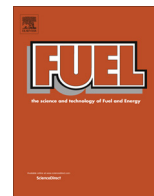




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A new rapid method for shale oil and shale gas assessment

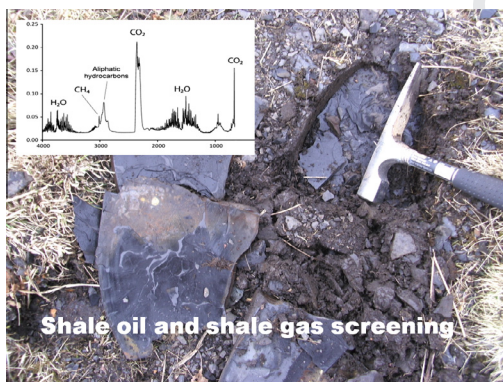
Miriam C. Wright, Richard W. Court, Fotios-Christos A. Kafantaris¹, Fivos Spathopoulos, Mark A. Sephton*

Department of Earth Science and Engineering, Imperial College London, SW7 2AZ, UK

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.

* Corresponding author. Tel.: +44 (0)20 7594 6542.

E-mail address: m.a.sephton@imperial.ac.uk (M.A. Sephton).

¹ Present address: Department of Earth Sciences, Indiana University – Purdue University Indianapolis, Indianapolis, IN 46202, USA.

These unconventional deposits are often difficult to access, more 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 with the shales either within 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 more 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 represent 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. The

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