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TRANSMISSION TECHNIQUE AS AN ANALYTICAL TOOL FOR MINERALOGICAL INVESTIGATION

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ABSTRACT
Transmission technique is one of the Fourier Transform Infrared (FTIR) Spectroscopy Technique that popularly serves as a tool for mineralogical investigation. Transmission technique was used in this work on two mineral samples namely; calcite and quartz to measure its spectral quality based on peaks height, repeatability and spectral resolution. Pellets of the minerals were made using KBr matrix and pellets making machine. The transmission spectra were obtained and analysed using OMNIC software.
KEYWORDS: FTIR, Calcite, KBr, OMNIC software, Transmission, Quartz.

INTRODUCTON.
Shale is a term that has been applied to describe wide variety of rocks that are composed of fine-grained particles, typically less than 4 microns in diameter but it may contain variable amounts of silt particles (up to 62.5 microns). Shales exhibit a wide range in composition (e.g. Quartz, feldspar, calcite, dolomite, illite etc) (Passey *et al.,* 2010).
In comparison, sandstones are rocks composed of grains (of variable composition) that are typically between 62.5 microns and 2000 microns in diameter. Just as sandstones can be composed of different mineral grains (e.g., quartz, feldspar, rock fragments, clays, etc.), shales (more properly referred to as mudstones) also exhibit a wide range in composition (clay, quartz, feldspar, heavy minerals, etc.). Moreover, the composition of a "typical" mudstone will vary much more than for typical sandstones, even though to the naked eye, many mudstones (i.e., shales) look similar (Passey *et al.,* 2010).
Gas shales refer to very fine-grained rock that is capable of storing significant amounts of gas. These fine-grained sediments were deposited in a low energy environment, such as a tidal flat or a deepwater basin. Gas may be present as free gas stored in the natural fractures and macro porosity, adsorbed onto the kerogen and internal surfaces, or dissolved in the kerogen and bitumen. They range from the organic rich, fine-grained rocks of the Antrim Shale in the Michigan Basin to the variable facies rocks of the Lewis Shale in the San Juan Basin (Ross and Bustin, 2008).
The information of minerals generally provides hints about the deposition and digenesis of rocks which aid in understanding the flow characteristics in a reservoir. General characterisation of the rock is needed to understand how to optimally recover oil and gas (Ballard, 2007). Shale has low permeability and therefore the production in commercial quantities require fractures to provide permeability hence knowledge of mineralogical composition of shale is needed. Fractures are necessary for creating high permeability pathways for gas migration from the matrix to the wellbore due to the extremely low permeability of shale (Manger *et al.,* 1991). The key to optimizing fracture stimulation treatments is a thorough understanding of the mechanical properties of the shale. The ability of the shale to fracture and maintain an open fracture is influenced by mineralogy and lithology. Poisson's ratio is a measure of the shale's ability to fail under stress. Young's modulus reflects its ability to maintain a fracture. Silica rich shales, like the Barnett and Woodford, have a high Young's modulus and low Poisson's ratio and tend to fail in a brittle manner. These types of shales will respond well to hydraulic fracture treatments. Calcite and clay rich shales, like the Caney Shale, fail in a ductile manner, tending to deform internally and resist fracturing. Changes in mineralogy and lithology result in a variable response of the Shale to stimulation treatments. Integration of these differences permits optimization of stimulation treatments (Manger *et al.,* 1991).

Infrared Spectroscopy is based on the fact that covalent bonds have resonant frequencies at which they vibrate. The fundamental vibrations of these bonds occur in the mid – infrared range (wave numbers between 4000 cm-1 to 400 cm-1) which is the range for absorption of most organic compounds and minerals, and are dependent on the type and the atoms bonded together (Chris *et al.,* 2008). Individual minerals have distinct atomic structures, allowing them to be identified by the bonds present. When a bond vibrating at a given frequency is exposed to radiation of the same frequency through infrared spectroscopy, it will absorb energy from the radiation and its magnitude will be amplified based on the principle of resonance. The amount of energy absorbed by the bond is its absorbance (Ballard, 2007). Infrared Spectroscopy is also called vibrational spectroscopy which measures bending and stretching vibrations of molecules having specific functional groups that are excited by an infrared beam. These vibrations produce bands in well defined regions which are characteristic for specific class of compounds (D'Sauza *et al.,* 2009).

Infrared spectroscopy has different techniques that can be used in identification of various minerals and organic compounds. The available techniques under infrared spectroscopy are Dispersive method which is the oldest technique, and Fourier transform infrared spectroscopy (FTIR). The FTIR technique is also categorised into diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), Transmission and Attenuated total reflectance (ATR). In transmission technique, samples to be run are generally ground and mixed with an IR transparent salt such as potassium bromide (KBr) and made into pellets prior to sampling; the KBr mix is usually made to reduce the concentration of the sample and obtain a better spectra. However, pressing of a KBr pellets with clays may alter the spectrum through absorption or exchange of the potassium ion (K+) into the clay structure (Karakassides *et al.,* 1997.) . Infrared Spectroscopy is generally effective in routine geochemical analysis for the estimation of total organic carbon (TOC) and major minerals in shales, coals and cement. In the estimation of TOC, IR is more advantageous when compared to other method like 'LECO' as there is no need for acid treatment, combustion, and there is less sample requirement and also is generally rapid (Ballard, 2007).

The aim of this work is to investigate the spectral quality and effects of the KBr matrix and grinding on the quality of mineral spectra recorded using transmission technique.

MATERIALS AND METHODS

Sample Preparation

Samples of Calcite (CaCO3) and Quartz (SiO2) were used in this work. The sample to KBr ratio used was 2.0 mg sample to 200 mg KBr making the mixture of about 202 mg (Madejova, 2003) for all the two mineral samples. The error of ±0.2 mg of both mineral samples and KBr powder was adopted during the weighing of the samples and KBr. The KBr pellets were formed from the powdered mineral samples (Quartz and Calcite) and KBr matrix. The required mineral sample and the KBr matrix were mixed and ground together for at least five minutes using agate mortar and pestle to ensure total homogeneity of the mixture. The powdered mixture was transferred in to KBr disc column, and the pressure of five tones was applied during the first five minutes and later increased to ten tones for another ten minutes. The pressure was released slowly to avoid the cracking of the pellets. The KBr pellets obtained were placed in the oven at 110oC over night in order to dry the absorbed water due to hygroscopic nature of the KBr, and later transferred to desiccators for further dryness of the KBr pellets. The FTIR Transmission spectra for the mineral samples (Quartz and Calcite) were obtained on a Nicolet 6700 FTIR spectrometer equipped with a transmission accessory. The spectra were recorded five times at 4 cm-1 resolution in order to measure the repeatability and reproducibility of the samples.

RESULTS AND DISCUSSION

Two different mineral samples (Calcite and Quartz) were analysed using transmission technique. Like other infrared techniques (DRIFTS and ATR) where mineral samples show their diagnostic bands at different wave numbers and absorbance, so also in transmission technique the mineral samples showed their characteristic bands.

Transmission spectra of the same aliquot calcite sample showed an excellent repeatability and smoothness as well as reproducibility as shown in the figure 1 below.

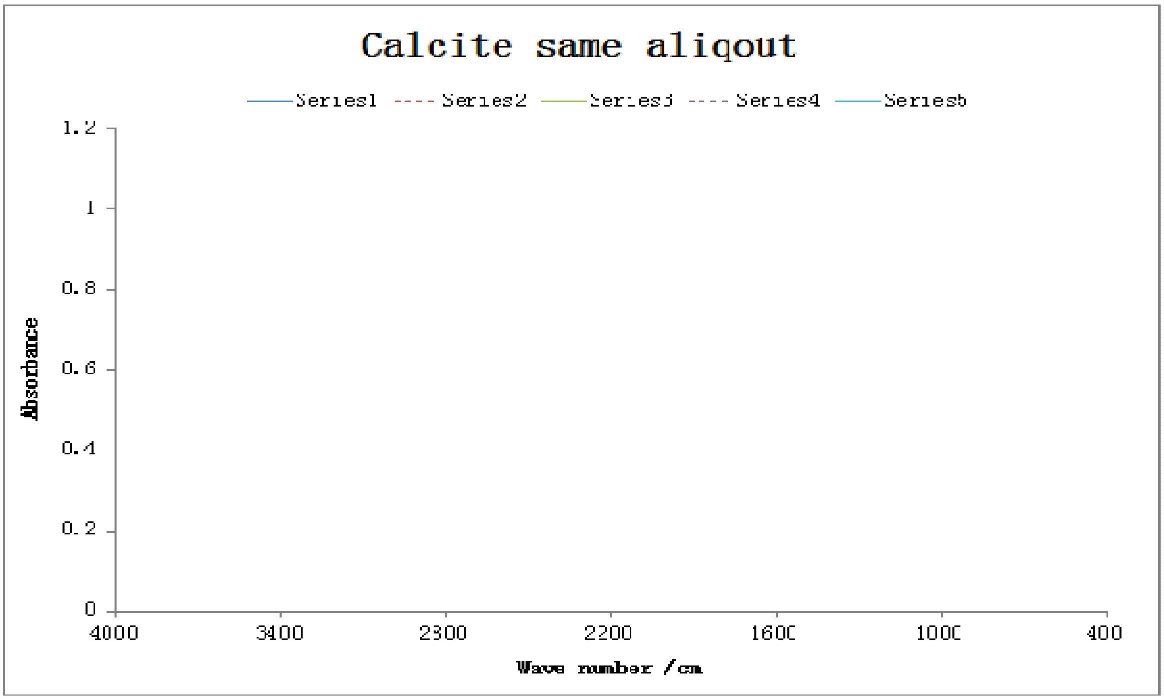

Figure 1. Transmission spectra of same aliquot of calcite sample.

However, different aliquots samples are not as repeatable as those of the same aliquots in transmission spectra (figure 2). This could be as a result of difference in quantity of sample to KBr ratio when the pellets were made.

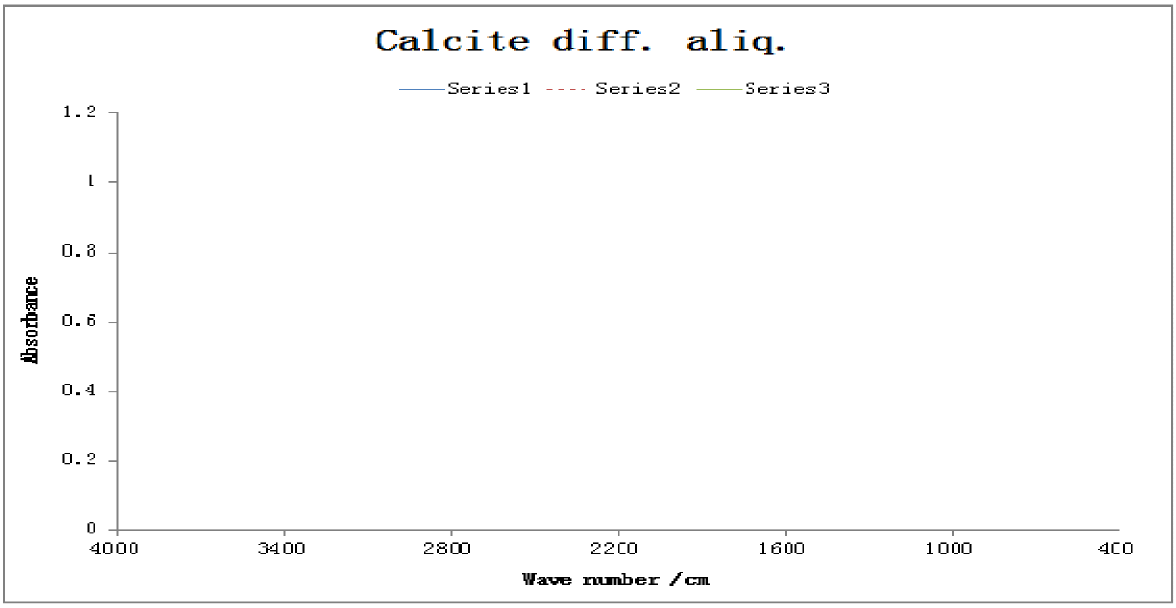

Figure 2. Transmission spectra of three different aliquots of calcite.

Quartz transmission spectra of same aliquot also showed excellent repeatability, reproducibility and the major diagnostic bands at their respective wave numbers. In Quartz transmission spectra, the diagnostic bands at 1076, 775 and 692 cm-1 are well resolved. Like transmission spectra of other mineral sample (calcite), also in quartz transmission spectra, there are some bands that are not pronounced well in transmission spectra.

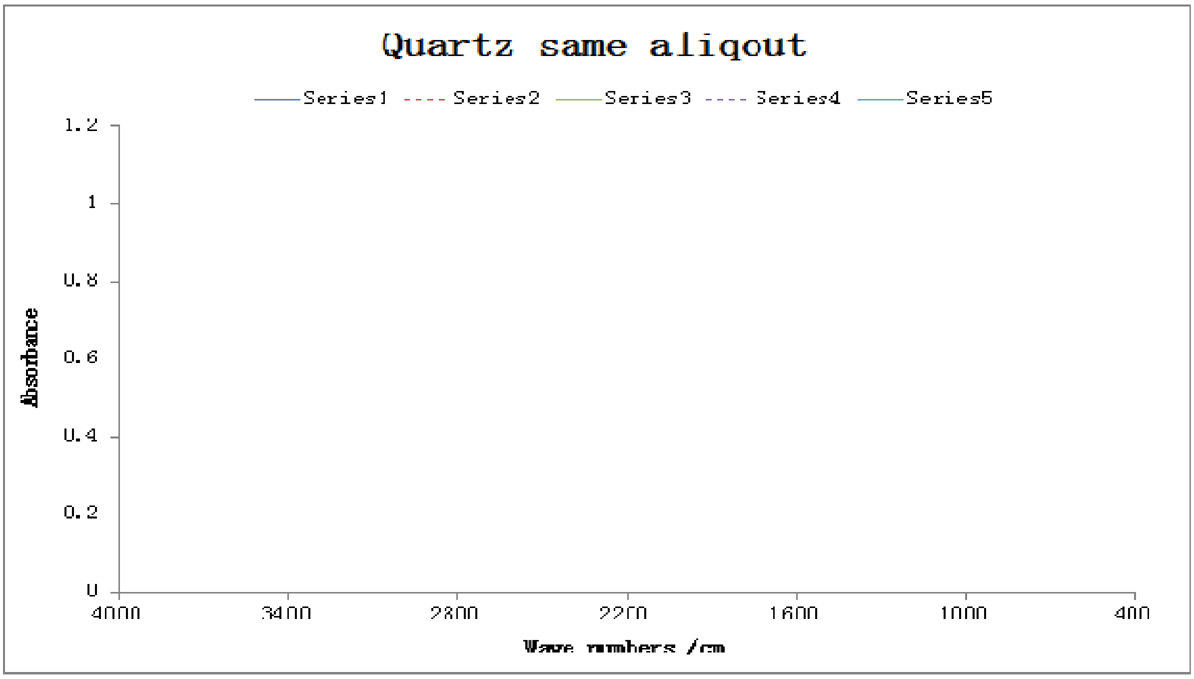

Figure 3. Transmission spectra of the same aliquots of Quartz sample.

The transmission spectra of different aliquots of quartz showed better repeatability and reproducibility when compared to the transmission spectra of other mineral (calcite) which might be as a result of difference in concentration of the samples.

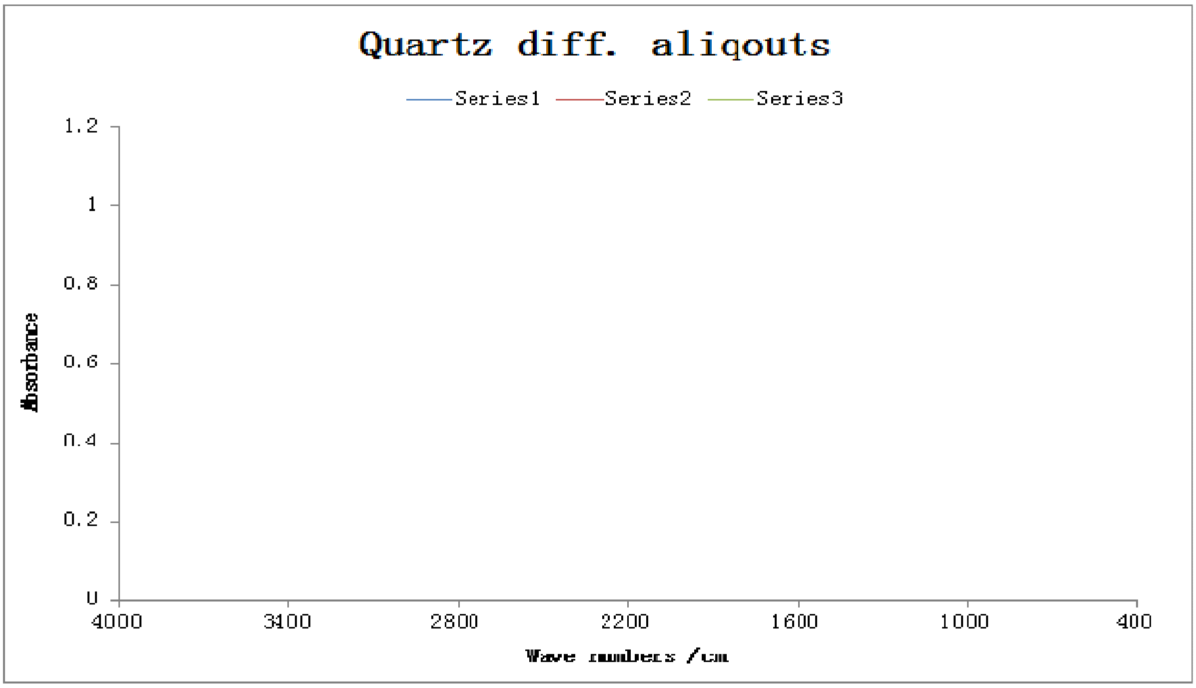

Figure 4. Transmission spectra of three different aliquots of Quartz sample.

In Transmission spectra of minerals, two sample concentrations are usually required to record high quality spectra over the range of 4000-400 cm-1. OH stretching region require 2-3 mg of sample dispersed in 200 mg of KBr while the region below 1200 cm-1 where intense Si-O absorptions and OH bending bands are present require less than 1 mg of the sample (Madejova, 2003).

However, the acquisition of high quality DRIFT spectra involves using 10%wt sample of 100%wt of KBr (Hughes *et al.,* 1995) . Despite the fact that DRIFTS technique is faster in mineralogical analysis than transmission technique due to sample preparation in transmission technique. However, in terms of shale mineralogical quantification, transmission technique is more reliable when compared to other techniques like DRIFTS, as transmission technique always obeys beers Lambert's law while reflection (DRIFTS) has to be converted to transmission in order to obey beers Lambert's law by using Kubelka-Munk algorithm (a mathematical function).

CONCLUSION

The knowledge of minerals provides information about the deposition and digenesis of rocks which aid in understanding the flow characteristics in a reservoir. Detail characterisation of the rock is essential to understand how to optimally recover oil and gas. Transmission technique is one of the most reliable techniques to be used in diagnosing organic rich shale through the identification of various functional groups which aid in identifying the type of mineral constitute in a particular rock. Based on the results obtained in this work it was generally observed that Transmission spectra of all the mineral samples displayed excellent repeatability and reproducibility. However, pressing of a KBr pellets with clays may alter the spectrum through absorption or exchange of the potassium ion (K+) in to the clay structure.

It is also concluded that in terms of mineralogical quantification, transmission technique is more reliable when compared to DRIFTS, as transmission spectra obeys beers Lambert law while reflectance spectra (DRIFTS) need to be transformed to transmission before it obeys beers lamberts law.

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