (Clegg, 1998). However, for each carbonate in the shale samples, the agreement between measured and derived values is better when the sum of the group is compared rather than when the minerals are considered individually. Analyses of variance (ANOVA) between the CLS predicted and XRD measured mineralogy conducted for the shale minerals at 95% confidence results in large p - values (Table 2). The p-values for all the mineralogy is greater than (0.05), which supports the conclusion that the means weights of the CLS predicted values do not differ significantly from the measured values.

Table 2: Errors of ATR-CLS model in prediction of mineral composition of reservoir shale samples (figures in parentheses denote the range of difference)

| Mineral | Average Difference (Wt %) | ANOVA p-values |
|--------------------|---------------------------|----------------|
| Illite-Smectite | -6.58 (+2.54/-15.97) | 0.55 |
| Kaolinite | -0.87 (+1.24/-4.92) | 0.897 |
| Quartz | 3.08 (+8.88/-3.04) | 0.739 |
| Calcite | 5.70 (+17.3/-7.46) | 0.917 |
| Dolomite | -4.55 (-2.59/18.24) | 0.08 |
| Calcite + Dolomite | -2.69 (+1.71/-5.99) | 0.879 |

Breen et al. (2008) developed a PLS model from the DRIFTS spectra of mixtures of seven mineral standards encountered in sandstone-type rocks; quartz, dolomite, montmorillonite, illite, kaolinite, chlorite and albite. The PLS-DRIFTS model was able to quantify the mineral components of independent mixtures with an absolute error of 1 wt. % for all the minerals (concentration range 0–30 wt. %) with the exception of quartz which exhibited an absolute error of 3 wt. % (concentration range 50–90 wt. %). Similarly, the results

obtained when they applied the PLS-DRIFTS model to several sandstone-type quarry rocks and a suite of oilfield reservoir rocks did not describe all the mineral components present in the samples. These findings compared well to results obtained in this study using the ATR-CLS model. The model was not able to differentiate between montmorillonite and illite probably due to the similarity of the DRIFTS spectra of these minerals, but it was able to quantify the combined (montmorillonite + illite) concentrations to

within 1 wt. %. They report over-prediction in the concentration of albite in the quarry rocks due to the presence of K-feldspar, which has a similar DRIFTS spectrum and was not included in their model. However, the model accurately predicted the total (albite and K-feldspar) concentration to within 4 wt. %. When they applied a separate PLS-DRIFTS model constructed using the DRIFTS spectra of the oilfield reservoir rocks for

the prediction, the carbonate components, calcite and dolomite could be differentiated and quantified to within 5.0 and 3.6 wt. %, respectively. This shows that more sophisticated models, which incorporates and describes a higher percentage of the variance in unknowns, would further improve the predictions. Such a model could be constructed from data set containing naturally varying minerals.

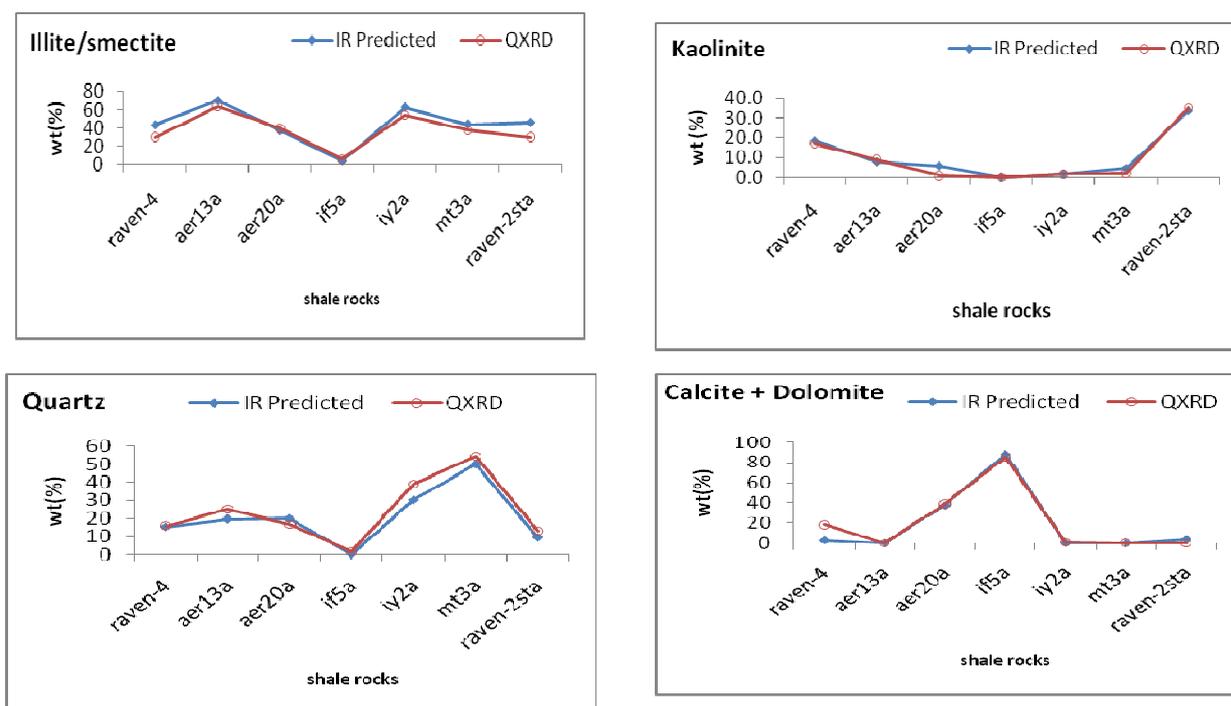


Fig.4. Comparison of ATR-CLS predicted mineralogy in shale rocks with those measured by QXRD.

Conclusions: This feasibility study confirmed the strong potential of combining ATR spectra with a multivariate statistical approach for quantitative mineralogical analyses. A set of mineral mixtures was prepared to develop prediction model using FTIR spectroscopy-multivariate statistical method. The mineral mixtures were designed to reflect the major mineral components found in clastic and

carbonates formations. Application of a CLS statistical tool on attenuated spectra of standard mineral mixtures generated predictive models with an average absolute error of less than 3 for illite/smectite, kaolinite and quartz and an average absolute difference of 3.8 for the combined carbonates (calcite and dolomite) in pure mineral mixtures. The degrees of similarity between the mineral group spectra indicate that it might be

difficult to determine individual mineral. The agreement between measured and known carbonates, calcite and dolomite is poor and leads to the conclusion that it is difficult to differentiate between them. On the other hand, the FTIR-derived concentrations between illite/smectite, kaolinite and quartz are in fairly good agreement with the known mineral concentrations. However, the agreement between the derived and known mineralogy is better when the sum of the carbonates are compared rather than when the individual carbonates are evaluated. The ATR-CLS model was able to quantify the minerals in natural reservoir rocks with an absolute average difference of 6wt%; which shows the evidence that applying multivariate non-linear regression analysis on attenuated spectra of shale rocks has high potential for quantifying its mineral components. ATR spectra predicted results compare reasonably well with predictions obtained using other techniques such as Transmission and DRIFT. The speed of spectral acquisition and data processing together with small sample size requirement makes the ATR technique more desirable than the other techniques.

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