



Investigation of Effect of KBr Matrix on Drift Infrared Spectra of Some Minerals

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ABSTRACT

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy was used in this work to investigate the effect of KBr on infrared spectra of calcite and illite/smectite. 30 mg of each of these minerals were dispersed in 270 mg of KBr and their drifts spectra were obtained and analysed using OMNIC software. Same minerals samples were also run in DRIFT spectroscopy without being dispersed in KBr matrix and their spectra were obtained and analysed. After the investigation it was observed that minerals dispersed in KBr have spectra that are better than those run without KBr in terms of peaks resolution, repeatability and peaks height. Therefore, KBr played a vital role for better DRIFTS spectra which aid for the diagnosis of functional groups of different minerals useful during shale gas exploration processes.

Keywords: Calcite, DRIFTS, illite/smectite KBr, Mineral samples

INTRODUCTION

The science of Infrared Spectroscopy is based on the fact that covalent bonds have resonance frequencies at which they vibrate. The fundamental vibrations of these bonds occur in the mid – infrared range (wave-numbers between 4000cm^{-1} to 400cm^{-1}) which is the range for absorption of most organic compounds and minerals. The exact frequency at which any bond resonate is dependent on the type of the bond 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 that 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 relative amount of energy absorbed by the bond is related to its absorbance (Ballard, 2007). Fourier transform infrared spectroscopy has different sampling techniques the most common of which are diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), Transmission and Attenuated total reflectance (ATR)

Diffuse reflectance is an excellent sampling tool for powdered or crystalline materials in the mid-IR and near IR spectral ranges. It can also be used for analysis of intractable solid samples. As with transmission analysis, samples to be run by diffuse reflectance are generally ground and mix with IR transparent salt such as potassium

bromide (KBr) prior to sampling, this is usually done to reduce the concentration of the sample and obtain a better spectra. DRIFT is an excellent technique as it eliminates the time consuming process of pressing pellets for transmission measurements. Other advantages of using DRIFT technique is that it provides a rapid technique for analysing samples without any interference through sample preparation (Frost and Johanson, 1998.) Samples can be analysed by diffuse reflectance infrared Fourier transform (DRIFTS) spectroscopy, in the form of undiluted or neat powders with very little preparation. However, spectra can be affected by crystal disorder and crystal symmetry causing changes to the number of observed peaks and to peak width and intensity hence the samples are dispersed in a KBr matrix and pulverised to a consistent fineness (Madejova, 2003). The IR technique works almost exclusively on samples with covalent bonds. Simple spectra are obtained from samples with few IR active bonds and high levels of purity. More complex molecular structures lead to more absorption bands and more complex spectra. The technique has been used for the characterization of very complex mixtures (Chris *et al.*, 2008).

Spectroscopic methods have been used for decades in different fields of research. In most cases light from the ultraviolet (UV) and visible ranges of the electromagnetic spectrum have been employed to assess changes in organic matter composition and mineral composition of the

sediments. Many studies were carried out using various techniques of spectroscopy. The mid-infrared spectroscopy has been used for the determination of quartz, clay and calcite in a range of deep sea sediments (Herbert *et al.*, 1992). Transmission and reflection FTIR techniques have been used to distinguish different types of materials and to derive information concerning their structure, composition and structural changes upon chemical modification. FTIR techniques (DRIFTS and ATR) were used to investigate the structure, bonding and chemical properties of clay minerals. (Madejova, 2003) (Madejova and Komadel, 2001.)

Infrared Spectroscopy is generally effective in routine geochemical analysis for the estimation of total organic carbon 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, in terms of minerals, IR is much cheaper than XRD, thin section and XRF (Ballard, 2007). Based on the advantages of this technique over other techniques, DRIFTS was used to investigate the effect of KBr matrix on the spectra of some minerals.

The aim of this work is to investigate the effects of the KBr matrix and grinding on the quality of Minerals DRIFTS spectra.

MATERIALS AND METHODS

Sample Preparation

Samples of calcite and illite/ smectite were used in this study. 30 mg (w/w) of each sample was mixed with 270 mg of KBr and ground using agate mortar and pestle for at least five minutes to ensure total homogeneity. Neat samples of the minerals

were also ground for at least five minutes to obtain a fine powder. The powdered mixtures were placed in the desiccators to dry the absorbed moisture.

The samples were packed into the sample cup to ensure reproducible spectra during the spectral scans (Breen *et al.*, 2008). Spectra were recorded by accumulating 100 scans at 4cm^{-1} resolution in the mid infrared region ($400 - 4000\text{cm}^{-1}$) of the IR on a Nicolet 6700 FTIR spectrometer.

Background KBr spectra were obtained during the spectral scans. Two different minerals were analysed and recorded in mid infrared region ($4000 - 400\text{cm}^{-1}$). The spectra were transformed to Kubelka-Munk algorithm; a mathematical function that transforms reflection spectra to transmission spectra which obeys Beer's Lambert law to provide spectra for comparison with absorption spectra (Frost and Johanson, 1998.). Spectral manipulations of baseline adjustment on all the spectra were performed using OMNIC software. All the spectra obtained from DRIFTS were normalised to a maximum absorption value of 1 in order to compare the reproducibility between the spectra.

RESULTS AND DISCUSSION

The DRIFTS spectra of the minerals (Calcite, illite/smectite) showed distinct bands at various wave-numbers with different absorbance. Calcite being the most common carbonate mineral in clays (Wilson, 1994) is recognizable with distinct bands at 1369 , 871 and 715cm^{-1} in neat calcite spectra without KBr as shown in Fig. 1. However, the spectra of calcite without KBr differ slightly to the neat spectra in terms of bands orientation and repeatability as it can be seen in Fig. 2.

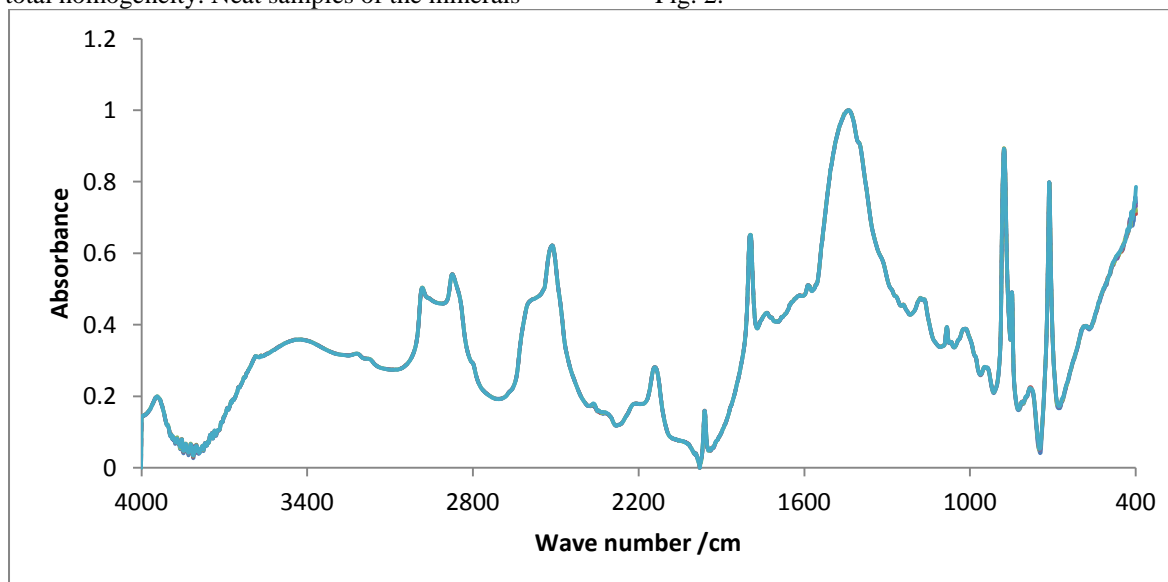


Fig. 1. Calcite infrared spectra with KBr.

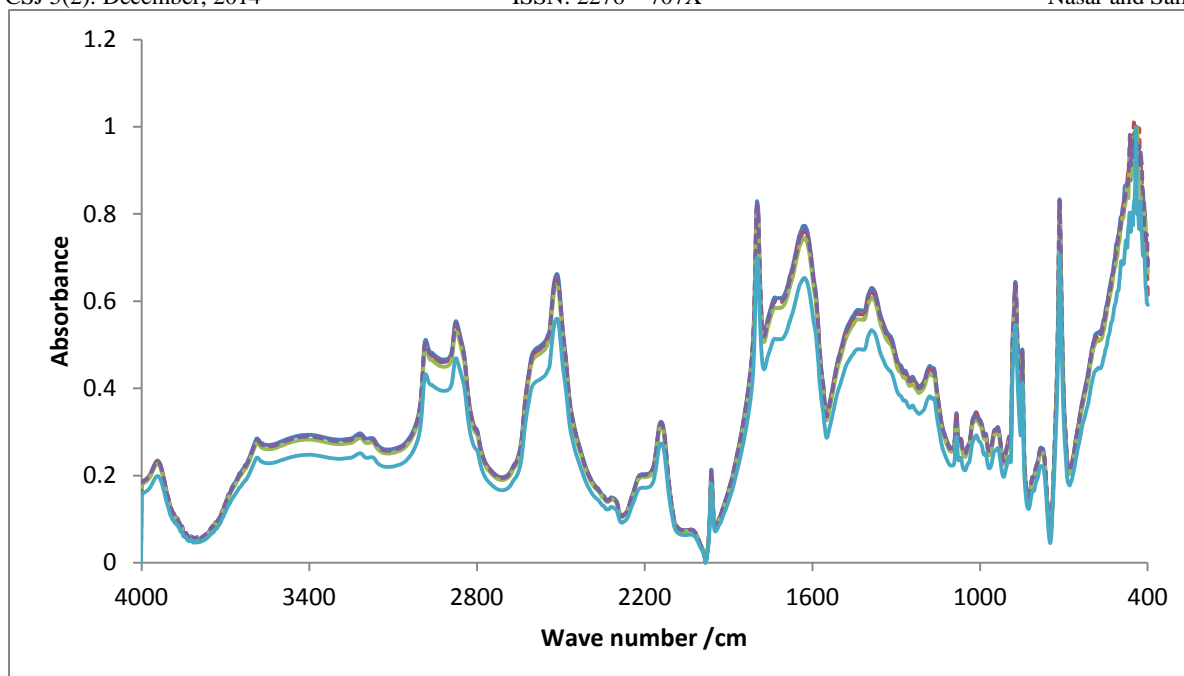


Fig. 2. Calcite infrared spectra without KBr.

There is no much difference between the calcite spectra with and without KBr, except in the region of 1600cm^{-1} to 1187cm^{-1} where the CO_3^{2-} bending at 1421cm^{-1} appear more pronounced in calcite with KBr than without KBr. The repeatability of the spectra with KBr is much better than one without KBr. In the spectra of calcite without KBr Fig. 2, the region below 500cm^{-1} showed derivative-shaped peaks or apparent absorbance dips (Restrahlen bands) appearing at very strong molecular vibration bands (such as Si-O) which is caused by specula reflectance (Madejova, 2003). In the process of forming “Restrahlen bands”, the component of radiation is reflected directly from the surface of the grains and has no absorptive interaction with the sample (Gates *et al.*, 2002). The other spectra of calcite sample with KBr Fig. 1 showed no any Restrahlen effect at the region of $500 - 400\text{cm}^{-1}$ which is as a result of dilution of the sample with KBr which have been observed to removes most of these effects (Gates *et al.*, 2002). However, to produce optimal DRIFTS spectral quality, the dilution with

KBr may differ from one mineral to another, as minerals differ in chemical composition (Madejova, 2003).

Apart from Restrahlen effect observed at the lower region of calcite spectra without KBr, another distinct difference between the two spectra (neat calcite spectra and calcite spectra without KBr) appeared in the regions of 1600cm^{-1} to 1300cm^{-1} Fig. 3 corresponding to two diagnostic bands at 1415cm^{-1} and 1369cm^{-1} , which both show CO_3^{2-} bending of calcite. The two bands differ slightly in the spectra of the neat calcite and calcite without KBr. However, the CO_3^{2-} stretching region of the two spectra matched having almost the same characteristic wave number at 871cm^{-1} and 715cm^{-1} respectively. These slight differences of the two spectra might be as a result of sample parking during the loading of the sample into the cup as the quantity of sample filled may have differed from one scan to another. The overtone of the C=O bands at 2497cm^{-1} and 2507cm^{-1} for calcite with and without KBr respectively is well diagnostic.

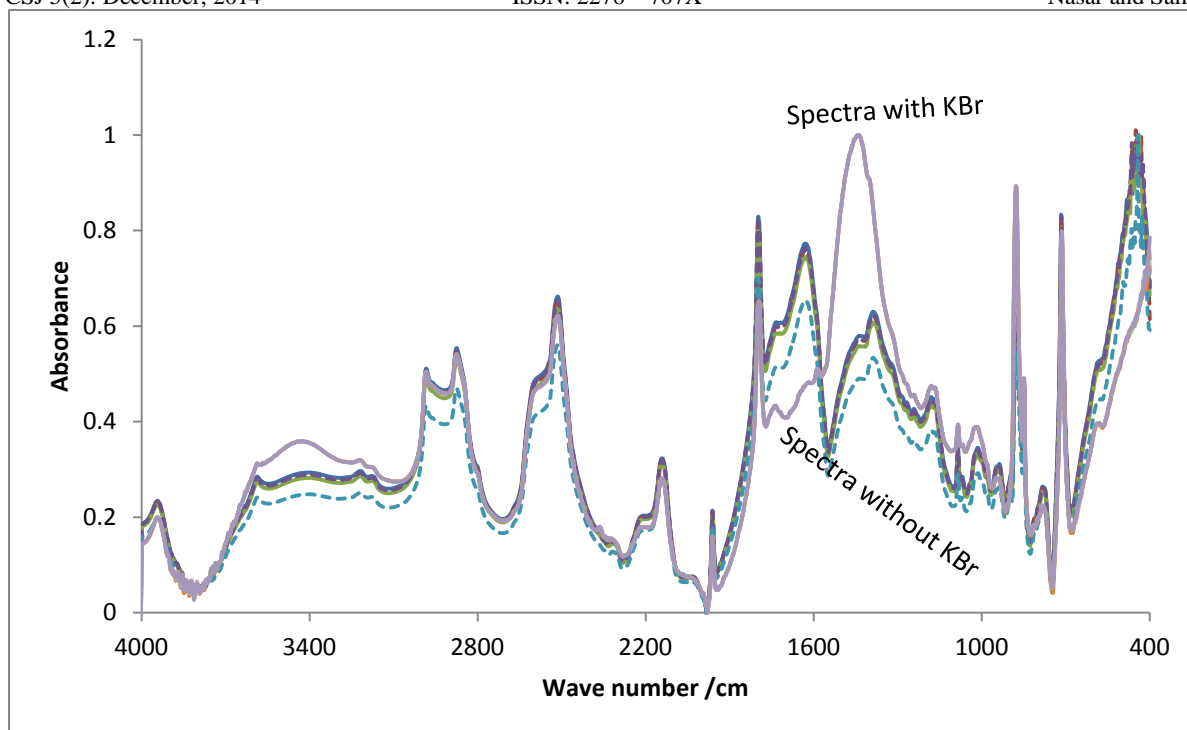


Fig. 3. Calcite Spectra With and Without KBr

Illite/smectite is generally made up of two different minerals as the name implies. Illite can be muscovite-like or phengite type. However, Phengite has much higher Mg content than muscovite and is the most commonly found in clays with weak bands between 850cm^{-1} to 750cm^{-1} . But generally, the broad OH-stretching band near 3608cm^{-1} ranging down to 3550cm^{-1} in some instances, coupled with the duplet between 1000cm^{-1} to 400cm^{-1} is certainly diagnostic. On the other hand, smectite contains Fe^{3+} , Al, Si and Mg from AlMgOH environment which usually results in broad OH-stretching band at 3622cm^{-1} in smectite spectra (Wilson, 1994). The two minerals (illite and smectite) combined together to form illite/smectite $(\text{Ca}, \text{K}, \text{Na})(\text{Al}, \text{Mg}, \text{Fe}, \text{Zn})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$.

The major diagnostic bands in illite/smectite spectra are 3604 , 1855 and 1619cm^{-1}

as can be seen in Fig. 4 and Fig. 5. The broad band at 3604cm^{-1} is indicating strong OH stretching region of illite/smectite which is common to both samples with and without KBr. The major differences between the two spectra lie between the regions of 2200 to 400cm^{-1} which shows distinct variation of bands between the sample diluted with KBr and the one without KBr in the spectra as clearly shown in Fig. 6. As in calcite spectra without KBr, illite/smectite spectra without KBr also showed derivative-shaped peaks (Restrahlen band) at the region of $500 - 400\text{cm}^{-1}$ of the spectra in Fig. 5. Although, there is excellent repeatability in the spectra of illite/smectite sample dispersed in KBr, still there are some noisy appearance that extended to the baseline of the spectra at 1390cm^{-1} region (Fig. 4). Similarly, another noisy appearance happened to be found in the lower region ($500 - 400\text{cm}^{-1}$) of the spectra without KBr (Fig. 5).

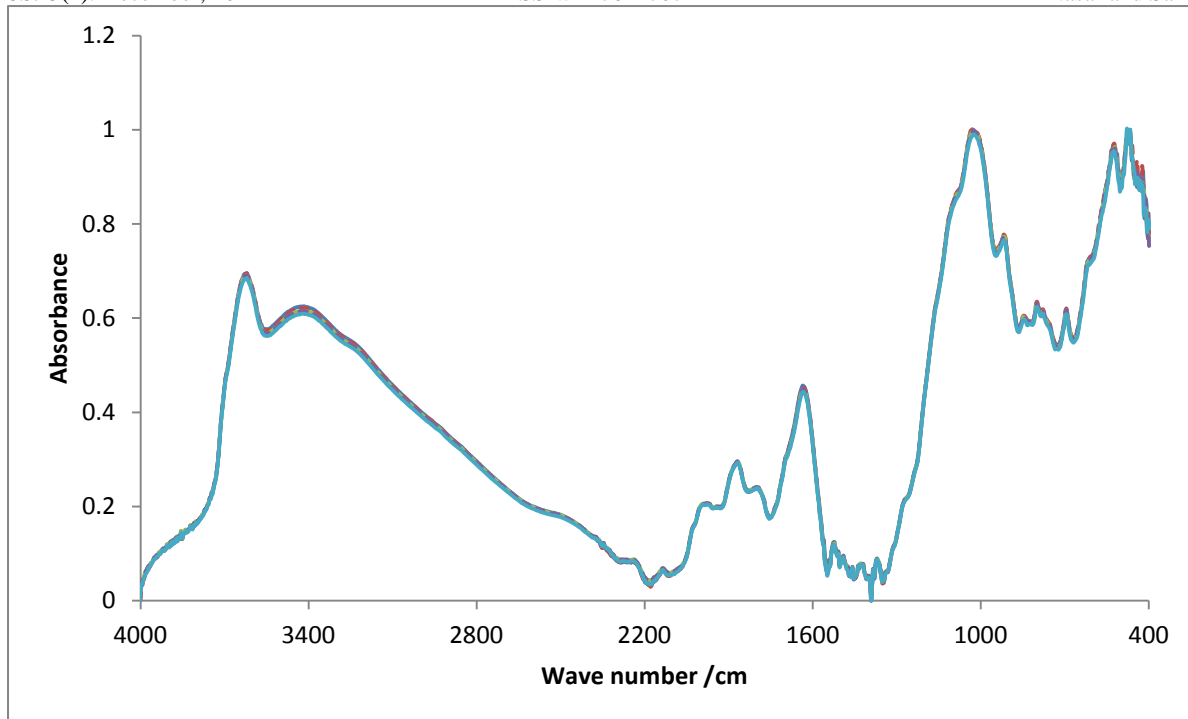


Fig. 4. Illite/smectite spectra with KBr

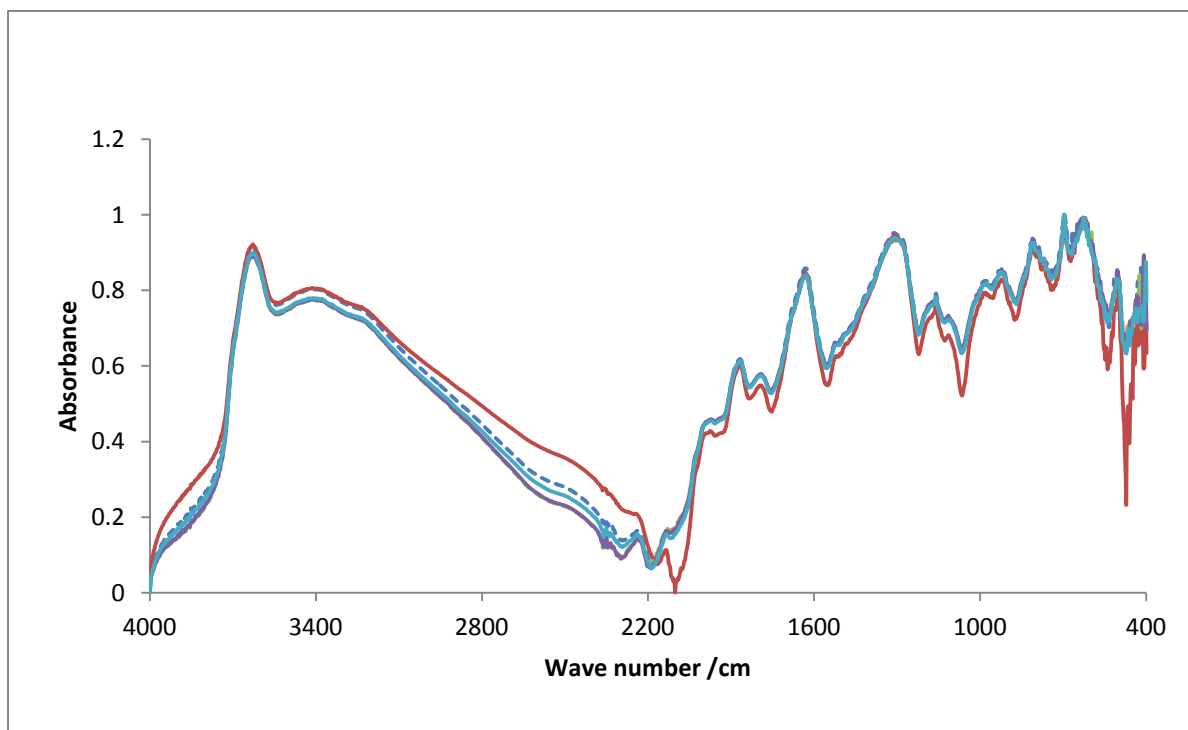


Fig. 5. Illite/smectite spectra without KBr

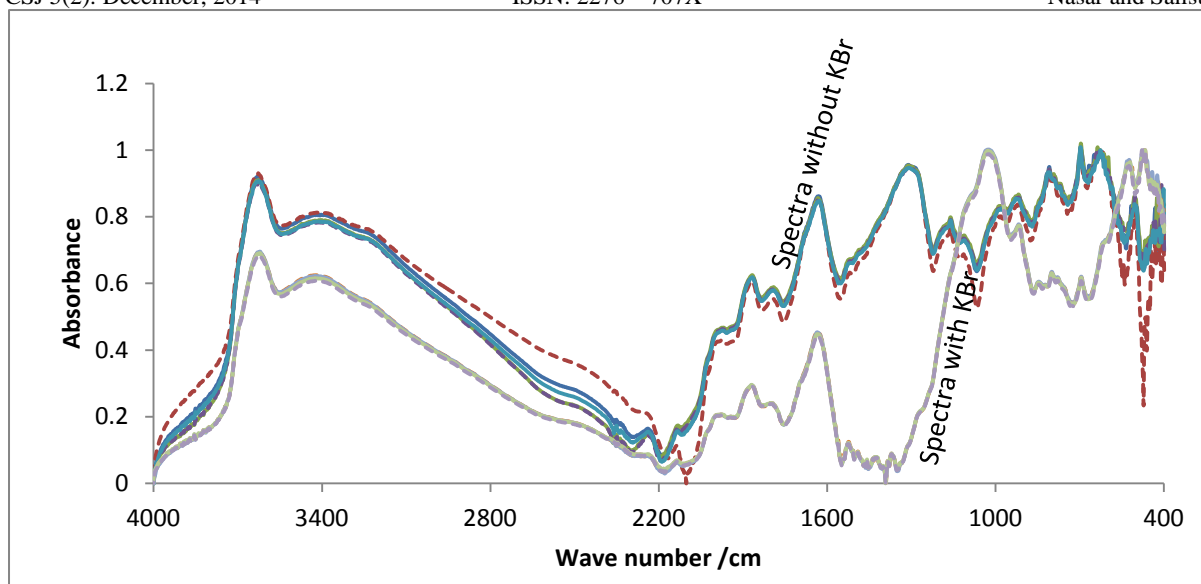


Fig. 6. Illite/smectite spectra with and without KBr.

CONCLUSION

The knowledge of minerals provides information about the deposition and diagenesis 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. DRIFTS is one of the most easiest technique to do so by diagnosing the various functional group contained in the organic rich shale which tremendously aid in determining the type of mineral constitute in that particular rock. Based on this work, the spectra of samples without KBr are not as good as spectra of neat samples in terms of resolution and repeatability considering the differences observed in the intensity of their absorbance which could be due to the effect of KBr matrix. The effect could be as a result of the differences in either grain size of the sample or concentration of the sample as a result of non dilution with KBr matrix.

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