



Full Length Article

Development of far-infrared attenuated total reflectance spectroscopy for the mineralogical analysis of shales



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ABSTRACT

Determining and understanding the geochemical properties of shale rocks is an important and essential aspect of hydrocarbon resource exploration and development. Although mid-infrared spectroscopy (MIR) has been widely used to characterize and provide chemical information of many different mineral components, mineral quantification of natural geological systems is still a major challenge that has not yet been satisfactorily achieved. Part of the problem is that many minerals which are frequently present in the shale rock in large amounts do not absorb and/or have characteristic absorption bands in the MIR region. We show for the first time that far-infrared spectroscopy (FIR) can be used to provide compositional information of the main mineral groups (i.e., carbonates, silicates and clays) in a shale. Furthermore, partial least square (PLS) methods were developed using seven mineral standards chosen to represent the most common minerals found in shale-type reservoir rocks. The developed PLS model was validated using 28 natural shale samples and a reasonable correlation was found between the FIR method and X-ray diffraction (XRD) analysis.

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1. Introduction

There has been significant interest over the last decade on geological formations generally referred to as shales. These serve as reservoirs for oil/gas in unconventional plays and also constitute the stratigraphic seals of conventional reservoirs. The extraction of gas from a shale formation, the assessment of their seal capacity and stability in wellbores are complex processes that require information and detailed knowledge concerning a number of different physical (porosity, permeability, rock strength, etc.) and chemical (organic matter content, etc.) properties [1,2]. The geochemistry of shales can be highly variable and an understanding of the organic and inorganic constituents is important in determining whether a particular shale is economically viable, and whether useful quantities of gas may be harvested from this heterogeneous material.

An important step in shale resource exploration and development is the determination of the rock properties, and a recent review has been published describing the different laboratory methods commonly employed to evaluate various physical attributes of shales [3]. In terms of characterizing and understanding the mineralogy and geochemistry, a number of techniques have

been traditionally used such as X-ray diffractometry, scanning electron microscopy, Rock Eval analysis and gas chromatography [4–6]. Similarly, infrared spectroscopy (IR) is another method that has been used for a number of years to provide chemical information and assess the structural properties of a wide range of inorganic and organic materials [7]. In particular, a wealth of qualitative and quantitative data pertaining to the mineralogical composition [8–11], hydrocarbon potential/yield [12,13], kerogen type/maturation [12], and total organic carbon content/geochemistry [14,15] has been obtained in the mid-infrared (MIR) region between 4000 and 400 cm^{-1} . The MIR spectrum comprises a number of fundamental modes of vibration (i.e., stretching and bending movements) that involve either a change in the bond length or bond angle [7]. Despite MIR spectroscopy being able to provide useful information regarding the chemical composition, a number of challenges still exist, particularly with respect to mineral and clay quantification [16]. Some IR absorption bands (i.e., Si–O stretch) that typically occur in many different mineral groups (i.e., silicates, clays) are broad and overlap with each other and this makes quantitative analysis extremely challenging. Multivariate methods have been developed to help improve the discrimination and quantification of many different mineral components [9,17,18]. However, the information generated from the IR spectra in heterogeneous materials can be complicated by various factors such as sample preparation and particle size effects [19]. In

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addition, many sulphide and oxide based minerals which are usually present in shales are not detected since they do not have characteristic absorption bands in the region between 4000 and 400 cm^{-1} [20]. It is clear that further research is needed to develop an analytical technique which is able to provide accurate quantitative information of all mineral components (i.e., both amorphous and crystalline) in a shale rock.

Some of the aforementioned problems and limitations with MIR may be addressed by far-infrared (FIR) spectroscopy which is able to provide compositional information over the wavelength range 400–10 cm^{-1} . The use of FIR has recently undergone a resurgence [21,22] and this is not surprising considering that many vibrational modes occur in this region such as phonon or lattice modes, low frequency torsional and rotational modes and functional group vibrations involving heavy atoms [23]. FIR spectroscopy has provided extensive structural information regarding proteins [24], molecular dynamics and intermolecular interactions of polymers [25], the phonon properties of semiconductors [26] and the characterization of cluster compounds [27]. In addition, many of the mineral components of shale rocks are expected to exhibit characteristic absorption bands in the FIR region. Although there is extensive literature on the vibrational spectroscopy of minerals [20,28], to our knowledge the application of FIR for the characterization of shales has to date received very little or no attention.

Despite many publications, it seems that a detailed understanding of the geochemical processes during the formation of shale systems are still largely unknown. In particular, quantitative analysis of shale rocks is a significant challenge that has not been satisfactorily addressed and further research is needed to develop a more reliable technique that provides *in situ* information with minimal sample perturbation and destruction. One of the aims of the present study is to determine if FIR methods can be used to provide compositional information of the mineral components which typically occur in a shale rock. It will address some of the uncertainties and limitations associated with the use of infrared spectroscopy for the characterization and mineralogical quantification of shale samples. Unravelling the chemical structure and properties of shales will allow better understanding of such systems and lead to improved decision-making processes regarding the development of shale resources and reduced impact on the environment during production.

2. Materials and methods

2.1. Minerals and shale samples

The reference minerals used in the study were obtained from a variety of sources. The calcite was obtained from SpiritRock Shop and is a large single crystal rhomb of near optical quality that originates from Mina Prieta Linda, Naica, Chihuahua, Mexico. A section of it was crushed to a fine powder using a mortar and pestle, and XRD revealed that its purity was >99%. The kaolinite (96% pure and containing 4% quartz) and smectite (98% pure and containing 1% quartz) were obtained from the Clay Mineral Society and more information is available elsewhere [29,30]. The quartz (99% pure) was collected from a vein at Muckinbudin (Western Australia) and the sample was pulverized followed by acid washing. Illite (68% pure) was obtained from Wards Natural Science and XRD revealed a significant quartz impurity (32%). Sodium feldspar (98% pure and containing 2% quartz) and dolomite (95% pure and containing 4% calcite) were purchased from Walker Ceramics Australia. A number of natural shales were used in this study and they originate from various geological settings ranging widely in time and space. A summary of the provenance, burial depth, age and typing of the natural shale samples is given in Table 1.

The preparation of calibration standards involved grinding each reference mineral in a mortar and pestle (if not already in powder form) followed by sieving it through a 20 μm mesh test sieve (Endecott's) and washing with dry ethanol (Aldrich). The suspension was dried under a stream of dry nitrogen followed by heating overnight in an oven at 50 °C. Mineral mixtures were prepared by weighing the sieved material (50 mg of each was prepared for the first calibration model and 100 mg for the second) into sample vials. The mixtures were thoroughly mixed with a spatula, followed by vigorous shaking.

2.2. Far-infrared (FIR) spectroscopy measurements

Far infrared spectra of the mineral standards and shales were recorded using a Bruker Vertex-80v FTIR spectrometer. The spectrometer was equipped with a mercury arc light source, Mylar multilayer beam splitter and DLaTGS detector with polyethylene window. The spectra were recorded under a vacuum of <2 hPa using a Bruker single-reflection diamond attenuated total reflectance (ATR) accessory. To ensure uniform and reproducible pressure, a spring-loaded mechanical anvil was used to compact the powdered samples onto the ATR. Data was recorded between 680 and 30 cm^{-1} (the spectral range of the beam splitter) at a resolution of 2 cm^{-1} and 128 scans were averaged for each spectra. All experiments were conducted at room temperature (20 ± 2 °C). The surface of the diamond ATR was cleaned with acetone followed by deionized water and wiped clean and dry with laboratory cleaning tissue (Kimwipe). Approximately 10 mg of the sample powder was loosely piled onto the 2 mm square diamond, enough to completely cover it. The anvil was clamped down and the instrument evacuated until a pressure of <2 hPa was reached, and then the spectrum recorded. All measurements were performed in triplicate.

2.3. Data processing

Initial processing including inspection and truncation of the spectra were performed using OPUS (Bruker). Spectra were loaded into Excel (Microsoft) and collated into a matrix form (X-data). This data, along with composition data in matrix form (Y-data), which was adjusted for the presence of impurities for the calibration mixtures, was then loaded into the PLS Toolbox (Eigenvector Research) for multivariate processing. Final graphs were generated using OriginPro 2015 (OriginLab).

2.4. X-ray diffraction (XRD) study

XRD patterns were recorded with a PANalytical X'Pert Pro multipurpose X-ray diffractometer using Fe filtered Co K α radiation, 1/4° divergence slit, 1/2° antiscatter slit and X'Celerator Si strip detector. The diffraction patterns were recorded in steps of 0.016° 2 θ with a 0.4 s counting time per step, and logged to data files for analysis. Quantitative analysis was performed on the XRD data using the commercial package SIROQUANT (Sietronics Pty Ltd). Further details of the XRD method can be found elsewhere [36]. For XRD analysis bulk samples were pre-ground for 15 s in a tungsten carbide mechanical mill to pass through a 0.5 mm sieve. A subsample (1 g) was further ground for 10 min in a McCrone micronizing mill under ethanol. The slurry was then dried in an oven at 60 °C and thoroughly mixed in an agate mortar and pestle before being lightly pressed into stainless steel sample holders for XRD.

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