Vibrational Spectroscopy for Hydrocarbon Resource Development

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SUMMARY

Determining the amount and geochemistry of organic matter in rocks is an important and essential step of hydrocarbon resource development. Despite extensive publications there still is a need for improved analytical methods for source rock evaluation and characterisation. Techniques based on infrared and Raman spectroscopy are promising in terms of providing qualitative and quantitative information on carbonaceous materials. However, the application of these methods for routinely determining parameters relevant to the organic geochemistry of petroleum systems has not been thoroughly addressed. The objective of this research is to evaluate the reliability of vibrational spectroscopic techniques for understanding the organic composition and geochemistry of shale rocks. It has been shown that infrared and Raman spectroscopy can be used to derive a number of important parameters such as the hydrocarbon generating potential, thermal maturity and total organic carbon.

Key words: shale; organic matter; infrared spectroscopy; Raman spectroscopy; geochemistry.

INTRODUCTION

The development of hydrocarbon resources to satisfy future energy needs is a topic that generates considerable interest. In recent years there has been a shift towards unconventional shale gas and liquid plays. Although fewer exploration wells are being drilled in Australia, there is still a great deal of activity in the Canning and Perth Basins in Western Australia which have been identified as locations with source potential and are considered hydrocarbon prospective (Ghori, 2018).

Information on the amount, type and maturity of organic matter present in source rocks is a crucial component of hydrocarbon resource development and general geological understanding. A number of techniques are available for characterising and determining the organic composition of geologic materials. Although these provide invaluable information, there is some concern that they have limited sensitivity particularly when investigating samples with low organic contents and high maturity. Recent effort has been devoted to the development of vibrational spectroscopic technologies based on Fourier transform infrared (FTIR) and Raman spectroscopy (Bonoldi *et al.*, 2016; Pejcic *et al.*, 2017; Wilkins *et al.*, 2018). These are relatively non-destructive techniques that can directly and rapidly assess the dispersed organic and carbonaceous materials which are present in a range of sedimentary rocks (Chen *et al.*, 2015; Olcott-Marshall and Marshall, 2015). However, very

little has been reported on the combined application of FTIR and Raman spectroscopy for determining the organic geochemistry of shales.

METHOD AND RESULTS

Given that the presence of organic solid materials in petroleum systems is an area of significant research, only a few studies have been published to date on the use of vibrational spectroscopy for understanding the organic content and composition of shale rocks. FTIR spectroscopy measurements were performed on powdered samples using a Vertex 80v Fourier transform infrared spectrometer (Bruker). Spectra were collected between 4000 to 400 cm^{-1} using 100 scans at a resolution of 2 cm^{-1} and a DLaTGS detector. Various methods are available for collecting infrared (IR) spectra and in this paper both attenuated total reflectance (ATR) and diffuse reflectance (DRIFT) techniques were used. Figure 1 shows typical IR spectra of shale samples obtained from the Canning Basin and it is evident that a number of peaks which arise from various molecular vibrations occur at characteristic frequencies (or wavenumbers). The features due to organic matter are observed at ~3000 and ~1600 cm^{-1} which appear as weak bands in Figure 1 whereas a number of intense peaks occur from 1400 to 400 cm^{-1} and this is attributed to a range of different minerals.
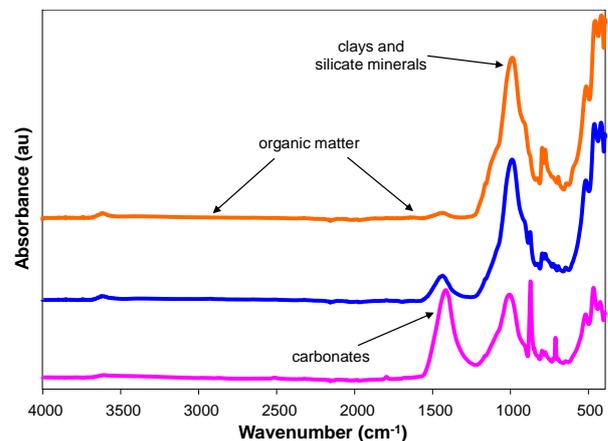

Figure 1. IR spectra of some typical shale samples obtained from the Canning Basin. The measurements were made using the attenuated total reflectance (ATR) method.

It has been previously established that the C-H stretching vibration between 2800 to 3000 cm^{-1} is a useful IR region for determining the total organic carbon (TOC) content of oil shales (Washburn and Birdwell, 2013). To investigate this for shale rocks from the Canning Basin, ATR-FTIR measurements were performed on a range of powdered samples and it is evident that the C-H intensity increases with TOC (see Figure 2). The C-H band was integrated and the relationship between peak area and TOC is shown in Figure 3. Although a reasonable correlation

was achieved, the regression coefficient was found to be much better when using the DRIFT method ($R^2 = 0.8623$) and is probably due to DRIFT being slightly more sensitive for powdered samples compared to ATR. This study shows that the C-H absorption band at 2800-3000 cm^{-1} can be directly related to TOC, however, the peak intensity depends on other factors such as the maceral type which also needs to be considered.
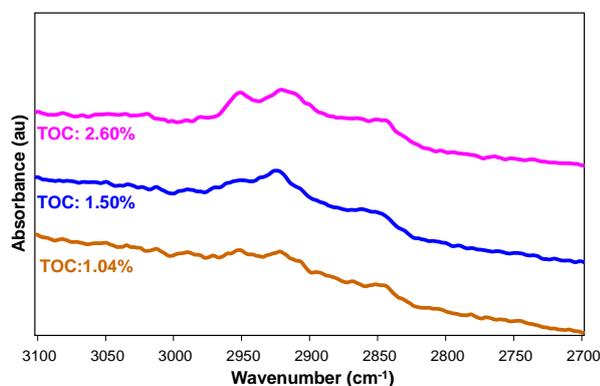
Figure 2. IR spectra of selected shale samples from the Canning Basin with different amounts of TOC. Measurements were made using the attenuated total reflectance (ATR) method.
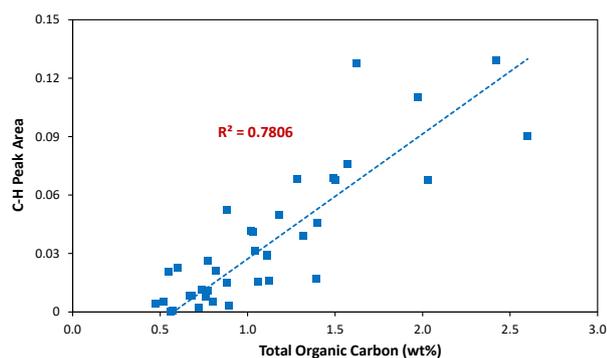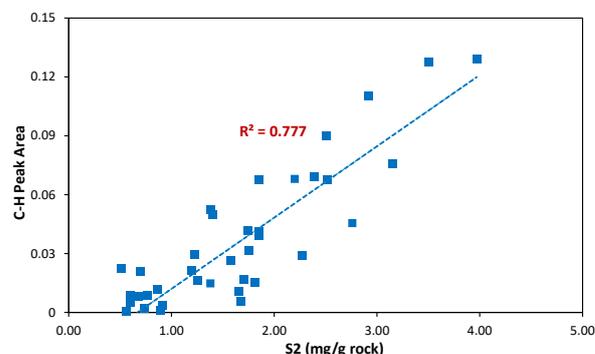

Figure 3. The relationship between the peak intensity at ~3000 cm^{-1} and TOC. Measurements were made using the attenuated total reflectance (ATR) method.

Rock-Eval pyrolysis is a common technique for assessing the kerogen types and evaluating the source rock potential of shales. The hydrocarbon generating potential (S2) is one of a number of parameters that can be derived from Rock-Eval. A plot was generated to investigate if a relationship exists between the aliphatic peak intensity obtained via FTIR spectroscopy and the hydrocarbon generating potential. Despite some scatter in the data, Figure 4 shows a general linear increase in the aliphatic peak area with S2. Compared to a previous study (Washburn and Birdwell, 2013) the correlation obtained herein appears slightly better ($R^2 = 0.777$ versus $R^2 = 0.543$) and is probably due to the presence of a similar type of kerogens.

The characterisation of organic matter in shales can be a significant challenge due to its low abundance and small particle size. However, micro-FTIR is able to provide chemical information of individual particles and measurements were performed on various dispersed organic materials (varying between 20 to 50 µm) which were of different maturities. A Vertex 70 spectrometer (Bruker) and Hyperion 3000 microscope was used to measure the IR spectra noting that the shale samples were obtained from different geological

formations. The microscope was operated in ATR mode using a Ge crystal and a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector. Measurements were performed with a 20x objective and all spectra were recorded in the 4000 to 600 cm^{-1} range using a spectral resolution of 2 cm^{-1} and a total of 64 scans were averaged for each spectrum. All IR spectra have been presented as raw data and were not processed. Figure 5 shows that the IR spectra contains a number of peaks at ~2900 cm^{-1}, ~1700 cm^{-1} and ~1600 cm^{-1} attributed to the C-H, C=O and C=C stretching vibrations, respectively.


Figure 4. The relationship between the hydrocarbon generating potential and the C-H peak intensity. Measurements were made on samples from the Canning Basin using the attenuated total reflectance (ATR) method.
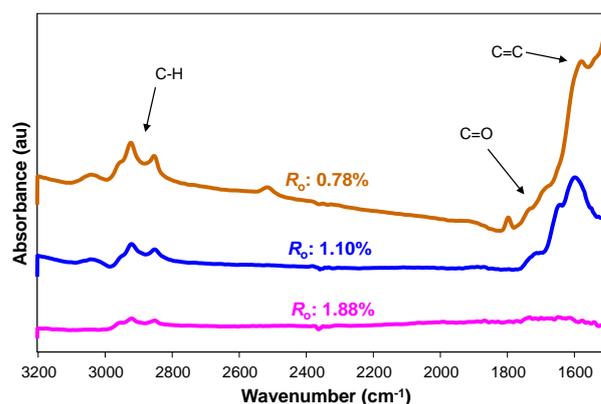
Figure 5. IR spectra of organic matter in shales rocks of different thermal maturity as determined using vitrinite reflectance (R_o). Micro-FTIR measurements were made on samples obtained from the Canning and Perth Basin using the attenuated total reflectance (ATR) method.

It is evident that the intensity of the aliphatic (C-H) and carbonyl (C=O) bands decreased significantly with increasing maturity/vitrinite reflectance and the changes observed in the IR spectra are consistent with intensity variations found elsewhere as a function of vitrinite reflectance (Chen, Mastalerz and Schimmelmann, 2012).

Raman spectroscopy technique has been recently evaluated for characterising the thermal maturation of organic matter in shales as an alternative of the vitrinite reflectance (VR) or equivalent methods. The Raman spectral features of organic material include a number of characteristic bands commonly referred to as disordered (D) and graphite (G) bands. A variety of lasers and spectral processing and spectral deconvolution methods were used in the different studies which leads to difficulty to compare existing published data. The most reported data is the D1 and G bands position separation.
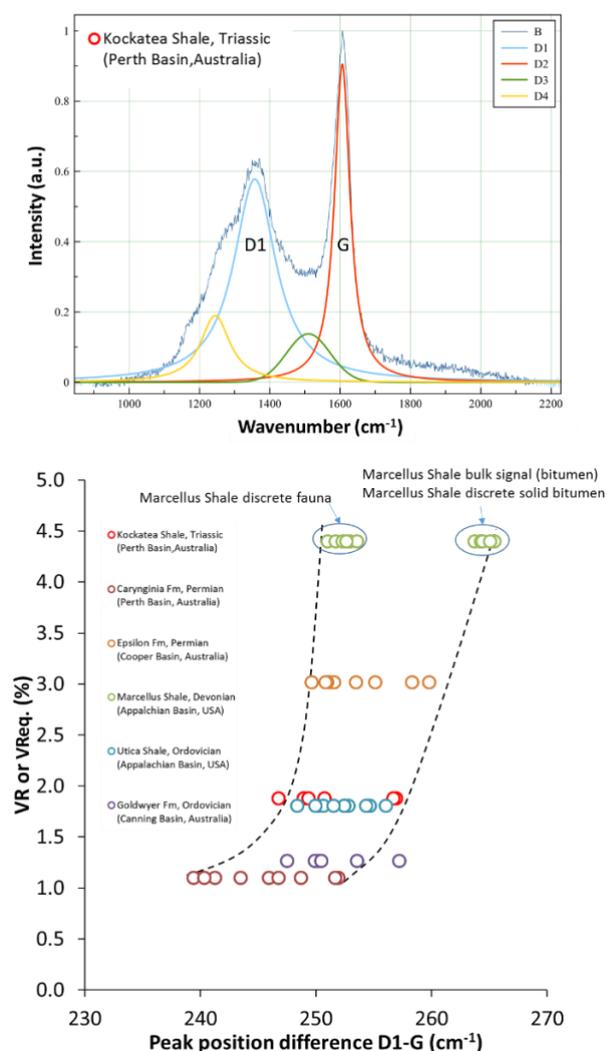
Figure 6. Top: Raman spectrum of organic matter from the Kockatea shale showing the deconvolution into 4 bands. Bottom: D1-G peak position difference organic matter from a series of shale samples plotted against their vitrinite reflectance value or equivalent.

Measurements of the Raman spectrum of organic matter from detrital kerogen, intergranular or fracture-fill bitumen are presented in Figure 6. A series of shale samples were used with variable source rock potential. Two samples are from the Appalachian Basin and the others are from onshore gas plays in Australia from Middle Ordovician, Early Permian and Triassic. The samples show a range of thermal maturity equivalent to VR values between 1 and 4. The samples were prepared as polished mounts of 25 mm diameter. The nature of the particles of organic material investigated (fauna, vitrinite, bitumen) were not always clearly identified but marginal highly reflective organic particles (inertinite) were avoided. The laser Raman spectra were acquired with a Horiba® LabRAM HR Evolution instrument using a 600 gr/mm grating, a Synapse visible detector and 532 nm incident radiation produced by a Torus 100 mW diode laser (Laser Quantum). A four band Gaussian–Lorentzian curve-fitting procedure was applied to the Raman spectra to resolve peaks as described by Kouketsu *et al.* (2014) using MagicPlot V2.5.1 software. Individual Raman spectra were background corrected by subtracting a spline baseline. In the Marcellus shale sample, the organic matter from fragments of fauna present a very consistent signature, different to the

bitumen signature. The separation of the bitumen points and the fauna points suggests differences in the molecular structure of the organic material between detrital (primary) organic matter and migrated bitumen. They also both show low variability within their cluster indicating a convergence of all the organic matter particles toward a similar molecular organisation at high maturity. Therefore, the variability of data points of the other samples at lower maturity is likely due to an inadequate distinction between detrital organic matter and bitumen and also a gradual separation process between bitumen and detrital organic matter.

CONCLUSIONS

FTIR and Raman spectroscopy are valuable techniques for the characterisation of carbonaceous materials that are found in shale rocks. Linear regression analysis revealed that FTIR is a promising method for investigating the geochemical properties of shales. It was shown that the C-H absorption band between 2800-3000 cm^{-1} can be related to the total organic carbon and hydrocarbon generating potential. However, further research is still needed to improve the correlation given that the peak intensity also depends on the organic matter type and maturity. The changes observed in the FTIR and Raman spectra of various shale rocks as a function of thermal maturity are consistent with literature trends and future work will involve the derivation of a quantitative relationship.

ACKNOWLEDGMENTS

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