

# Potential of emission Fourier transform infrared spectroscopy for in situ evaluation of kerogen in source rocks during pyrolysis

Craig P. Marshall<sup>a</sup>, Michael A. Wilson<sup>a,\*</sup>, Birgitta Hartung-Kagi<sup>b</sup>, Gwenda Hart<sup>b</sup>

<sup>a</sup> *Organic Geochemistry Group, Department of Chemistry Materials and Forensic Science, University of Technology, Sydney, P.O. Box 123, Broadway 2007, Australia*

<sup>b</sup> *Geotech Pty Ltd, Locked Bag 27, Cannington 6107, Australia*

Received 2 November 1999; accepted 25 August 2000

## Abstract

Eleven petroleum source rock samples have been examined by Emission Fourier transform infrared spectroscopy (FTIRES) and by Rock-Eval thermal analyses. FTIRES has been used to estimate the amount of C–H aliphatic and C–H aromatic signal lost during thermal treatment at Rock-Eval temperatures. In particular, the loss of signal from 150°C to 300°C has been monitored and compared to the yield of oil obtained over this range by Rock-Eval analysis. Likewise, signal loss between 300–500°C and 500–700°C was monitored. Correlations of FTIRES changes with Rock-Eval pyrolysis derived parameters were not found because FTIRES reflects changes in composition of undistilled material during pyrolysis. However, by relating Rock-Eval and FTIRES derived parameters a source rock quality index can be derived. This index can be useful as a quick routine method for scanning samples to determine if the free oil in the source rock was generated by thermal maturation of the same source rock. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Kerogen; Pyrolysis; Infrared spectroscopy; Source rocks; Petroleum

## 1. Introduction

Rock-Eval pyrolysis is a method used to evaluate the oil and gas potential and the maturity of source rocks during petroleum exploration (Espitalie et al., 1977). The sample is heated, and the yield of material volatilised below 300°C (termed S1) is a measure of the hydrocarbon present in the rock in a free or absorbed state. The yield of volatile material generated by thermal cracking at 300–500°C (S2) measures the potential of the source rock to yield oil. In a more recent variant (Rock-Eval pyrolysis II), the

material evolved after this temperature (S3) is determined by oxidation and used to calculate total carbon content. During pyrolysis, the temperature  $T_{\max}$ , recorded at the maximum rate of volatile release is also measured and used to evaluate thermal maturity of the source rock.

Rock-Eval pyrolysis does not give information on the composition of the source rock or the oil derived from it other than yields of volatile material at different temperatures. Oil quality is usually measured by gas chromatography mass spectrometry (GC/MS). GC/MS provides useful information, but is unsuitable for a quick routine methodology for screening large numbers of geological samples. Moreover, only materials that can pass through a GC

\* Corresponding author. Fax: +61-2-9514-1628.

E-mail address: mick.wilson@uts.edu.au (M.A. Wilson).

column are identified. Solid state  $^{13}\text{C}$  Nuclear Magnetic Resonance spectroscopy can also be useful. It is possible to estimate the aromaticity of a petroleum prone source rock and the oil that is evolved from that rock at different temperatures (Maciel et al., 1978; Miknis et al., 1982; Wilson et al., 1994). However,  $^{13}\text{C}$  NMR spectroscopy is insensitive and measurements on source rocks involve overnight runs on individual samples. Other workers have used conventional thermogravimetric analysis (TGA) for source rock evaluation, however it gives little additional information than Rock-Eval pyrolysis. Huang et al. (1999) found better correlations of  $T_{\text{max}}$  derived from TGA analysis with respect to vitrinite reflectance ( $\%R_o$ ) measurements than that of  $T_{\text{max}}$  derived from Rock-Eval pyrolysis but there seems a priori no molecular reason why this should be so. Thermogravimetric Fourier transform infrared spectroscopic (TG-FTIR) analysis of petroleum source rocks (Whelan et al., 1990) or thermogravimetric (TG) mass spectrometry may offer greater potential.

A desirable methodology would involve in situ evaluation of oil quality during pyrolysis. In addition it would be useful to measure the quality of the organic matter in the residual source rock as the oil is evolved. Previous conventional FTIR spectroscopic studies (Landais, 1995; Espitalie et al., 1985; Schenk et al., 1986; Verheyen et al., 1984; Ganz and Kalkreuth, 1987; Solomon and Miknis, 1980; Snyder et al., 1983) have found a linear correlation between the intensity of the aliphatic C–H stretching bands between 2700 and 3000  $\text{cm}^{-1}$  and the volatile matter generated between 300°C and 500°C. The method involves analysis of samples at room temperature and so does not monitor oil changes during pyrolysis. Conventional infrared (IR) spectroscopy can be used as a screening method for oils, especially when combined with chemometric techniques. However, like GC/MS its application involves collecting oils generated by Rock-Eval pyrolysis experiments and then independently studying the individual oils.

Emission Fourier transform infrared spectroscopy (FTIRES) enables thermal degradation studies to be carried out in real time. Moreover, sample sizes of only 0.1 mg are needed to acquire high quality spectra. The methodology employs an IR emission cell, from which emitted light electromagnetic radiation generated by heating the sample in a graphite

furnace is directed to a Fourier transform IR spectrometer. FTIRES has been used to study the thermal transformations of organic matter of oil shales, coals and kerogens (Cole-Clark and Vassallo, 1991; Rose et al., 1993, 1998). The changes in the intensity of absorptions such as alkyl bands (aliphatic C–H stretch) of the source rock or kerogen samples with increasing temperature from 50°C to 700°C have been monitored. Its advantage over the TG-FTIR analysis is that source rock or kerogen composition can be measured at evolution temperature.

This paper compares Rock-Eval pyrolysis data (S1, S2, S3 and  $T_{\text{max}}$  values) and FTIRES of kerogen samples in order to evaluate its potential as a new exploration tool. Ideally, one measurement by Rock-Eval pyrolysis and one measurement by FTIRES could provide a powerful matrix of complementary information.

## 2. Experimental

### 2.1. Samples

The 11 samples used in this comparative study were supplied by Geotech Services. Their geographical locations are not reported because of commercial sensitivities. Analytical details are given in Table 1. Samples were ground to fine powders before study.

### 2.2. Rock-Eval pyrolysis

This was carried out on a commercial instrument using established methodology reported elsewhere (Espitalie et al., 1977). Details of yields and source rock potential parameters are listed in Table 1. These parameters are defined as: S1 = Volatile hydrocarbons, S2 = hydrocarbon generating potential, S3 = organic carbon dioxide, S1 + S2 = potential yield,  $T_{\text{max}}$  = temperature of maximum oil yield during S2 oil generation, PI = production Index = S1/(S1 + S2), TOC = total organic carbon (mg/g), HI = hydrogen index (mg/g TOC) and OI = oxygen index (mg  $\text{CO}_2$ )/g TOC).

### 2.3. Fourier transform infrared emission spectroscopy

FTIRES was performed using a modified Digilab FTS 60A spectrometer. The emission cell consists of

Table 1  
Source rock potential parameters determined from Rock-Eval pyrolysis experiments

Sample	Group number	S1 (mg/g)	S2 (mg/g)	S3 (mg CO <sub>2</sub> /g)	S1 + S2 (mg/g)	S2/S3	T <sub>max</sub> (°C)	PI	TOC (mg/g)	HI [(mg/g)/(mg/g TOC)]	OI (mg CO <sub>2</sub> /mg/g TOC)
1	1	0.05	0.18	1.22	0.23	0.15	N/D	0.22	0.51	35	239
2	1	0.10	0.59	3.06	0.69	0.19	416	0.14	1.14	52	268
3	1	0.09	0.64	2.19	0.73	0.29	414	0.12	2.22	29	99
4	2	1.32	8.10	0.07	9.42	115.71	454	0.14	4.00	203	2
5	1	3.02	25.37	0.84	28.39	30.20	442	0.11	7.21	352	12
6	2	5.05	16.17	1.68	21.22	9.63	457	0.24	14.76	110	11
7	2	6.04	57.17	1.93	63.21	29.62	438	0.10	23.70	241	8
8	2	3.53	49.00	9.68	52.53	5.06	427	0.07	32.20	152	30
9	2	3.87	49.05	10.50	52.92	4.67	427	0.07	40.50	121	26
10	2	7.57	84.94	2.12	92.51	40.07	465	0.08	52.76	161	4
11	2	3.71	135.23	8.28	138.94	16.33	438	0.03	64.30	210	13

S1 = Volatile hydrocarbons, S2 = Hydrocarbon generating potential, S3 = Organic carbon dioxide, S1 + S2 = Potential yield, T<sub>max</sub> = Maximum temperature, PI = Production index S1/(S1 + S2), TOC = Total organic carbon (mg/g), HI = Hydrogen index (mg/g TOC), OI = Oxygen index (mg CO<sub>2</sub>/g TOC), N/D = no data.

an atomic absorption graphite rod furnace. The furnace was driven by a thyristor-controlled AC power supply with a maximum output of 150 A at 12 V. A 6-mm platinum disc was used as a hot plate to heat the samples. An insulated 0.125-mm type R thermocouple was embedded inside the platinum. A Eurotherm Model 808 proportional temperature controller, coupled to the thermocouple was used to control the temperature to an accuracy of  $\pm 10^\circ\text{C}$  at the maximum operating temperature ( $1500^\circ\text{C}$ ) and an accuracy of  $\pm 3^\circ\text{C}$  at lower temperatures ( $< 500^\circ\text{C}$ ).

The emitted IR radiation was captured by an off-axis paraboloidal mirror with a focal length of 25 mm mounted above the heater and directed into the modified Digilab FTS 60A Fourier transform IR spectrometer. The heater assembly was located so that the surface of the platinum disc was above the focal point of the mirror of the off-axis paraboloidal mirror, which gives an area 3 mm in diameter to be sampled by the spectrometer. The mirror was mounted at an angle of  $45^\circ$ , enabling it to direct the IR radiation into the interferometer. The interferometer is heated but does not contribute any emission signal. A liquid nitrogen cooled mercury–cadmium–telluride broad range (MCT) detector was used. The sample furnace was encased with a perspex box, which was purged with nitrogen. This eliminates water vapour and carbon dioxide in the path of sample emission. Spectra were acquired at temperatures from  $150^\circ\text{C}$  through to  $700^\circ\text{C}$  at increments of  $50^\circ\text{C}$  at a heating rate of a  $1^\circ\text{C}/\text{s}$ . For this temperature range, the spectra were computed from 64 co-added interferograms prior to transformation, having a resolution of  $4\text{ cm}^{-1}$ . It would have been more appropriate to study samples from  $50^\circ\text{C}$  thermal temperature since, although these are not organic, small weight losses may occur between  $50^\circ\text{C}$  and  $150^\circ\text{C}$ . However, FTIRES spectra are poor below  $150^\circ\text{C}$  and hence, of no quantitative value.

The FTIR emission technique requires a finely ground sample, as large particles become blackbody-like emitters. In this study, the rock samples were hand ground using an agate mortar and pestle. The ground sample was transferred to the platinum disc, which was then placed into the sample furnace, and then analysed. Triplicate analyses were performed on each sample to ensure consistent and repeatable results.

Table 2  
Emission infrared spectroscopy peak assignments

Wavenumber ( $\text{cm}^{-1}$ )	Assignment
3300	O–H stretch
3030–3050	Aromatic C–H stretch
2930	Antisymmetric $\text{CH}_2$ stretch
2860	Symmetric $\text{CH}_2$ stretch
1640	O–H bend
1600	Aromatic ring stretch
1440–1450	$\text{CH}_2$ and $\text{CH}_3$ bend
1000–1100	Silicates
700–900	Aromatic C–H out-of-plane bending modes

Peak assignments (Table 2) were based on previous investigations of coals, kerogens, and oil shales (Painter et al., 1985; Solomon and Carangelo, 1987; Vassallo et al., 1992; Vassallo and Attalla, 1992; Rose et al., 1993). Peak areas of aliphatic groups and aromatic groups were integrated using SPECTRAL-CALC FT-IR SOFTWARE 1989 (Galactic Industries), by drawing connecting lines across the baseline of the absorption and integrating the area under the line.

#### 2.4. IR spectroscopic parameters

Rock-Eval equivalent IR spectroscopic parameters, S1FTIRES, S2FTIRES, and S3FTIRES were calculated from the integrated peak areas from the emission spectra from the temperature range  $150$ – $700^\circ\text{C}$ , by plotting the peak area obtained for the various absorbances at different temperatures against temperature. Only the bands between  $2700$ – $3000$  and  $3000$ – $3100\text{ cm}^{-1}$  were used to calculate parameters. S1FTIRES was determined by subtracting the peak area left at  $300^\circ\text{C}$  from that obtained at  $150^\circ\text{C}$  and dividing this by total signal from peak between  $2700$ – $3000$  and  $3000$ – $3100\text{ cm}^{-1}$ . Likewise, S2FTIRES was determined by subtracting the peak area left at  $500^\circ\text{C}$  from that obtained at  $300^\circ\text{C}$  and dividing this by total signal and S3FTIRES was calculated from the peak area lost from  $500^\circ\text{C}$  to  $700^\circ\text{C}$ .

Table 3 shows the fraction of signal lost peak calculated at each temperature range by for the aliphatic C–H stretching region ( $2700$ – $3000\text{ cm}^{-1}$ )

Table 3  
Normalised peak area values used in determining S1FTIRES, S2 FTIRES and S3 FTIRES for the aliphatic C–H stretching region

Sample number	Fraction of signal lost at 300°C	Fraction of signal lost at 300–500°C	Fraction of signal lost at 500–700°C
1	0.401	0.443	0.155
2	0.054	0.936	0.010
3	0.126	0.785	0.089
4	0.148	0.589	0.263
5	0.191	0.667	0.137
6	0.164	0.597	0.240
7	0.100	0.734	0.163
8	0.177	0.645	0.177
9	0.119	0.661	0.220
10	0.082	0.523	0.392
11	0.027	0.769	0.204

and Table 4 shows the equivalent data for the aromatic C–H stretching mode (3000–3100  $\text{cm}^{-1}$ ). These numbers are calculated from the peak area changes shown in the appendix. Peak area changes are normally negative, since volatiles are lost, but for aromatic carbon they can be positive as some of the aliphatic carbon is aromatised. Thus, the fraction of signal lost can be negative, i.e. signal is gained, as well as positive.

$T_{\text{max}}$  FTIRES was determined by measuring the point of inflection of the curve shown by the thermal decomposition of the organic matter by extrapolating down to the abscissa in the S2 range 300–500°C. Table 5 shows the  $T_{\text{max}}$  FTIRES values derived for the 11 samples, for both the decomposition of

Table 4  
Normalised peak area values used in determining S1FTIRES, S2FTIRES and S3FTIRES for the aromatic C–H stretching region

Sample number	Fraction of signal lost at 300°C	Fraction of signal lost at 300–500°C	Fraction of signal lost at 500–700°C
4	0.052	0.309	0.639
6	0.357	–0.175	0.818
7	0.117	–0.104	0.987
8	0.826	–0.542	0.716
9	–0.194	–0.157	1.35
10	–0.902	0.465	1.44
11	0.100	22.3	–21.4

Table 5  
 $T_{\text{max}}$  values derived from the aliphatic and aromatic C–H stretching region

Samples	Aliphatic $T_{\text{max}}$	Aromatic $T_{\text{max}}$
1	ND	ND
2	300	–
3	370	–
4	450	475
5	400	–
6	400	500
7	450	550
8	450	500
9	450	550
10	450	550
11	450	550

ND = not determined.

aliphatic C–H stretching region (2700–3000  $\text{cm}^{-1}$ ), decomposition of the aromatic C–H stretching region (3000–3100  $\text{cm}^{-1}$ ).

### 3. Results and discussion

#### 3.1. Samples and Rock-Eval pyrolysis data

Samples were chosen which reflect the range of Rock-Eval thermal data that may be encountered. The TOC content of these samples varied from 0.51% to 64.30% TOC by weight. Samples were chosen which had both high (sample 11, Table 1) and low (sample 1, Table 1) free oil contents (S1), and variable hydrocarbon generating potential (S2) (compare samples 1 and 11, Table 1). Likewise, the production index  $PI = S1/(S1 + S2)$  of samples examined varies from 0.03 to 0.24 and the hydrogen index  $S2/TOC \times 100$  can be very high sample 5, (Table 1) or very low sample 1 (Table 1). Similarly, the oxygen index,  $OI = S3/TOC \times 100$  varies considerably.

#### 3.2. Thermal transformations as observed by FTIRES

The samples fall into two groups, namely those, which show aliphatic peaks only (Group 1), and those which also show aromatic character (Group 2). Some of these samples have low hydrogen indexes

(Table 1). Typical thermal transformations observed by FTIRES for Group 1 are shown in Fig. 1, which is data obtained from sample 3 (other samples in this group include 1, 2 and 5). They have aliphatic C–H bands from 2700 through to 3000  $\text{cm}^{-1}$  with dual maxima arising at 2860 and 2930  $\text{cm}^{-1}$  assigned to symmetric  $\text{CH}_2$  stretching modes and anti-symmetric  $\text{CH}_2$  stretching modes, respectively. These samples also show corresponding  $\text{CH}_2$  and  $\text{CH}_3$  bending modes maximising around 1440–1450  $\text{cm}^{-1}$ .

Spectra for samples 4, 6, 7, 8, 9, 10 and 11 contain the above, however they also show aromatic C–H stretching mode absorptions maximising between 3000 and 3100  $\text{cm}^{-1}$ . These typical spectra also show a peak maximising at 1600  $\text{cm}^{-1}$  due to

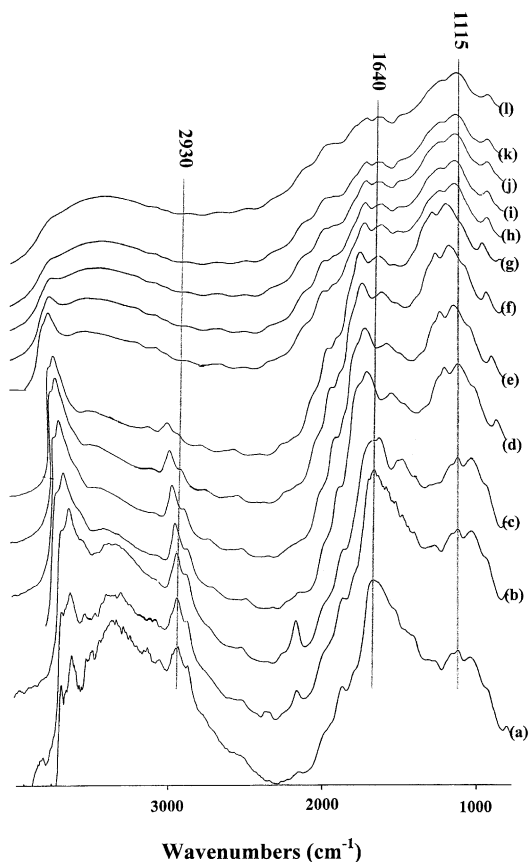


Fig. 1. Typical emission FTIR spectra of aliphatic samples from Group 1 (sample 3) in the region 800–4000  $\text{cm}^{-1}$ . (a) 150°C, (b) 200°C, (c) 250°C, (d) 300°C, (e) 350°C, (f) 400°C, (g) 450°C, (h) 500°C, (i) 550°C, (j) 600°C, (k) 650°C and (l) 700°C.

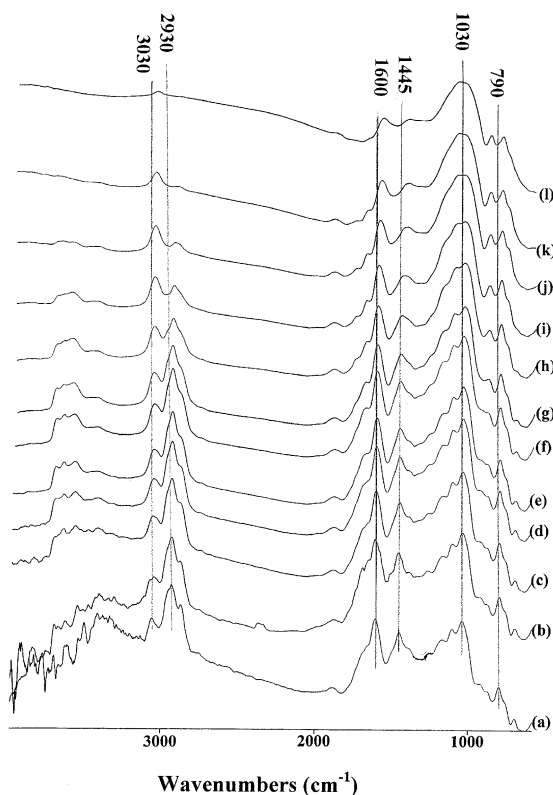


Fig. 2. Typical emission FTIR spectra of aromatic samples from Group 2 (sample 10) in the region 400–4000  $\text{cm}^{-1}$ . (a) 150°C, (b) 200°C, (c) 250°C, (d) 300°C, (e) 350°C, (f) 400°C, (g) 450°C, (h) 500°C, (i) 550°C, (j) 600°C, (k) 650°C and (l) 700°C.

aromatic ring stretching absorptions. Typical spectra for Group 2, such as those obtained for sample 10 are shown in Fig. 2.

All samples behave individually with change in temperature and this is reflected in their FTIRES spectra. Aliphatic peaks decrease with increasing temperature, at different rates, and subsequently completely disappear at  $\sim 600^\circ\text{C}$ . In the Group 2 samples, the aromatic C–H stretching mode (3000–3100  $\text{cm}^{-1}$ ) pervades until 700°C but the behaviour is dissimilar for different samples. The band maximising at 1600  $\text{cm}^{-1}$  due to aromatic ring stretching absorption shows a gradual decrease in peak area with increasing temperature, until 700°C but the rate of loss is not identical in all samples. This is because aromatic volatiles are lost at different temperatures in the sample and have different structures and/or

can be generated as involatiles by transformation of aliphatics. Fig. 3 illustrates changes in the aliphatic C–H stretch *from* 2700 through to 3000  $\text{cm}^{-1}$ , for Group 1 and Group 2 samples, respectively. For brevity, the aromatic plot is not shown.

### 3.3. Correlations with Rock-Eval pyrolysis parameters

If the total area of organic absorbance was a quantitative measure of the organic matter still in the

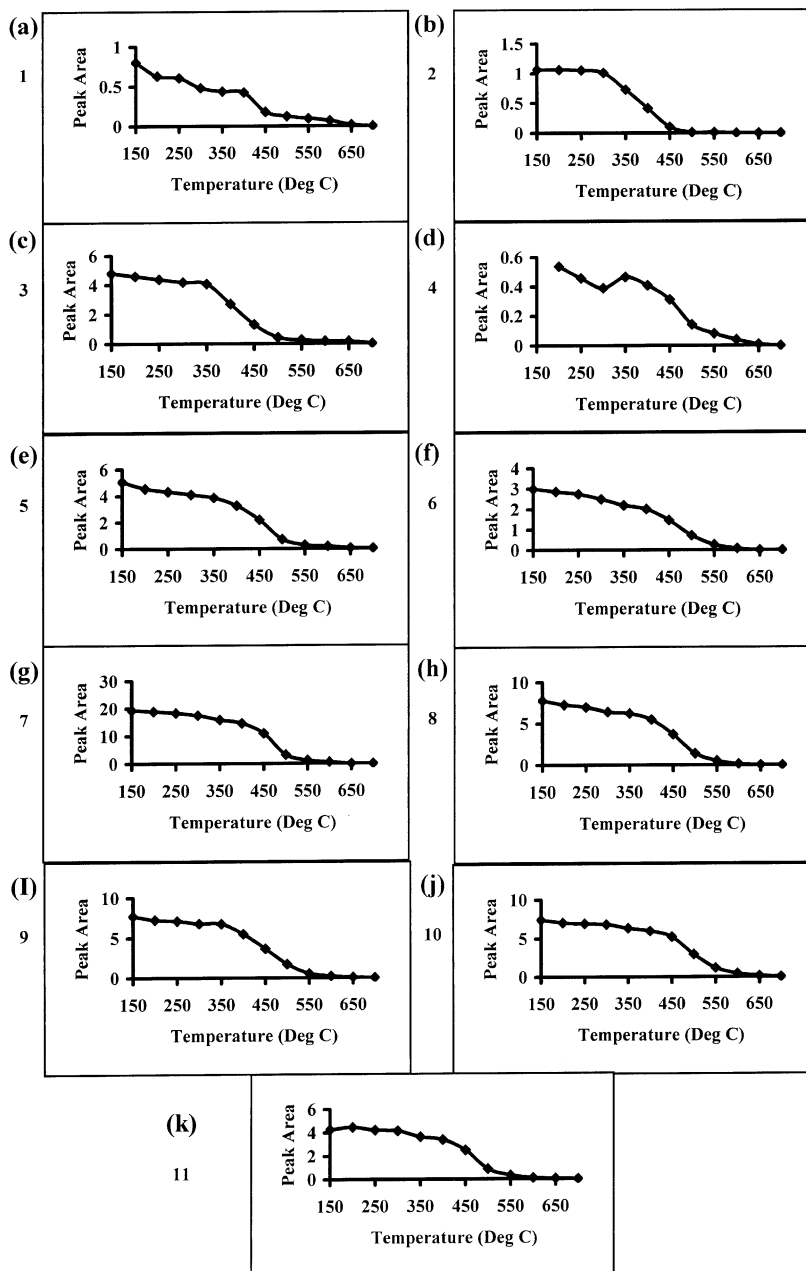


Fig. 3. Emission FTIR signal intensity of the aliphatic C–H stretch signal  $2700\text{--}3000\text{ cm}^{-1}$  with increasing temperature. (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4, (e) sample 5, (f) sample 6, (g) sample 7, (h) sample 8, (i) sample 9, (j) sample 10 and (k) sample 11.

source rock, FTIRES could be used as an alternative to Rock-Eval pyrolysis. However, as the organic material pyrolyses, contributions to the IR absorbance could change since during pyrolysis the molecular composition of the residues and oil change, and hence a good correlation is not necessarily expected.

Fig. 4a, b and c compares S1, S2, S3 values by FTIRES for the aliphatic C–H stretching region (2700–3000  $\text{cm}^{-1}$ ) with those obtained by Rock-Eval. They show that there is little correlation. This is also true of aromatic absorbance or  $T_{\text{max}}$  FTIRES (not shown). While the correlations of S1 + S2 are better (Fig. 5), they are not necessarily good.

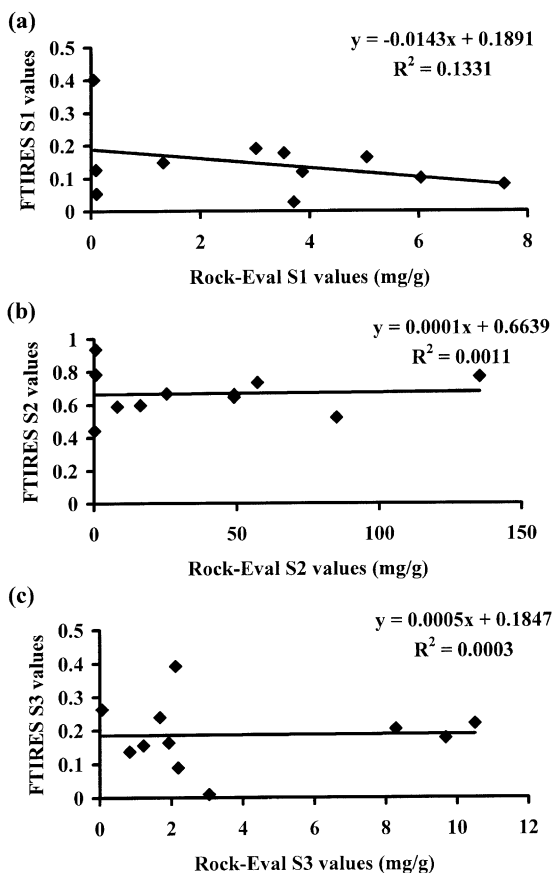


Fig. 4. Correlation between Rock-Eval pyrolysis and FTIRES parameters calculated from the aliphatic C–H stretch data. (a) Rock-Eval pyrolysis S1 plotted against S1FTIRES. (b) Rock-Eval pyrolysis S2 plotted against S2FTIRES. (c) Rock-Eval pyrolysis S3 plotted against S3FTIRES.

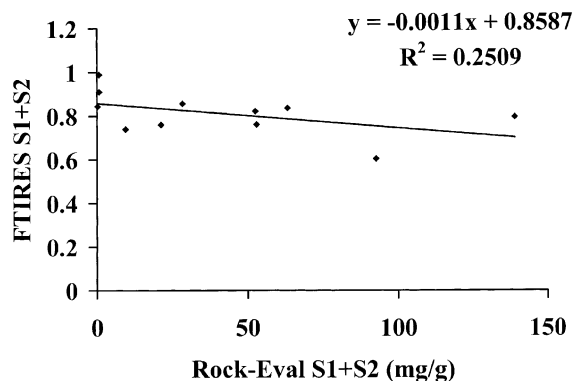


Fig. 5. Plot of Rock-Eval pyrolysis S1 + S2 against S1FTIRES + S2FTIRES. Plot derived from aliphatic C–H stretch data.

### 3.4. New quality parameters from FTIRES

S1FTIRES and S2FTIRES are respectively a measure of the gross molecular changes in the source rock as free oil and available oil are removed. Thus, S1FTIRES/S1 and S2FTIRES/S2 are measures of source rock quality. When two source rocks have the same free oil but in different quantities, then S1FTIRES/S1 values is the same. Likewise, source rocks that have similar material, which can be thermally matured to oil, will have the same S2FTIRES/S2. If the free oil in a source rock is the same as oil obtained by further thermal maturation of that source, then S1FTIRES/S1 = S2FTIRES/S2.

If we define a constant  $k$  where,

$$(S1FTIRES/S1)k = S2FTIRES/S2 \quad (1)$$

then  $k$  is a measure of the difference in quality between available oil in the sample and that, which may be found when appropriate geochemical temperature gradients are present. The value  $k$  can be expressed for any FTIRES absorption area, but here, we confine ourselves to that obtained for aliphatic  $k_{\text{ali}}$ , aromatic  $k_{\text{arom}}$ , and aromatic plus aliphatic absorbance  $k_{\text{ali}}$ . When  $k = 1$  or thereabouts then the free oil in the sample is the same as the oil that could be produced by thermal maturity. That is, the oil has been generated from the same rock.

Values of S1FTIRES/S1 and S2FTIRES/S2 and  $k$  for the samples are shown in Table 6. Values of S1FTIRES/S1 and S2FTIRES/S2 and  $k$  are listed for aliphatic absorbances, and aromatic absorbances.



Table 6  
Values of S1FTIRES/S1 and S2FTIRES/S2 for the samples of Group 1 and Group 2

Sample	Aliphatic S1FTIRES/S1	Aliphatic S2FTIRES/S2	Constant $k_{\text{ali}}$ obtained for aliphatic HC	Aromatic S1FTIRES/S1	Aromatic S2FTIRES/S2	Constant $k_{\text{arom}}$ obtained for aromatic HC	$k_{\text{ali}}/k_{\text{arom}}$
1	8.028	2.463	0.307	–	–	–	–
2	0.535	1.587	2.966	–	–	–	–
3	1.403	1.226	0.874	–	–	–	–
4	0.112	0.073	0.649	0.039	0.038	1.03	0.630
5	0.063	0.026	0.417	–	–	–	–
6	0.032	0.037	1.139	0.071	–0.011	–6.45	–0.177
7	0.017	0.013	0.777	0.019	–0.002	–9.50	–0.082
8	0.050	0.013	0.263	0.283	–0.011	–25.72	–0.010
9	0.031	0.014	0.440	–0.050	–0.003	16.67	0.026
10	0.011	0.006	0.574	–0.119	0.005	–2.38	–0.241
11	0.007	0.006	0.781	0.027	0.165	0.164	4.762

The  $k_{\text{ali}}$  constant approaches 1 for samples 3 > 6 > 7 > 4 and hence the free oil is similar to the oil generated from pyrolysis. Samples 1, 2, 5, 8, 9 and 10 (Table 6) have  $k_{\text{ali}} \neq 1$ . These cases show that the material, which is free (i.e., volatile between 150°C and 300°C) in the source rocks, is very different in composition from that which can be made by thermal generation by heating above 300°C. These results could be interpreted as just simply implying the sample studied had not been heated to thermal maturity in its geological setting, which is obvious. However, it could also be that free material has not been generated at the same geological location but has come from a different geological source with different composition.

Similar arguments can be made concerning aromatics. When aromatics are similar in free and generated oils, then, S1FTIRES/S1 and S2FTIRES/S2 are similar and the value of  $k_{\text{arom}}$  will approximate 1. This relationship is shown by sample 4 (Table 6), while the other aromatic samples show  $k_{\text{arom}}$  values differing widely from 1 (samples 6, 7, 8, 9, 10 and 11 — Table 6). It can be seen from Table 6 that sample 4 has the same type of aliphatics ( $k_{\text{ali}}$  approximates 1) and the same type of aromatics ( $k_{\text{arom}}$  approximates 1) in both free and generated oil. This suggests the free oil is from the same source rock but was formed at a geological setting that had been under higher geothermal gradients and then had migrated to the area from which the sample was obtained.

#### 4. Conclusions

1. FTIRES is shown to be a valuable method for obtaining additional information during the pyrolysis of source rocks to evaluate their hydrocarbon generation potential.

2. While correlations with Rock-Eval pyrolysis derived parameters are not found, equivalent parameters derived from FTIRES when combined with Rock-Eval pyrolysis data can give a measure of oil quality. During Rock-Eval analysis when the sample is heated the yield of material volatilised below 300°C (termed S1) is a measure of the hydrocarbon present in the rock in a free or absorbed state. The yield of volatile material generated by thermal cracking at 300–500°C (S2) measures the potential of the source rock to yield oil. If S1FTIRES and S2FTIRES are the Rock-Eval pyrolysis equivalent FTIRES derived parameters then S1FTIRES/S1 and S2FTIRES/S2 can be used as source rock quality indexes.

3. The constant  $k$  derived from the relationship (S1FTIRES/S1)  $k$  = S2FTIRES/S2 can be useful in determining whether oil migration has occurred.

#### Acknowledgements

We thank Dr. A. M. Vassallo, CSIRO, North Ryde Australia for the use of the FTIRES spectrometer.

## Appendix A

Table A1. Calculation of the fraction of peak area lost at 150–300°C

Sample	Peak area change aliphatic 150–300°C = $I_a$	Peak area change aliphatic 150–700°C = $I_a$ total	$I_a/I_a$ total	Peak area change aromatic 150–300°C = $I_b$	Peak area change aromatic 150–700°C = $I_b$ total	$I_b/I_b$ total
1	-0.322	-0.802	0.401	-	-	-
2	-0.057	-1.065	0.054	-	-	-
3	-0.606	-4.797	0.126	-	-	-
4	-0.079	-0.537	0.148	-0.018	-0.346	0.0520
5	-0.965	-5.066	0.190	-	-	-
6	-0.488	-2.987	0.163	-0.100	-0.280	0.357
7	-1.948	-19.397	0.100	-0.149	-1.276	0.117
8	-1.380	-7.790	0.177	-0.361	-0.437	0.826
9	-0.917	-7.712	0.119	0.132	-0.680	-0.194
10	-0.604	-7.411	0.082	0.339	-0.376	-0.902
11	-0.114	-4.252	0.027	0.002	0.020	0.100

Table A2. Calculation of the fraction of peak area lost at 300–500°C

Sample	Peak area change aliphatic 300–700°C = $I_a$	Peak area change aliphatic 150–700°C = $I_a$ total	$I_a/I_a$ total	Peak area change aromatic 300–500°C = $I_b$	Peak area change aromatic 150–700°C = $I_b$ total	$I_b/I_b$ total
1	-0.355	-0.802	0.443	-	-	-
2	-0.997	-1.065	0.936	-	-	-
3	-3.764	-4.797	0.785	-	-	-
4	-0.316	-0.537	0.589	-0.107	-0.346	0.309
5	-3.380	-5.066	0.667	-	-	-
6	-1.783	-2.987	0.597	0.049	-0.280	-0.175
7	-14.236	-19.397	0.734	0.133	-1.276	-0.104
8	-5.026	-7.790	0.645	0.237	-0.437	-0.542
9	-5.098	-7.712	0.661	0.107	-0.680	-0.157
10	-3.872	-7.411	0.523	-0.175	-0.376	0.465
11	-3.269	-4.252	0.769	0.446	0.020	22.3

Table A3 Calculation of the fraction of peak area lost at 500–700°C

Sample	Peak area change aliphatic 500–700°C = $I_a$	Peak area change aliphatic 150–700°C = $I_a$ total	$I_a/I_a$ total	Peak area change aromatic 500–700°C = $I_b$	Peak area change aromatic 150–700°C = $I_b$ total	$I_b/I_b$ total
1	-0.125	-0.802	0.155	-	-	-
2	-0.011	-1.065	0.010	-	-	-
3	-0.427	-4.797	0.089	-	-	-
4	-0.141	-0.537	0.263	-0.221	-0.346	0.639
5	-0.694	-5.066	0.137	-	-	-
6	-0.715	-2.987	0.240	-0.229	-0.280	0.818
7	-3.163	-19.397	0.163	-1.260	-1.276	0.987
8	-1.381	-7.790	0.177	-0.313	-0.437	0.716
9	-1.697	-7.712	0.220	-0.919	-0.680	1.351
10	-2.906	-7.411	0.392	-0.540	-0.376	1.436
11	-0.868	-4.252	0.204	-0.428	0.020	-21.4

## References

- Cole-Clark, P.A., Vassallo, A.M., 1991. Infrared emission spectroscopy of coal. *Fuel* 71, 469–470.
- Espitalie, J., Laporte, J.L., Madec, M., Marquis, F., Leplat, P., Paulet, J., Boutefeu, A., 1977. Methode rapide de caracterisation des roches meres de leur potentiel petrolier et de leur degre d'evolution. *Rev. Inst. Fr. Pet.* 32, 23–42.
- Espitalie, J., Deroo, G., Marquis, F., 1985. La pyrolyse Rock-Eval et ses applications. *Rev. Inst. Fr. Pet.* 40, 755–784.
- Ganz, H., Kalkreuth, W., 1987. Application of infrared spectroscopy to the classification of kerogen-types and the evaluation of source rock and oil shale potentials. *Fuel* 66, 708–711.
- Huang, H., Wang, S., Wang, K., Klein, M.T., Calkins, W.H., 1999. Thermogravimetric and Rock-Eval studies of coal properties and coal rank. *Energy Fuels* 13, 396–400.
- Landais, P., 1995. Statistical determination of geochemical parameters of coal and kerogen macerals from transmission micro-infrared spectroscopy data. *Org. Geochem.* 23, 711–720.
- Maciel, G.E., Bartuska, V.J., Miknis, F.P., 1978. Correlation between oil yields of oil shales and  $^{13}\text{C}$  nuclear magnetic resonance spectra. *Fuel* 57, 505–506.
- Miknis, F.P., Smith, J.W., Maughan, E.K., Maciel, G.E., 1982. Nuclear magnetic resonance: a technique for direct nondestructive evaluation of source-rock potential. *Am. Assoc. Pet. Geol. Bull.* 66, 1396–1401.
- Painter, P.C., Snyder, R.W., Starsinic, M., Coleman, M.M., Kuehn, D.W., Davis, A., 1985. Concerning the application of FT-IR to the study of coal: a critical assessment of band assignments and the application of spectral analysis programs. *Appl. Spectrosc.* 35, 475–485.
- Rose, H.R., Smith, D.R., Vassallo, A.M., 1993. An investigation of thermal transformations of the products of oil shale demineralisation using infrared emission spectroscopy. *Energy Fuels* 7, 319–325.
- Rose, H.R., Smith, D.R., Vassallo, A.M., 1998. Study of the oxidation of oil shale and kerogen by Fourier transform infrared emission spectroscopy. *Energy Fuels* 12, 682–688.
- Schenk, H.J., Witte, E.G., Muller, P.J., Schwochau, K., 1986. Infrared estimates of aliphatic kerogen carbon in sedimentary rocks. *Org. Geochem.* 10, 1099–1104.
- Snyder, R.W., Painter, P.C., Cronauer, D.C., 1983. Development of FT-i.r. procedures for the characterisation of oil shale. *Fuel* 62, 1205–1214.
- Solomon, P.R., Carangelo, R.M., 1987. FT-ir analysis of coal. *Fuel* 67, 949–959.
- Solomon, P.R., Miknis, F.P., 1980. Use of Fourier transform infrared spectroscopy for determining oil shale properties. *Fuel* 59, 893–896.
- Vassallo, A.M., Attalla, M.I., 1992. Studies of thermal transformations of fulvic acids using Fourier transform-infrared emission spectroscopy. *J. Anal. Appl. Pyrol.* 23, 73–85.
- Vassallo, A.M., Cole-Clark, P.A., Pang, L.S.K., Palmisano, A.J., 1992. Infrared emission spectroscopy of coal minerals and their thermal transformations. *J. Appl. Spectrosc.* 46, 73–78.
- Verheyen, T.V., Johns, R.B., Esdaile, R.J., 1984. Structural investigations of Australian coals — IV: A characterisation of the variation in rank of bituminous coal fractions by elemental analysis and I.R. spectroscopy. *Geochim. Cosmochim. Acta* 47, 1579–1587.
- Whelan, J., Carangelo, R., Solomon, P.R., Dow, W.G., 1990. TG/plus — A pyrolysis method for following maturation of oil and gas generation zones using  $T_{\text{max}}$  of methane. *Org. Geochem.* 16, 1187–1201.
- Wilson, M.A., La Fargue, Gizachew, D., 1994. Solid state  $^{13}\text{C}$  NMR for characterising source rocks. *Aust. Pet. Explor. Assoc. J.* 210–215.