



## A new rapid method for shale oil and shale gas assessment



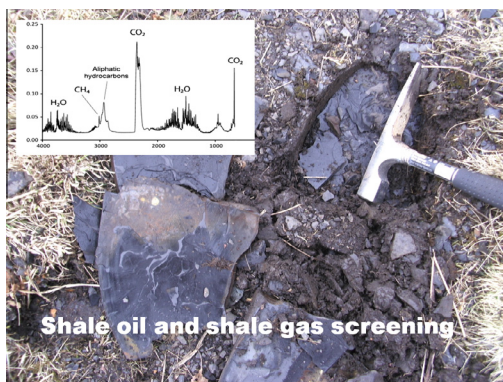
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### HIGHLIGHTS

- Shale gas and shale oil targets require rapid screening methods.
- Pyrolysis-FTIR has been assessed as a quick and information-rich technique.
- Application to Midland Valley shale samples demonstrates efficacy as analytical survey tool.
- Data reveal actual and potential liquid and gas contents.
- Quantification is possible by utilisation of calibration curves.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Unconventional hydrocarbons represent the future of fossil fuel supply. Arguably the most exciting unconventional deposits are those provided by shale gas and shale oil, hydrocarbons generated and retained by fine grained sedimentary rocks. Effective exploration for shale gas and shale oil requires screening of large numbers of samples in a time and cost effective manner. The most promising samples are then selected for more sophisticated and time consuming procedures. We have examined a new screening technique for shale gas and shale oil. Pyrolysis-FTIR provides a substantial amount of information related to shale quality in a single analysis including the types of gases present (including methane) and the nature of any liquid hydrocarbons released. Construction of calibration curves allows the rapid determination of gas quantities and the average chain length of aliphatic hydrocarbons present. Application of pyrolysis-FTIR to Carboniferous oil shales from the Midland Valley of Scotland reveal percentage levels of methane. Following pyrolysis at 600 °C, immature Type III kerogen containing shale has relative gas abundances in the order water > carbon dioxide > methane, mature Type I kerogen containing shales have gas abundances that follow the order water > methane > carbon dioxide and post mature Type I kerogen containing shales have relative abundances in the order carbon dioxide > water > methane. Multistep pyrolysis-FTIR reveals carbon speciation and the relative responses at low and high temperatures reflect sample maturity. The new pyrolysis-FTIR technique can provide a relatively simple and labour saving, but information-rich, technique for the assessment of shale oil and shale gas targets.

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### 1. Introduction

The Earth contains large amounts of hydrocarbons that are not contained within what might be called conventional reservoirs.

These unconventional deposits are often difficult to access, relatively expensive to develop and require advanced technologies to make production possible [1]. With conventional hydrocarbon reserves being rapidly utilised, a future in which demand for conventional deposits outstrips supply is inevitable [2]. Hence, attention is turning to unconventional resources to satisfy our present and future oil and gas needs.

Shale gas deposits are unconventional resources in which gas has been generated from a fine grained sedimentary rock rich in organic matter and retained within that same sedimentary rock. Gas is located within the shales either in pore spaces or adsorbed onto organic or inorganic surfaces. In contrast to more conventional petroleum systems, the shales have acted as source rock, reservoir and trap concurrently [3]. Where maturity levels are less elevated, shale oil deposits may exist, where liquid hydrocarbons have been generated and then retained by the shale. In the case of shale gas and shale oil the technologies that make their recovery economical are hydraulic fracturing and horizontal drilling.

Although shale oil and shale gas reservoirs share many similarities they also exhibit numerous differences [4]. Variations are partly the results of the higher relative maturities associated with shale gas reservoirs. In the higher maturity reservoirs, swelling clays in the mineral fraction have been transformed to non-swelling clays and organic porosity and permeability is more well-developed owing to the formation of pyrobitumen and char. Also in the higher maturity reservoirs, hydrocarbon fluids are less viscous. The variations in rock permeability and fluid viscosity have significant influence on the production characteristics of shale oil and shale gas.

The exploration for unconventional hydrocarbons involves many of the same methods used in the search for conventional deposits. An issue that is common to both types of deposit is the need to screen large numbers of samples in a relatively rapid and inexpensive manner. Assessment techniques such as total organic carbon (TOC) analysis and programmed pyrolysis provide information that allows the quality of the target rock to be assessed [5]. The best samples are then selected for more sophisticated and time consuming further analysis by techniques such as gas chromatography–mass spectrometry and pyrolysis–gas chromatography–mass spectrometry.

Organic matter is present in rocks in both low molecular weight or “free” and high molecular weight or “kerogen” forms. Organic matter can be liberated from the rock by various methods. Solvent extraction solvates the free compounds and isolates them from the kerogen and mineral matrix. Thermal methods at lower temperatures can also evaporate the free compounds and liberate them from the immobile kerogen and mineral phases. Thermal methods at higher temperatures begin to degrade the kerogen and transform it into low molecular weight fragments. Once organic units are extracted, either by solvent or thermal methods, they can be detected and characterised by a number of techniques. Gas chromatography separates complex mixtures into individual compounds and flame ionisation detection can quantify compounds while mass spectrometry can identify any unknowns.

Current methods for rapid assessment of the required characteristics are somewhat discrete and data must be combined to obtain an effective assessment of shale quality. A new method that provides a variety of information on shale quality in a single analysis would be a valuable addition to the screening techniques currently available. Petroleum geochemists need to identify shale gas and shale oil deposits that have potential commercial viability. There is a requirement for a technique that is quick, inexpensive and which provides indications of the rock’s ability to host and generate oil and gas. Moreover, a technique that can be applied directly to unextracted whole rock samples would have the

advantage of analytical simplicity and the benefit of reflecting the overall constitution of the organic inventory.

A currently unexploited method for the assessment of shales is pyrolysis-Fourier transform infrared (FTIR) spectroscopy. Previous work has demonstrated the utility of pyrolysis-FTIR for the assessment of the gas generation potential of extra-terrestrial organic materials [6–8]. Pyrolysis-FTIR has also been proposed as an exploration tool for the triage of future samples return missions aimed at detecting life on Mars [9]. Thermal degradation is an analytical staple of organic geochemical research but its combination with FTIR is relatively uncommon. The technique can be made quantitative by constructing calibration curves for products of interest [10]. In this paper we assess the utility of pyrolysis-FTIR for the rapid assessment of shale gas and shale oil target rocks. We examine the responses of four organic-rich shale samples of varying maturity to establish proof of concept for the method. The approach swiftly provides a great deal of information, some of which would normally only become available following more sophisticated and time consuming analytical steps.

## 2. Methods

### 2.1. Samples

A series of shales of various maturities and organic constitution were collected from field exposures in the Midland Valley of Scotland (Table 1). The shales were deposited in a large rift valley formed between the Highland Boundary and the Southern Upland faults [11]. During the Carboniferous a tropical lake complex experienced thermal stratification and associated anoxic conditions leading to the deposition of organic rich shales [12]. All shale samples were obtained from the Lower Carboniferous Subsystem, Visean Stage, Strathclyde Group sedimentary rocks. Port Edgar (PEE), South Queensferry (SQB) and Society Beach (SB) represent shales from the Queensferry Beds, Pumpherston Shale Member. Broxburn Riverside (BR) is from the Upper Oil Shale Group, Broxburn Shale Member. The stratigraphic relationships of these beds are available in the literature [12].

Comprehensive organic geochemical and microscopic investigations have led to the definition of four organic facies in these shales [12]. Organic facies 1 occurs in silty mudstones, has a mean TOC of only 2% and Type III–IV gas-prone or inert kerogen indicating oxic conditions that were unsuitable for preservation of planktonic organic matter. Organic facies 2 is transitional between the oxic facies described above and the anoxic facies described below. Organic matter contents in organic facies 2 are similar to those in the oil shales but are less well preserved owing to more variable redox conditions. Organic facies 3 represents the true oil shales with high TOC values and Type I or Type I/II kerogens formed in a distal, low energy and anoxic environment. Organic facies 4 represents marine band deposition with high sulfur contents.

### 2.2. Sample preparation and screening

Each shale was crushed to a fine powder (clay-grade) using a pestle and mortar. Aliquots of the powdered samples were analysed for total organic carbon (TOC), and Rock-Eval (RE6). Any liquid hydrocarbon content of the shales was extracted by placing a measured amount of crushed sample in a test tube to which a 93:7 v/v dichloromethane/methanol solvent mixture was added. The tube was then placed in an ultrasonic bath for 15 min followed by 5 min at 2500 rpm in a centrifuge. The supernatant solvent was collected by pipette, the process repeated three times, and the extracts combined. The final extract was subjected to a stream of nitrogen gas to remove solvent and weighed when dry.

**Table 1**  
Samples used in the pyrolysis FTIR study and their geochemical characteristics.

Abbrev.	Name	TOC (%)	S1 (mg)/ (g)	S2 (mg)/ (g)	S3 (mg)/ (g)	HI	OI	Tmax (°C)	EOM (%)	Ali (mg)	Aro (mg)	Pol (mg)	Alkane mode
PEE	Port edgar east	19.90	3.54	145.93	0.84	733	4	450	0.69	1.1	1	0.5	18,22
SQB	South queensferry beach	4.95	0.57	3.66	0.98	74	20	434	0.41	0.8	1	1.6	18
SB	Society beach	15.97	1.31	21.27	1.13	133	7	503	0.44	0.7	4.4	0.9	18
BR	Broxburn riverside	22.42	0.95	161.65	2.45	721	11	450	0.41	0.6	1.1	–	14

The extracts were fractionated using column chromatography where a pipette was plugged with quartz wool and filled with a 3 cm bed of silica gel that was previously activated overnight in a 450 °C furnace. A weighed amount of sample was then placed on top of the column and the fractions eluted using 3 column volumes of hexane (aliphatic fraction), dichloromethane (aromatic fraction) and methanol (polar fraction).

### 2.3. Gas chromatography–mass spectrometry and pyrolysis-gas chromatography–mass spectrometry

Extracts were dissolved in 1 ml dichloromethane and 1 µl was introduced via splitless injection onto a HP-5 (0.25 mm × 30 m × 0.25 mm) capillary column fitted to an Agilent 6890 gas chromatograph. The column oven was operated with a temperature programme starting at 50 °C for 1 min followed by a ramp of 5 °C min<sup>-1</sup> until 310 °C where the temperature was held for 20 min. Helium was used as a carrier gas. Individual compounds were identified by introducing the column effluent into an Agilent technologies 5973 inert mass selective detector operated with a 12 min solvent delay and a scan range of *m/z* 50–550. For pyrolysis analyses, the gas chromatography–mass spectrometer conditions were identical to those above but with analytes introduced via split injection following pyrolysis of approximately 10 mg of shale in a 2500 autosampler with the quartz pyrolysis tube heated at 20,000 °C s<sup>-1</sup> to 600 °C. Samples were not pre-extracted before pyrolysis so as to simulate a screening technique.

### 2.4. Pyrolysis-FTIR

The equipment used for this project has been described previously [10]. Pyrolysis was performed using a CDS Pyroprobe 5200. Accurately weighed samples of approximately 10 mg were held inside a quartz pyrolysis tube and heated at 20,000 °C s<sup>-1</sup> to the required temperature, with the products of pyrolysis introduced to a CDS Analytical Brill Cell™ and analysed using a Thermo Nicolet 5700 FTIR spectrometer. In this study, single-step pyrolysis was performed at 600 °C. Multistep pyrolysis was conducted for all samples, at temperatures of 350 °C, 600 °C and 1000 °C, all at atmospheric pressure.

## 3. Results and discussion

### 3.1. Conventional analyses

Table 1 presents basic organic geochemical data for the analysed samples. Total organic carbon (TOC) data for the Midland Valley samples vary from ~5 to ~23%. The relatively high TOC values are consistent with previous work [11] and provided the basis for the historical oil shale industry in this region. Almost all samples represent excellent (TOC >4%) source rocks. Programmed pyrolysis (RockEval6) S2/S3 ratios indicate that all but SQB are dominated by Type I kerogen (>15) reflecting deposition of algal remains in a lacustrine environment; SQB represents Type III kerogen reflecting the input of land plant material. Programmed

pyrolysis data also show that most samples are at maturities corresponding to peak oil generation (Tmax 445–450 °C). The exceptions are SQB which is immature and SB which is post mature.

Solvent-extraction allows for the weight of the extractable organic matter (EOM) to be calculated and implies that the samples contain significant amounts of liquid hydrocarbons. The relative abundance of the chemical fractions resulting from column chromatography of the extracted organic matter varies. The difference in relative proportions of chemical fractions can reflect a variation in both source of organic matter (land plant material is relatively polar) and maturity (immature organic matter is normally relatively polar). Gas chromatography–mass spectrometry can reveal the individual organic constituents within the extractable organic matter. The envelope of the *n*-alkane distributions obtained by gas chromatography–mass spectrometry can be used to characterise the organic matter input [13] and alkanes with modes of C<sub>18</sub> support the proposed input of algal organic matter (Fig. 1). Sample BR has the highest maturity, and because more extensive cracking of kerogen has occurred, the *n*-alkane carbon number mode corresponds to a shorter chain length than the other samples.

On-line pyrolysis rapidly thermally dissociates any high molecular weight kerogen present thereby rendering it amenable to analysis by gas chromatography–mass spectrometry. The combined pyrolysis-gas chromatography–mass spectrometry method can reveal the source of organic matter for the kerogen and in this study provides similar information to that from the extractable organic matter suggesting that for most samples algal organic matter dominates all solubility fractions (Fig. 2). Overall the samples reflect mainly algal organic matter deposited in a lacustrine environment and postburial processes have raised most of the samples to maturities that correspond to oil generation temperatures.

### 3.2. Single step pyrolysis-FTIR

Single-step pyrolysis can be performed at 600 °C because at this temperature the carbon–carbon bonds are thermally dissociated and pyrolysis yield is likely to be high. An example of data generated from pyrolysis experiments is provided in Fig. 3. Each absorption band represents the presence of a functional group [14] which in the case of gases usually corresponds to the whole molecule. Carbon dioxide is recognised from its characteristic strong absorptions around 2350 cm<sup>-1</sup> and 669 cm<sup>-1</sup> with four further weak absorption bands between 3600 and 3750 cm<sup>-1</sup>. Carbon monoxide is indicated by a weak dual band around 2150 cm<sup>-1</sup>. Water absorbs between 3500 and 4000 cm<sup>-1</sup> and also around 1300–1900 cm<sup>-1</sup>. Methane produces a strong band around 3015 cm<sup>-1</sup> and a weak absorption band around 1305 cm<sup>-1</sup>. Absorptions resulting from aliphatic methyl (–CH<sub>3</sub>) and methylene (–CH<sub>2</sub>–) carbon-hydrogen bonds produce bands at 2900–3000 cm<sup>-1</sup>.

Fig. 4 displays data from single step pyrolysis at 600 °C for all Midland Valley shale samples. The shales that contain Type I kerogens in the oil window (PEE, BR) produce abundant aliphatic hydrocarbons following pyrolysis-FTIR. The responses are the

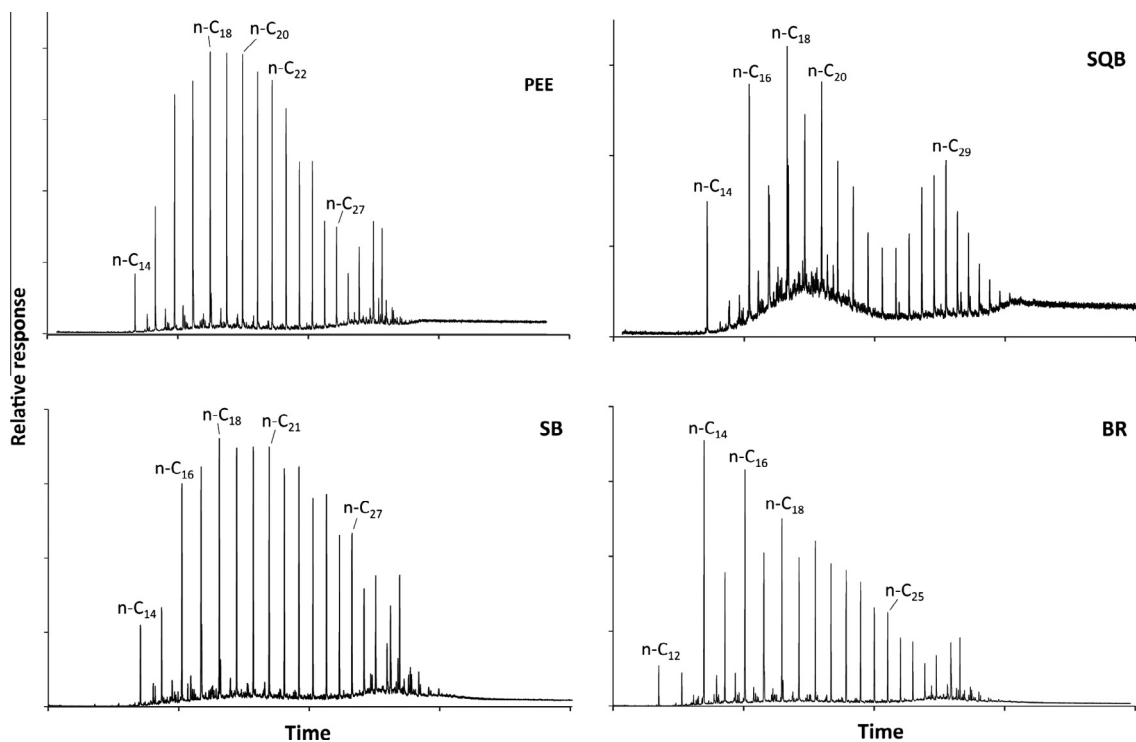


Fig. 1. Gas chromatography–mass spectrometry total ion currents for the aliphatic fractions of solvent extracts of the studied shales.

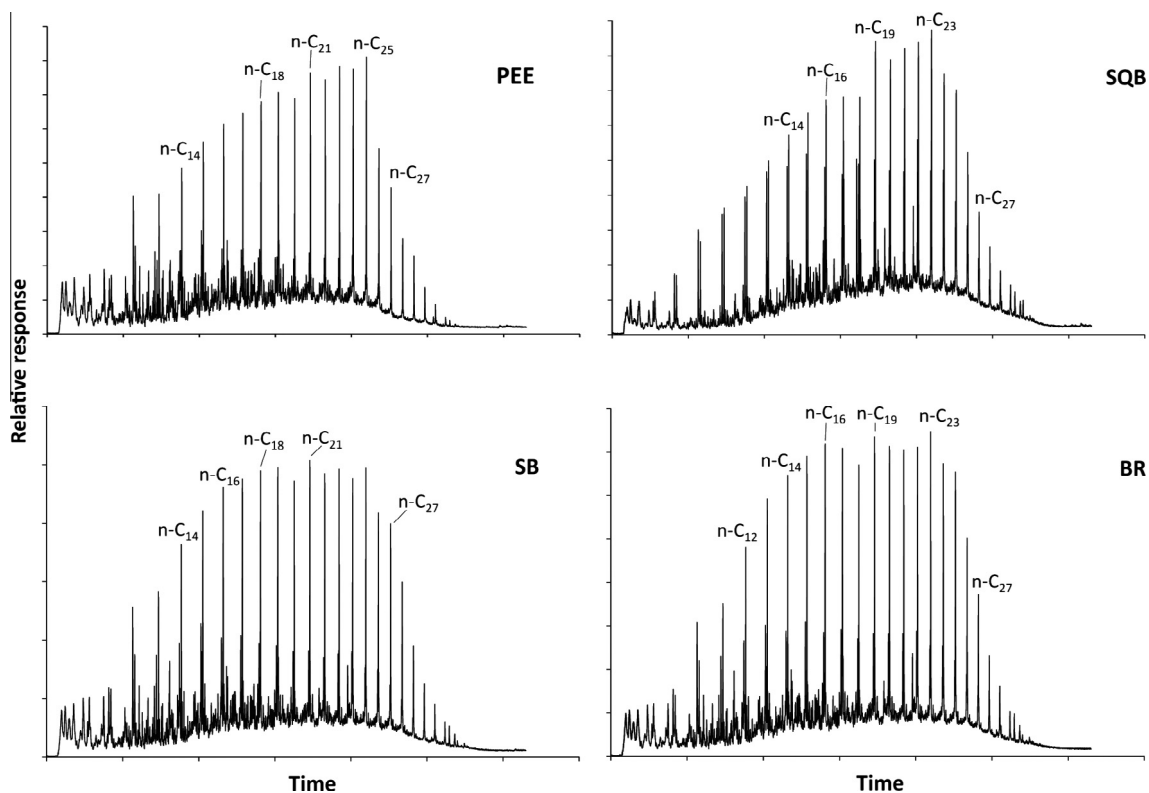


Fig. 2. Pyrolysis-gas chromatography–mass spectrometry total ion currents for the non-solvent extracted shales.

products of evaporated oil and newly generated oil from the pyrolysis of kerogen. All of the oil window shale samples also release substantial amounts of methane, presumably a combination of interstitial and adsorbed gas and the thermal fragmentation

products of pre-existing oil and kerogen. The oil window shale samples also release carbon dioxide and water most likely derived from both the desorption of volatiles from minerals and organic matter surfaces, decarboxylation of organic matter and

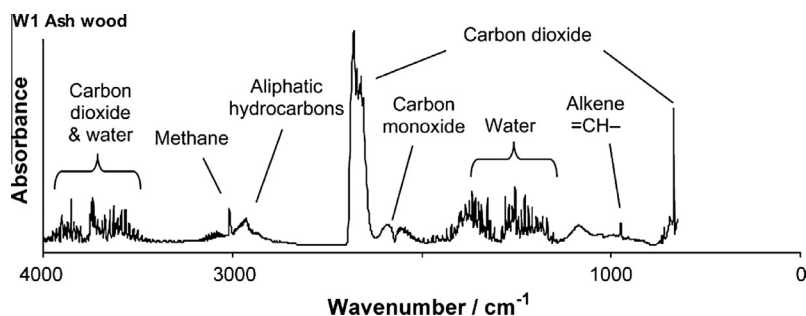


Fig. 3. FTIR spectrum of the pyrolysis products of ash wood pyrolysed at 1000 °C [10].

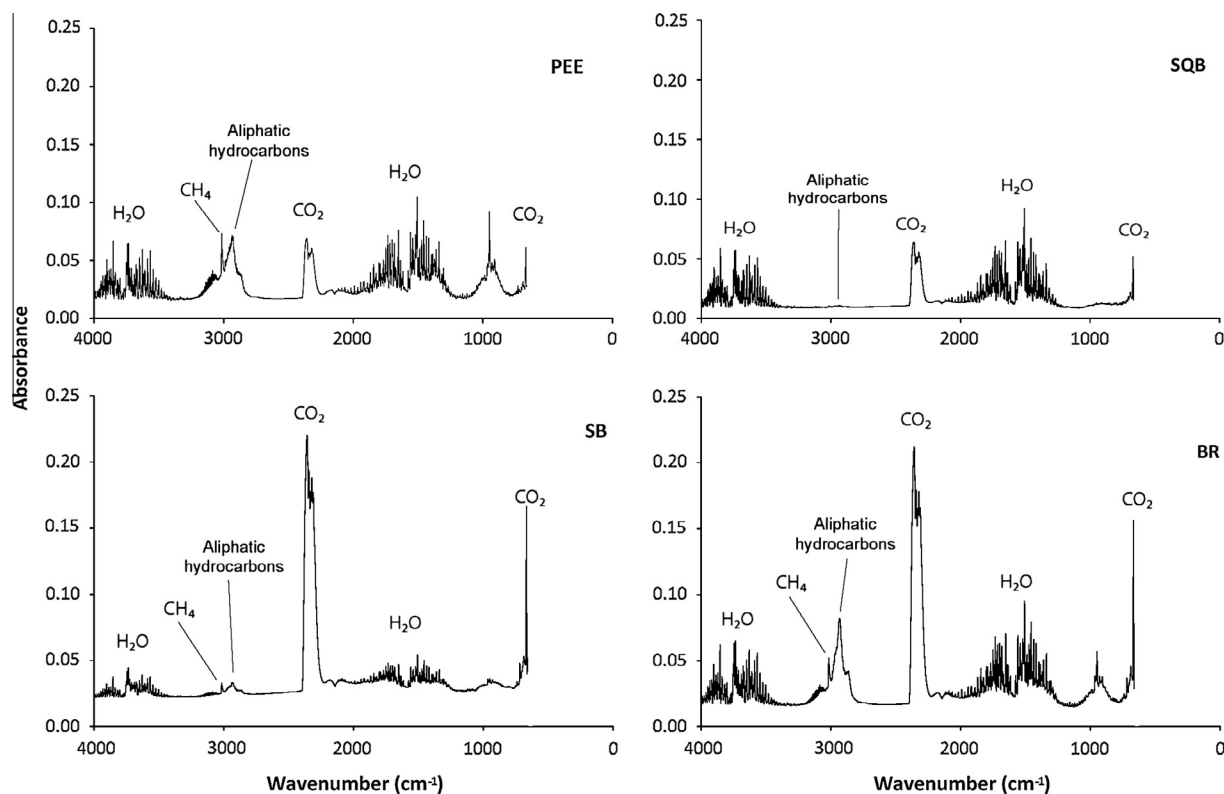


Fig. 4. Infrared spectra for single-step pyrolysis at 600 °C for 15 s for PEE, SQB, SB and BR.

decomposition of hydrated minerals. The immature Type III shale sample (SQB) produces no significant aliphatic hydrocarbon signal following pyrolysis implying that this kerogen is not predisposed to oil or gas generation. The post mature Type I shale sample (SB) produces only limited aliphatic hydrocarbon and methane signals consistent with the natural generation and loss of hydrocarbons from the sample prior to its analysis.

### 3.3. Gas quantification

Quantification of the components in the gas phase is possible by the construction and use of calibration curves [10]. Calibration curves require direct injection of gas or decomposition of thermally unstable materials. As long as the quantity of the sample analysed is known then the concentration of the individual product in the pyrolysis cell can be calculated. Calibration in the gas-phase is aided, because there are minimal molecular interactions as in the case of liquid-phase FT-IR [10].

A calibration curve for C<sub>5</sub> to C<sub>15</sub> *n*-alkanes is presented in Fig. 5. Data from the quantification steps following pyrolysis of the

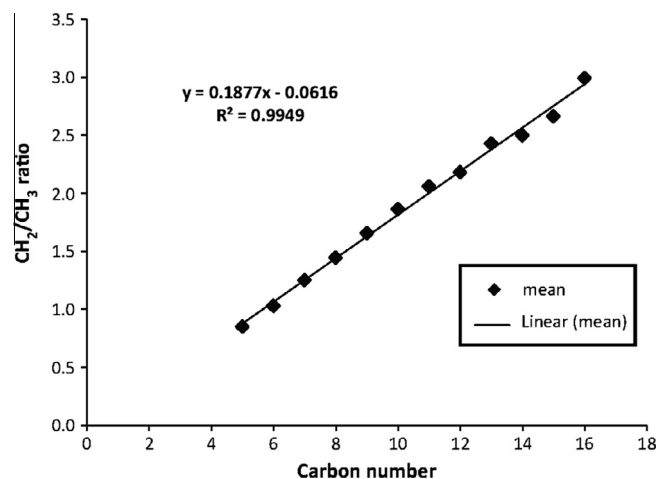


Fig. 5. Calibration curve for *n*-alkanes, from pentane through to pentadecane, produced by their pyrolysis at 600 °C and their subsequent detection by FTIR.

various samples at 600 °C is presented in Table 2. All shales that reflect Type I kerogens in the oil window (PEE, BR) produce the greatest quantities of methane following pyrolysis at 600 °C. The immature Type III kerogen-containing shale sample (SQB) and post mature Type I kerogen-containing shale sample (SB) produce the least amounts of methane following pyrolysis at 600 °C. Methane is present at percentage levels and varies by an order of magnitude depending on the history of the sample. The shales that contain Type I kerogens in the oil window (PEE, BR) produce significant amounts of water following pyrolysis at 600 °C. The Type III kerogen-containing shale sample (SQB) also generates substantial amounts of water, consistent with the presence of volatile rich immature organic matter. Perhaps expectedly the post mature Type I kerogen-containing shale sample (SB) produces the least amount of water following pyrolysis at 600 °C. The Type I kerogen dominated shales in the oil window (PEE, BR) produce significant amounts of carbon dioxide following pyrolysis at 600 °C. The Type III kerogen-containing shale sample (SQB) generates the least amount of carbon dioxide. The post mature Type I kerogen-containing shale sample (SB) produces the greatest amount of carbon dioxide following pyrolysis at 600 °C implying that some of the methane that is seen in the other samples has been transformed to carbon dioxide by interaction with minerals surfaces, consistent with proposed chemical reactions in postmature rocks. The relative abundances of the various gases appears to reflect the history of the sample. The shales that contain Type I kerogens in the oil window (PEE, BR) have gas abundances that follow the order water > methane > carbon dioxide. Post mature Type I kerogen displays the following relative abundance carbon dioxide > water > methane. Immature Type III kerogen has an order of relative abundance that is water > carbon dioxide > methane.

### 3.4. Oil hydrocarbon average chain length

The complexity of the compounds present in natural oil shale samples does not facilitate the quantification of whole oil. However, one useful piece of information that is readily obtained by pyrolysis-FTIR is the average carbon number of the aliphatic hydrocarbons released [15]. All *n*-alkanes contain a fixed number of methyl units, but the number of methylene units varies. Hence, a longer *n*-alkane will produce a methylene absorption band that is more prominent relative to its methyl counterpart. Chain length information is achieved with the use of calibration curves. The curves are constructed by pyrolysing different volumes of each *n*-alkane (pentane through to pentadecane), and relating the average ratio of methylene/methyl band heights to an aliphatic compound with a specific carbon number. It must be noted that calibration curves must be used for a distinct temperature because the choice of pyrolysis temperature will have an influence on average chain length. At lower temperatures only evaporative extraction will occur and the measured chain length will reflect that of the free hydrocarbons, at moderate temperatures the measured chain length will reflect a mixing of free hydrocarbons and hydrocarbons generated by thermal dissociation of kerogen, at the highest temperature the measured chain length will reflect secondary cracking of any hydrocarbons present.

Data from the chain length calculation steps following pyrolysis of the various samples at 600 °C is presented in Table 3. Chain lengths range between 7.5 and 9.1. It is notable that the average chain lengths are less than the modes of the *n*-alkanes displayed in the gas chromatography mass spectrometry data. Possible explanations for this discrepancy are that the pyrolysis steps lead to the production of shorter chains by thermal fragmentation of pre-existing oil. Alternatively the pyrolysis-FTIR measurement may also reflect the presence of branched and cyclic compounds that exist in the unresolved complex mixture that underlies the

**Table 2**

Quantitative pyrolysis-FTIR applied to oil shale samples, single-step pyrolysis at 600 °C.

	PEE	SQB	SB	BR
Sample mass (mg)	18.19	20.3	11.71	12.37
Sample mass after pyrolysis (mg)	15.11	18.71	8.39	8.99
Loss upon pyrolysis (%)	16.9	7.8	28.4	27.3
<i>Methane</i>				
Absorbance (band area)	0.333	0.008	0.067	0.181
Projected mass (mg)	0.10	0.00	0.02	0.06
Yield (% of sample mass)	0.7	0.0	0.3	0.6
Yield (% of sample mass lost)	3.4	0.2	0.7	1.7
<i>Water</i>				
Absorbance (band area)	0.223	0.219	0.067	0.199
Projected mass (mg)	0.84	0.81	0.17	0.68
Yield (% of sample mass)	5.6	4.4	2.1	7.5
Yield (% of sample mass lost)	27.3	51.2	5.2	20.0
<i>Carbon dioxide</i>				
Absorbance (band area)	0.178	0.164	0.515	0.527
Projected mass (mg)	0.05	0.04	0.43	0.45
Yield (% of sample mass)	0.3	0.2	5.1	5.0
Yield (% of sample mass lost)	1.7	2.5	13.0	13.2
Sum of masses (mg)	1.00	0.86	0.63	1.18
Sum of masses as% of mass lost	32.4	53.8	18.9	34.9

**Table 3**

Determination of average chain length number using an *n*-alkane calibration curve (single-step pyrolysis at 600 °C).

	PEE	SQB	SB	BR
<i>CH<sub>2</sub></i>				
Absorbance (band height)	0.0549	–	0.0091	0.0653
<i>CH<sub>3</sub></i>				
Absorbance (band height)	0.0407	–	0.0059	0.0395
<i>CH<sub>2</sub>/CH<sub>3</sub></i>				
Absorbance ratio	1.35	–	1.54	1.65
Projected average carbon number	7.5	–	8.5	9.1

more noticeable discrete peaks in the gas chromatography–mass spectrometry total ion current. Irrespective of the appearance of gas chromatography–mass spectrometry data it is the actual integrated average as represented by quantified FTIR data that should be most important for shale gas and shale oil production considerations.

### 3.5. Multistep pyrolysis

Shales contain various organic fractions that can be accessed by the application of different temperatures providing the ability to determine maturity. Hence a multistep pyrolysis-FTIR approach can provide detailed information on speciation of organic matter [9]. Firstly desorption and evaporation can reveal the presence of solvent soluble materials and volatiles either adsorbed onto mineral or organic matter surfaces or present in pore spaces. Secondly higher temperatures can degrade organic networks to produce detectable fragments. Finally, the highest temperature steps can perform complete gasification of the sample.

Both programmed pyrolysis and multistep pyrolysis-FTIR are thermal extraction and degradation techniques that exploit incremental temperature increases. Hence some responses from pyrolysis-FTIR may be comparable to those observed during conventional programmed pyrolysis. The free hydrocarbon or S1 fraction in programmed pyrolysis [16] will correspond to the lower temperature steps of multistep pyrolysis-FTIR; the kerogen degradation or S2 fraction in programmed pyrolysis [16] will relate to the higher temperature steps of multistep pyrolysis-FTIR.

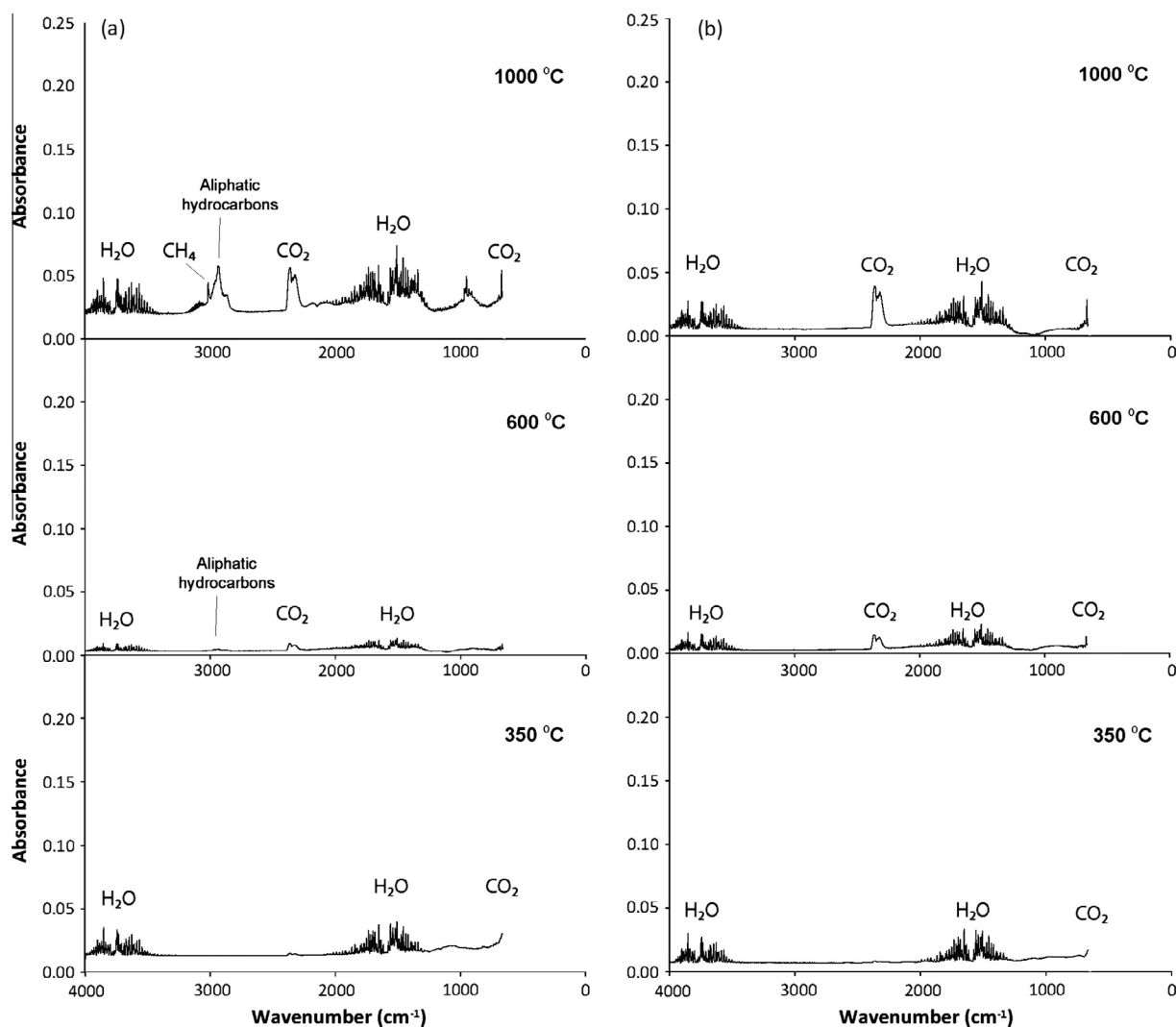


Fig. 6. Infrared spectra for natural oil shale samples (a) PEE and (b) SQB pyrolysed for 15 s at 3 different temperatures: 350 °C, 600 °C and 1000 °C.

In this study, multistep pyrolysis was performed at temperatures of 350 °C, 600 °C and 1000 °C. Pyrolysing the samples at three different temperatures produces three distinct spectra for any given sample. At 350 °C most samples will release some CO<sub>2</sub> (669 cm<sup>-1</sup>), and also most of the water that is adsorbed onto the sample (583 cm<sup>-1</sup>). 600 °C simulates the conditions found within the oil window, and most samples should produce aliphatic compounds (e.g. *n*-alkanes). At the 600 °C step some gases such as methane are released and these indicate the shale gas potential of the rock. In other words, the pyrolysis steps represent the generation of methane that would be occurring for a lateral equivalent of the rock in a deeper part of the sedimentary basin. At 1000 °C greater amounts of carbon dioxide are released, which correspond to the breakdown of carbonate phases in the rocks, and the release of water from clays which also occurs at this temperature.

All samples produced distinct responses from carbon dioxide and water at the lowest 350 °C temperature step (Figs. 6 and 7). The responses probably reflect the liberation of desorbed volatiles from the surfaces of the shale constituents. Noticeably there are no hydrocarbon responses at this temperature. The lack of methane or other hydrocarbon gases may reflect the fact that the sample was powdered before introduction into the pyrolysis unit and any interstitial gas may have been lost. Future work could examine

the effects of sample grain size on the 350 °C evaporative step. The shales that contain Type I kerogens in the oil window (PEE, BR) produce small aliphatic hydrocarbon responses following pyrolysis at 600 °C. All shale samples also release carbon dioxide and water at 600 °C. The immature Type III shale sample (SQB) and the post mature Type I shale sample (SB) produce no significant aliphatic hydrocarbon signal following pyrolysis at 600 °C. At 1000 °C all shales that reflect Type I kerogens in the oil window (PEE, BR) produce substantial aliphatic hydrocarbon and methane responses. The immature Type III shale sample (SQB) produces no methane following pyrolysis at 1000 °C. The post mature Type I shale sample (SB) produced some methane at 1000 °C. All shales produce significant amounts of carbon dioxide and water following pyrolysis at 1000 °C.

When single step pyrolysis is conducted at a relatively high temperature (600 °C or 1000 °C), the absorbance values recorded are higher than for the corresponding step in a multistep pyrolysis experiment (Figs. 5 and 7). Single step pyrolysis at the highest temperature represents all detectable products in a single analysis. For multistep pyrolysis the individual temperature steps will contain temperature fractions, i.e. only portions, of the complete response observed for single step pyrolysis. It is sensible therefore to suggest single step analysis for organically lean or very small-sized samples. Where sample size or organic contents are sufficient,

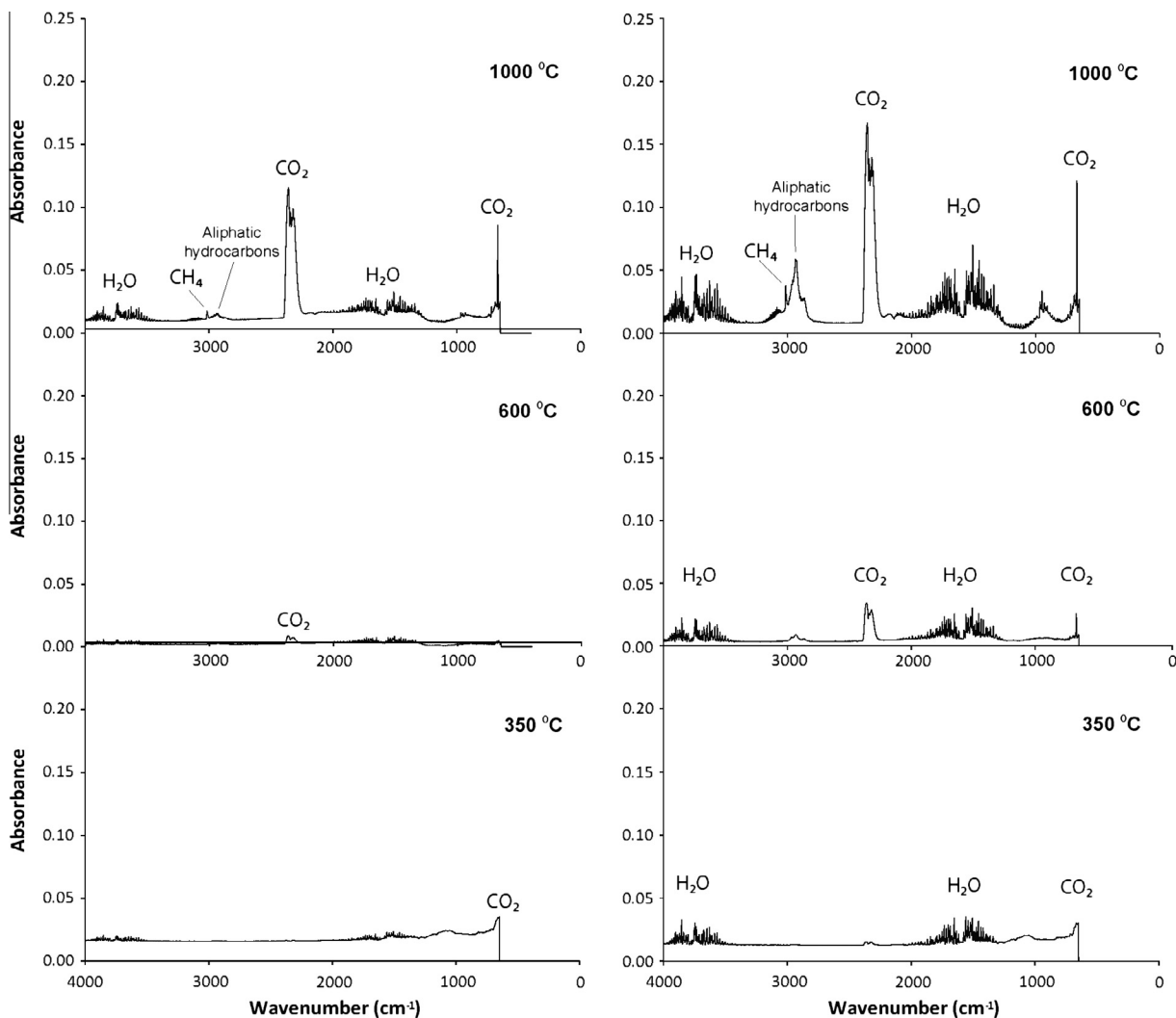


Fig. 7. Infrared spectra for a natural oil shale samples (a) SB and (b) BR pyrolysed for 15 s at 3 different temperatures: 350 °C, 600 °C and 1000 °C.

multistep analysis appears to provide important information on organic speciation, with the highest maturity sample (SB) only producing aliphatic hydrocarbon responses at the highest temperature step. Such observations are useful for maturity assessment and a standard geochemical approach used to assess the maturity of shales is to recognise the temperature at which the maximum amount of products appear during a temperature programmed analysis Ref. [17]. Natural metamorphism progressively removes more heat sensitive fractions and the temperature at which the maximum amount of products are generated moves to higher values. For instance, substantial hydrocarbon responses at 600 °C represent immature or mature samples (PEE, BR), Limited responses at 600 °C but significant responses at 1000 °C reflects post-mature samples (SB).

### 3.6. Shale gas and oil resource evaluation

Our data indicate that pyrolysis-FTIR rapidly provides much of the necessary information used to make decisions when exploring and assessing shale oil and shale gas target rocks in a rapid single analytical method. The data generated by pyrolysis-FTIR is easy to interpret and can be compared with pre-constructed calibration curves for the generation of quantitative information. The quantitative nature of pyrolysis-FTIR (Table 2) allows direct

calibration of the results with other geochemical data such as extractable organic matter and programmed pyrolysis S1 and S2 data (Table 1) providing valuable diagnostic utility for the technique.

Our Midland Valley shale samples can be used as an example of an analytical survey. The mature Type I kerogen-containing samples (PEE and BR) provide strong methane responses and evaporated and generated oil is relatively light with the pyrolysis-FTIR determined average hydrocarbon (straight, branched and cyclic compounds) chain length corresponding to the gasoline range (<C<sub>10</sub>). The PEE and BR data suggest that these rocks represent good shale oil and shale gas targets. The immature Type III kerogen-containing sample (SQB) and postmature Type I kerogen containing sample (SB) produce weak methane responses. The SQB and SB data imply they are relatively poor shale oil and shale gas targets. Multistep pyrolysis-FTIR reveals confirmatory information. SQB produces similar responses in all temperature steps and generally poor aliphatic signals indicating immaturity and a relative lack of hydrocarbon structures that can degrade to produce substantial amounts of oil and gas. SB only releases hydrocarbons at high temperatures indicating high maturity and the loss of much of its presumably good original shale oil and shale gas potential.

Using the pyrolysis-FTIR method, two approaches can be considered for shale oil and gas assessments [17]. The first is the



volume method by which geochemical and other data are used to calculate the prospectivity of a shale gas resource from first principles. The second is the analogue method where the shale oil and gas assessment is performed by comparison of the studied resource to well-known economic shale gas fields. Both approaches can be followed with the new pyrolysis-FTIR data. The oil and gas hosting and generation capability of the rock can be implied from pyrolysis data. Comparison with a catalogue of analogue samples from classic shale gas fields can be made so that rapid indications of shale gas potential of new study areas are provided. In the context of shale oil and shale gas, pyrolysis-FTIR can also inform choice of depths at which horizontal drilling and hydraulic fracturing occur.

Future work will involve the construction of a catalogue of classic shale oil and gas responses to pyrolysis-FTIR. Moreover, because of the relationship between heat and fluid viscosity the use of pyrolysis-FTIR has the potential to reveal the producible hydrocarbons in shale reservoirs, i.e. those that are the most economically relevant. Following calibration of pyrolysis-FTIR results with production data produceable hydrocarbon assessment represents an additional potential application for this method.

#### 4. Conclusions

Pyrolysis-FTIR method is a rapid method for the characterisation and quantification of liquids and gases released following the pyrolysis of organic-rich samples. This method can be applied to shale oil and shale gas targets to quickly assess their potential. A series of Carboniferous oil shales from the Midland Valley area of Scotland have been used to demonstrate the efficacy of the technique. Pyrolysis-FTIR can be applied using a single step approach where any present hydrocarbons are evaporated and mixed with newly generated hydrocarbons from the degradation of kerogen. Pyrolysis-FTIR can also be used using a multiple step approach where a series of increasing temperatures are used to reveal information on the speciation of organic carbon. Multiple step pyrolysis-FTIR also reveals maturity of the sample being investigated. Pyrolysis-FTIR data can be useful for volumetric or analogue approaches to assess the shale gas and shale oil potential or organic-rich rocks.

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