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Multidimensional and comprehensive two-dimensional gas chromatography of dichloromethane soluble products from a high sulfur Jordanian oil shale

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ABSTRACT

A high sulfur Jordanian oil shale was converted into liquid hydrocarbons by reaction at 390 °C under N_2, and the dichloromethane soluble fraction of the products was isolated then analyzed by using gas chromatography (GC). Comprehensive two-dimensional GC (GC × GC) and multidimensional GC (MDGC) were applied for component separation on a polar – non-polar column set. Flame-ionization detection (FID) was used with GC × GC for general sample profiling, and mass spectrometry (MS) for component identification in MDGC.

Multidimensional GC revealed a range of thiophenes (**th**), benzothiophenes (**bth**) and small amounts of dibenzothiophenes (**dbth**) and benzonaphthothiophenes (**bnth**). In addition, a range of aliphatic alkanes and cycloalkanes, ethers, polar single ring aromatic compounds and small amounts of polycyclic aromatics were also identified. Some of these compound classes were not uniquely observable by conventional 1D GC, and certainly this is true for many of their minor constituent members. The total number of distinct compounds was very large (ca. > 1000). GC × GC was shown to be appropriate for general sample profiling, and MDGC-MS proved to be a powerful technique for the separation and identification of sulfur-containing components and other polar compounds.

1. Introduction

Oil shale is an alternative source of hydrocarbon fuel which has attracted researchers for many years. There has been a surge of interest recently because of increased oil prices and the realization that liquid oil resources are limited. This is particularly important for countries without indigenous crude oil deposits such as Jordan [1]. Oil shale is an organic rich sedimentary rock which, when heated to high temperature, produces oil [2]. The organic material in the shale can be divided into two types depending on its solubility in organic solvents at room temperature; the soluble material is defined as bitumen, and the non-soluble material is called kerogen [2]. Jordanian oil shale is derived from marine algae; it is rich in sulfur (9.8 wt% dry mineral matter free; dmmf) and consequently, the organic matter released at high temperature is more complex (ca. > 1000 identifiable compounds) than that from low-S oil shales [3,4]. Gas chromatography–mass spectrometry (GC–MS) is a primary method used to identify compounds in liquid fuel [5], but the complexity of shale-derived organic material generates chromatograms with an abundance of overlapping peaks, making identification of organic material in oil shale analytically difficult.

Chromatographic methods with increased separation power are required for the resolution and identification of compounds in complex matrixes. One method, introduced more than 40 years ago [6] but somewhat neglected since, is multidimensional GC (MDGC) [7]. Conventional 'heart-cut' (H/C) MDGC instrumentation enables the transfer of selected bands of overlapping compounds from a primary (^{1}D) to a secondary (^{2}D) column, connected by means of an interface (either a switching valve or a Deans switch). The ^{1}D effluent bands, subjected to this re-injection process, may be selected through preliminary one-dimensional GC experiments [8]. Recently, technologies and applications studies in both MDGC and comprehensive two-dimensional GC were reviewed, and a continuum in technical implementation of the two approaches suggested [9]. Maikhunthod et al. [10] developed, applied and validated a dual GC × GC/MDGC method (termed switchable GC × GC/targeted MDGC) with H/C for the analysis of essential oils. H/C MDGC was employed for identification of oxygenated compounds in gasoline and in algae-derived jet fuel [7,11].

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Yang et al. investigated an approach that employed sequential MDGC analysis by taking 1.00 or 1.50 min fractions from a first column and applied each to a second column analysis [12]. Recently, Mitrevski et al. [13] used GC × GC with an FPD detector to quantify the S containing compounds in the reaction products from a high S oil shale, although generally class-compositions were derived and little detailed chemical speciation was conducted.

The aim of this work is to apply the GC × GC method with FID detection for general sample profiling, and then to conduct a sequential heart-cut MDGC-qMS method for detailed identification of organic material derived from the oil shale and for comparison of the results with those obtained by conventional 1D GC–MS.

2. Experimental

2.1. Materials

Oil shale from the El Lajjun deposit in Jordan derived from marine algae in the Campanian–Maastrichtian age (65–84 million years ago) [4] was received as 2 mm particles and was ground to 180 μm. An ash yield of 75.8 wt% dry basis (db) (organic material 24.2 wt% db) was determined by heating in air to nearly constant mass. A low ashing temperature (490 °C) was used to minimize carbonate–silica reactions and ensure ash yields were similar to the inorganic content of the shale. A solid state ^{13}C NMR CP/MAS spectrum of the acid-washed shale showed a C_{ar} to C_{aliph} of 0.21:0.79, indicating a high aliphatic content, as implied by the hydrogen-to-carbon atomic ratio for the total organic material of 1.44 [14]. N_2 was purchased from BOC Australia Ltd. Dichloromethane (DCM; liquid chromatography grade) was purchased from Merck (Kilsyth, Australia).

2.2. Sample preparation procedure

Reactions were carried out in 27 mL stainless steel autoclaves fitted with a stainless steel liner charged with 2.1 g of oil shale dried at 105 °C and 3 MPa (cold) of N_2. The autoclave was evacuated and weighed before and after the gas was charged, so that the free space in the autoclave could be calculated. The autoclave was lowered into a preheated sand bath and came to the required temperature (390 °C) in 2–4 min. The autoclave was continuously shaken while in the sand bath. The autoclave was held at temperature for the required time (1 h), removed, allowed to cool, then weighed. A fraction of the DCM soluble material was taken for subsequent analysis. A detailed reaction and workup procedure is given in Amer et al. [14].

2.3. Instrumentation

A sample of DCM soluble material was analyzed by GC–MS using a HP6890 instrument (Agilent Technologies, Mulgrave, Australia) in splitless mode. For GC separation, a HP-5 ms capillary column (5% phenylmethylsiloxane), 30 m long, 0.25 mm internal diameter (ID), 0.25 μm nominal film thickness (d_f), was used. The inlet temperature was 230 °C. The oven temperature was initially held at 50 °C for 2 min then raised to 200 °C at a rate of 4 °C/min, held at 200 °C for 2 min, then raised to 300 °C at 8 °C/min and held at 300 °C for 3 min. For MS, the electron ionization (EI) energy was 70 eV, the accelerating voltage 1.9 kV, the mass scan range of 45–600 m/z, with an ion source temperature of 200 °C.

An Agilent 7890A GC coupled to an Agilent 5975C quadrupole MS (qMS; Agilent Technologies) was used for all MDGC analyses in the EI mode at 70 eV over the mass range 45–350 m/z at 4.57 scans/s. A flame-ionization detector (FID) fitted to the same system was used for all GC × GC-FID analyses. Injection and detection (FID) temperatures were 270 °C and 280 °C, respectively. The National Institute of Standards and Technology NIST08 MS database and NIST search algorithm (NIST, Gaithersburg, MD, USA) were used for peak identification. A Deans switch (DS) assembly (part number G2855-60100, Agilent) enabled H/C in MDGC operation. Modulation for the GC × GC-FID mode and cryofocusing of H/C in MDGC were performed by using the longitudinally modulated cryogenic system (LMCS, Doncaster, Victoria, Australia), with liquid carbon dioxide as a coolant.

For MDGC, the ^{1}D column was 30 m × 0.25 mm ID × 0.25 μm d_f Supelcowax 10 (Supelco, Bellefonte, USA) with poly(ethylene glycol) as a polar (P) stationary phase, while the ^{2}D NP column was Rxi-5Sil MS (20 m × 0.18 mm × 0.18 μm d_f) with 5% phenyl (equivalent)/95% dimethylpolysiloxane (Restek, Bellefonte, USA). The usual DS restrictor column was used as the ^{2}D column in GC × GC mode, which in the present case was 2 m × 0.1 mm × 0.1 μm d_f BPX5 phase (rather than a length of deactivated fused silica column) from SGE Analytical Science (Ringwood, Victoria, Australia). The same column set and the same GC system were used for both MDGC and GC × GC modes, with only one operational difference: for MDGC mode, modulation was performed on the beginning of the 20 m ^{2}D column (Rxi-5Sil MS), while for GC × GC modulation was performed on the beginning of the 2 m ^{2}D column (BPX5). Column configurations and a schematic of the systems used are given in Fig. 1.

Due to the complexity of the sample matrix, it was decided to sample very narrow H/C zones of the ^{1}D eluate, followed by fast separation on the ^{2}D column. Subsequent to preliminary experiments using different H/C durations, a H/C duration of 0.2–0.3 min was chosen here to sample effluent from ^{1}D. From the maximum retention on ^{2}D ($^2t_{R,max}$), the regular period H/C sampling cycle could be set to be just greater than this value so that sequential H/C can be applied. Therefore, H/Cs were sampled every 2.00 min in order to allow repetitive sampling during a single GC run and to prevent components from a current H/C eluting after the commencement of the next H/C cycle. For the next injection, the whole sampling protocol is incremented by 0.20 min as described recently [7]. In this manner, six analyses provided coverage of the total sample.

The same oven temperature program was applied in both modes: 60 °C (1 min) to 280 °C (hold 2 min) at 8 °C/min. One microliter of the DCM soluble oil sample was injected at a split ratio of 50:1. In GC × GC-FID mode, modulation was performed at −20 °C with 6 s modulation period (P_M), and a FID data acquisition rate of 50 Hz. For the H/C mode, 10–13 H/C of ^{1}D effluent were taken for each single run, with a cut duration of 0.20 min conducted periodically with a 2.00 min interval between each cut. This operation was accomplished automatically. The transferred effluent from each H/C was refocused by cryotrapping at the LMCS (−20 °C) with release of the trapped components 6 s after each H/C was finished. One G size cylinder of liquid CO_2 was sufficient for about 30 analyses. For comparison purposes, H/C was also diverted to the long ^{2}D column without cryotrapping, but this was deemed to be inefficient since broad peaks resulted arising from peak dispersion on the ^{1}D column. In one instance the cryofocused H/C was analyzed on the ^{2}D column by cooling the oven and slowly raising the temperature in a similar manner as reported previously [7]; this provided significantly greater separation and is proposed for the discovery process of determining the complete component composition of each H/C, but it is very time-consuming (data not shown).

3. Results and discussion

3.1. GC–MS

The total ion chromatogram (TIC) and selected extracted ion chromatograms (EIC) for a sample of DCM-soluble organics are

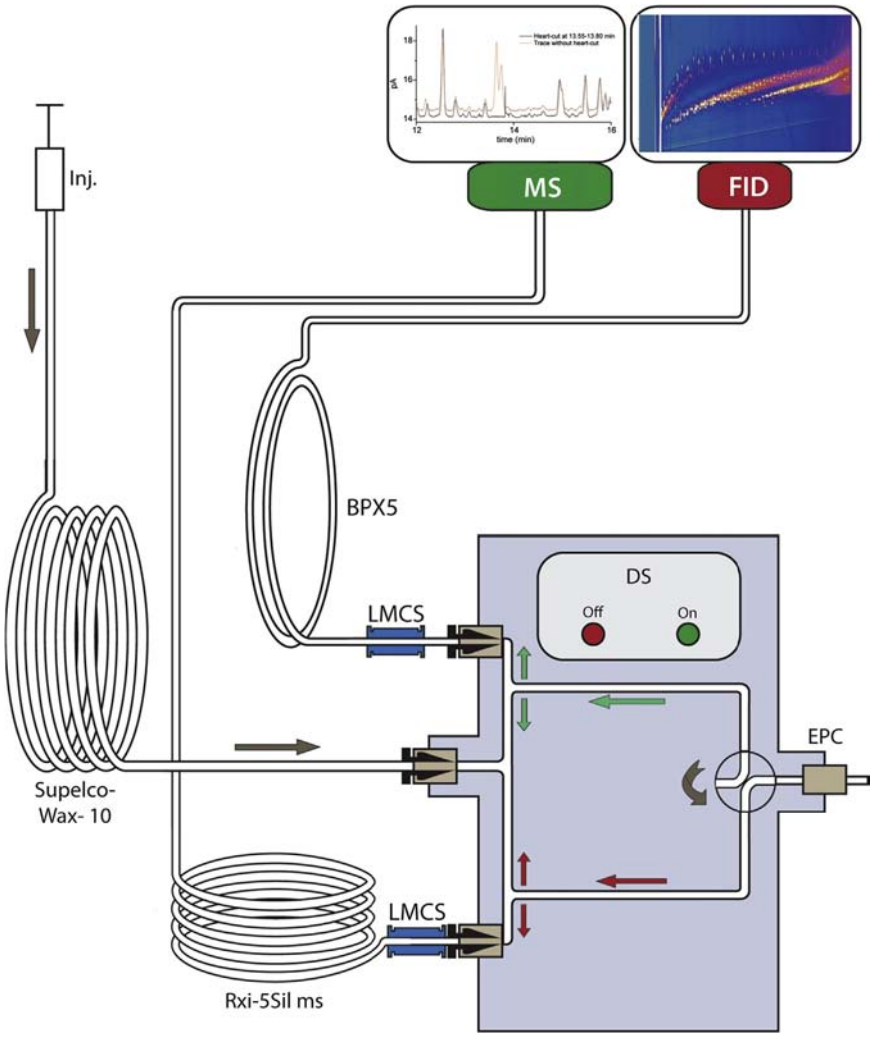

Fig. 1. Schematic of the instrumental arrangement. GC × GC-FID was performed using fast modulation (cryotrapping) applied at the beginning of the short ^{2}D column (red arrow flow-path), and MDGC–qMS for multiple heart-cutting where target modulation occurs at the beginning of the long ^{2}D column (green arrow flow-path). EPC: electronic pressure control for the Deans switch (DS) operation. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

shown in Fig. 2. GC–MS data indicate a highly complicated TIC with straight chain *n*-alkanes (and some branched compounds) giving the most prominent peaks. A homologous series ranging from C_{10}–C_{32} (*m*/*z* 57) and match quality ranging from 580 to 862 (on the scale 0–999) was noted. No cycloalkanes were detected, which most likely is due to co-elution with other higher-abundance compounds such as abundant alkanes, branched alkanes, and thiophenes. The short chain *n*-alkane peaks ($< C_{22}$) were more prominent, suggesting the oil shale originated from algae [15]. The cracking of high molecular weight compounds may also contribute to this effect.

Pristane (Pr) and phytane (Phy) are isoprenoids derived from phytol [16] and other biological precursors. Both compounds gave observable peaks in the TIC. Phytol is preferentially degraded to Pr under oxic conditions and to Phy under anoxic/reducing conditions [16].

Monocyclic aromatics were identified from the EIC *m*/*z* 91 (C_n-benzene) trace although with poor match quality ranging from 523 to 678, which is probably again largely due to co-elution with other high-abundance compounds such as alkanes. No peaks from polycyclic compounds such as hopanes or steranes were found in either the TIC or the EIC. These compounds have been identified in algae derived materials whose composition has been reported in the literature [17], but their absence here may be due to low sampled mass, upper temperature limits, and insufficient component abundance.

Fig. 3 shows the EIC for S-containing compounds, with *m*/*z* 97 (C_n-thiophene) and *m*/*z* 161 (C_n-benzothiophene). It shows an homologous series of substituted thiophenes from C_1 to C_{19}, with match quality ranging from 545 to 829. The *m*/*z* 161 EIC in Fig. 3 indicates the presence of an homologous series of benzothiophenes ranging from C_1 to C_3, again with a relatively poor match quality, 522 to 654. In all cases, both class of the compound, and precise attribution of a molecular ion is difficult due to overlapping components. The high organic sulfur content in the shale (see above) agrees with previous reports [5], and is probably related to the marine algal origin of the oil shale.

The GC–MS results for the shale oil indicate the strongly aliphatic character of the shale oil, and also the presence of a large number of S compounds (thiophenes and benzothiophenes), which contribute to the complexity of the chromatogram resulting in a significant overlapping of peaks over most of the chromatogram. This makes the secure identification of individual compounds present in the sample difficult, and explains the poor mass spectral match quality. These reasons led to the proposed development of multicolumn GC for further characterization of the shale products.

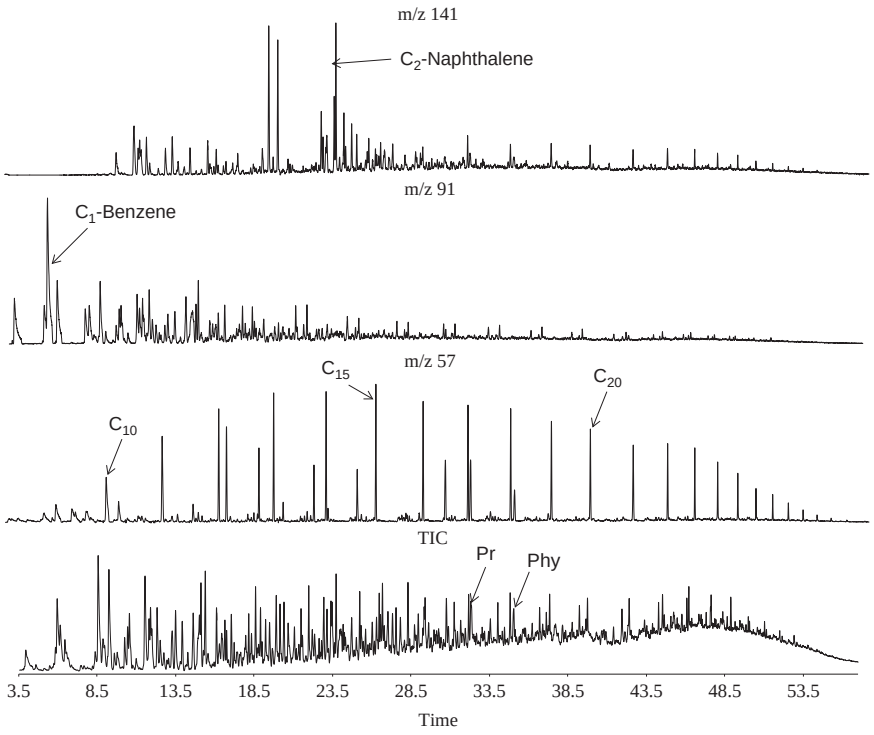

Fig. 2. Total ion chromatogram of 1D GC–MS of El-Lajjun oil shale of DCM soluble compounds at 390 °C under N_2, with EIC of alkanes (*m/z* 57), C_n one-ring aromatics (*m/z* 91) and two-ring aromatics (*m/z* 141).

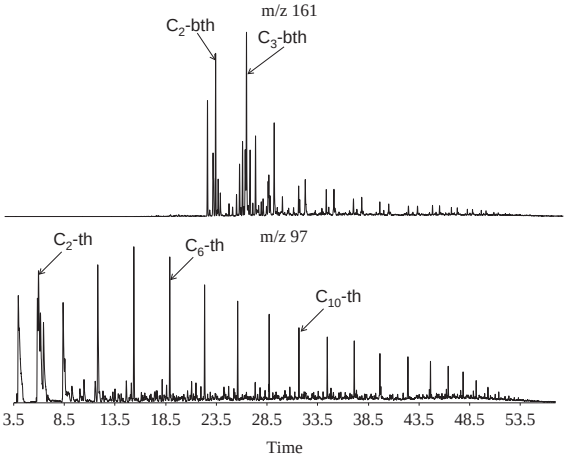

Fig. 3. The EIC for 1D GC–MS analysis for different sulfur compound classes, substituted thiophenes (*m/z* 97) and substituted benzothiophenes (*m/z* 161).

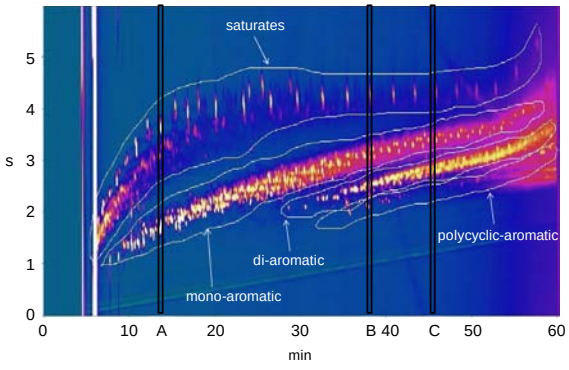

Fig. 4. GC × GC-FID 2D plot of a shale oil sample using a slow oven temperature program. Several classes of components are clearly distinguished. Refer to text for the marked zones A, B and C.

3.2. GC × GC-FID

The DCM-soluble materials comprise components with a wide range of boiling points. ^{1}H–NMR results imply that the concentration of cyclic and aromatic compounds is relatively low, and the analysis of these low abundance compounds, poorly separated in conventional GC–MS (see above), contribute to uncertainty in identification. In GC × GC, effluent from the ^{1}D column is 'modulated' (sampled) into a large number of contiguous fractions of small time packets, and each is immediately separated on the ^{2}D column. Separation on the ^{2}D column is very fast, so the sampled fractions can be narrow and the separation obtained on the ^{1}D column is largely maintained. The modulator interface between the two columns performs the collection/re-injection function of narrow fractions from ^{1}D to ^{2}D columns.

GC × GC-FID analysis on the polar/non-polar (P/NP) column set of DCM-soluble material extracted from oil shale is shown in Fig. 4, and illustrates the impact of the unique selectivity and separation power of the GC × GC method. A polar ^{1}D column elutes alkanes at relatively lower elution temperature (T_e) so, when delivered to the non-polar ^{2}D column, they have relatively higher retention factors than polar compounds on this phase. Thus, the impact of retaining these components is to extend their ^{2}D elution time, to make greater use of the retaining power and increase non-polar (saturate) peak resolution. This is reflected in the 2D position of the series of saturate compounds. Conversely, components of greater polarity are more strongly retained on the ^{1}D column; they have higher T_e, and this facilitates very short ^{2}D retention times, as demonstrated by the ^{2}D position of the polycyclic aromatics, which have low retention factors. Thus, in this column setup, retention is increased and resolution for saturated hydrocarbons is greatly improved compared to the NP/P column set [18]. The aromatics elute over a narrower ^2t_R time range. This may be an

Table 1
Compounds identified by sequential MDGC-MS.

Saturates	Cycloalkanes	Ethers	Mono-aromatic	Di-aromatic	Sulfur-compounds
C_{10}–C_{32}	Cyclopentanes (C_1–C_6) Cyclohexanes (C_1–C_8)	Cyclic (furans) Aliphatic (C_8–C_{18})	Benzenes (C_1–C_6)	Indenes Naphthalenes (C_1–C_6)	Thiophenes (C_1–C_{19}) Benzothiophenes (C_1–C_6) Dibenzothiophenes (C_1–C_3) Benzonaphthothiophene

advantage when group-type determination is desired, or a larger number of classes of analytes have to be distinguished, as in this matrix. It should be added that, under properly optimized experimental conditions – primarily temperature control – not only can alkanes be separated from cycloalkanes (which could not be uniquely confirmed in the 1D GC–MS TIC result), but a detailed separation within each class in the form of sub-classes can also be obtained (Fig. 4). A modulation ratio ($M_R = {}^1w_b/P_M$) [19] of 1.2 was noted, with average first dimension peak width (^1w_b) of ~7 s, and this has ramifications on peak capacity (^1n_c) and potential reduced separation performance on the first column as a consequence of the modulation process. The 6 s P_M setting ensures each ^{2}D analysis is completed within one modulation cycle. The added peak capacity arising from the second column and the structured retention for different chemical classes – as clearly displayed in Fig. 4 – more than offsets this ^1n_c reduction. However, this report chooses to focus on the MDGC approach, for qualitative interpretation of shale-oil composition.

The major saturate peaks distributed from left to right parallel to the abscissa of the GC × GC chromatogram is an homologous series of C_{10} to C_{32} *n*-alkanes. Bands from top to bottom on the *y*-axis, separated according to chemical class, are homologous series of saturates (normal, branched and cyclic alkanes), and homologous series of mono-, di- and polycyclic aromatics. In this manner, GC × GC is effective at separating, grouping, and identifying the important classes of DCM-soluble material in a complex shale oil sample. In order to better qualitatively identify these classes in this complex sample, MDGC-MS was applied with narrow H/C to improve component separation in each class. Most probably, S-containing aromatic compounds will overlap aromatic hydrocarbon (polyaromatic) bands.

3.3. MDGC-MS

GC × GC-FID was applied for preliminary sample profiling using FID as above. Then detailed sample composition using MDGC-MS was performed by using an Agilent Deans switch with diversion of the flow from the ^{1}D column to a long ^{2}D column for further separation. Narrow H/C (0.2–0.3 min) was selected approximately every 2 min, giving 13–15 H/C per run. In the next injection of the same sample, H/C timings were shifted by 0.2–0.3 min, to provide a further 13–15 heart-cuts, but for these slightly different selected ^{1}D regions. In total, six runs were conducted to provide a detailed overall sample composition.

The recently developed sequential MDGC-MS method with cryofocusing of narrow selected ^{1}D heart-cuts for analysis of oxygenated products in algae-derived fuel oil [7] was applied here to obtain a more detailed sample composition of the shale oil sample. The restrictor normally used with DS devices was replaced with a short ^{2}D column, and provided modulation for GC × GC-FID operation described above. The 2D plot of a shale oil sample given in Fig. 4 can now be overlaid with H/C zones to indicate regions sampled into the ^{2}D column. About 13 successive H/Cs are taken. Here, only three regions are taken as examples for further discussion, and to illustrate the differences between different H/C regions and the molecular heterogeneity that can be observed.

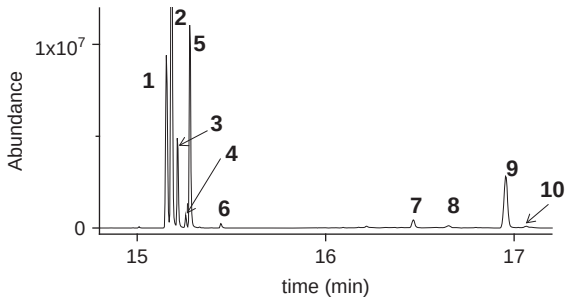

Fig. 5. A typical chromatogram of a single H/C obtained from the early region A in Fig. 4 result, by sequential MDGC-MS. Up to 10 components were tentatively identified from the narrow single H/C of 0.3 min. See Table 2 for component identification.

After the 0.2–0.3 min H/C transfer to the start of the long ^{2}D column (every 2 min), the transferred band is cryofocused. After a delay of 6 s, it is immediately released as a sharp band to the ^{2}D long column under the prevailing temperature *i.e.* no oven cooling was incorporated into the method, even though this significantly increases the separation achieved on the ^{2}D column as reported elsewhere [7]. All peaks elute within 2 min, at which time the next H/C can be performed. More than 70 H/Cs were performed from six separate runs for the same sample, giving tentative MS identification of many hundreds of components. The most abundant were alkanes (normal, branched and cyclic), ethers, one- and two-ring aromatics, thiophenes, benzothiophenes, dibenzothiophene and benzonaphthothiophene. Some lower abundance polyaromatics were present.

A list of component classes identified in the shale oil samples is given in Table 1. Although this approach may not be practical for routine analysis because of the multiple analyses required per sample, it does give an exquisitely detailed sample composition, and so is useful for the discovery phase of sample analysis. Up to 10 well-resolved components were tentatively identified in the MDGC-MS chromatogram of a single heart-cut of 0.3 min shown in Fig. 5, but many minor components were still observed at higher signal amplification. The marked region A on the 2D plot in Fig. 4 corresponds to the chromatogram shown in Fig. 5. The last eluted peak here is the low polarity branched alkane, so no components should elute later than this (having about a 2 min ^2t_R elution time from the sampling point). Identified components together with their structure, mass spectra and match quality against the NIST08 MS library are given in Fig. 6, and clearly show decreasing polarity with increased retention on the non-polar ^{2}D column. They range from thiophenes (A1, A2, A4, A5), monoaromatics (A3), thiophane (A6), methylether (A7), a cyclic alkane (A8), to alkanes (A9, A10). These compound matches are considered tentative due to lack of authentic standards, but the general compound class assignments should be acceptable. Cryotrapping and sharp release of each H/C on the ^{2}D column greatly improves separation, signal magnitude and consequently identification. Note that the response scale in Fig. 5 (10^7) can be expanded significantly to display minor peaks. Thus while thiophanes, ethers and cyclics are less abundant peaks here, and are minor components in the sample, they are still

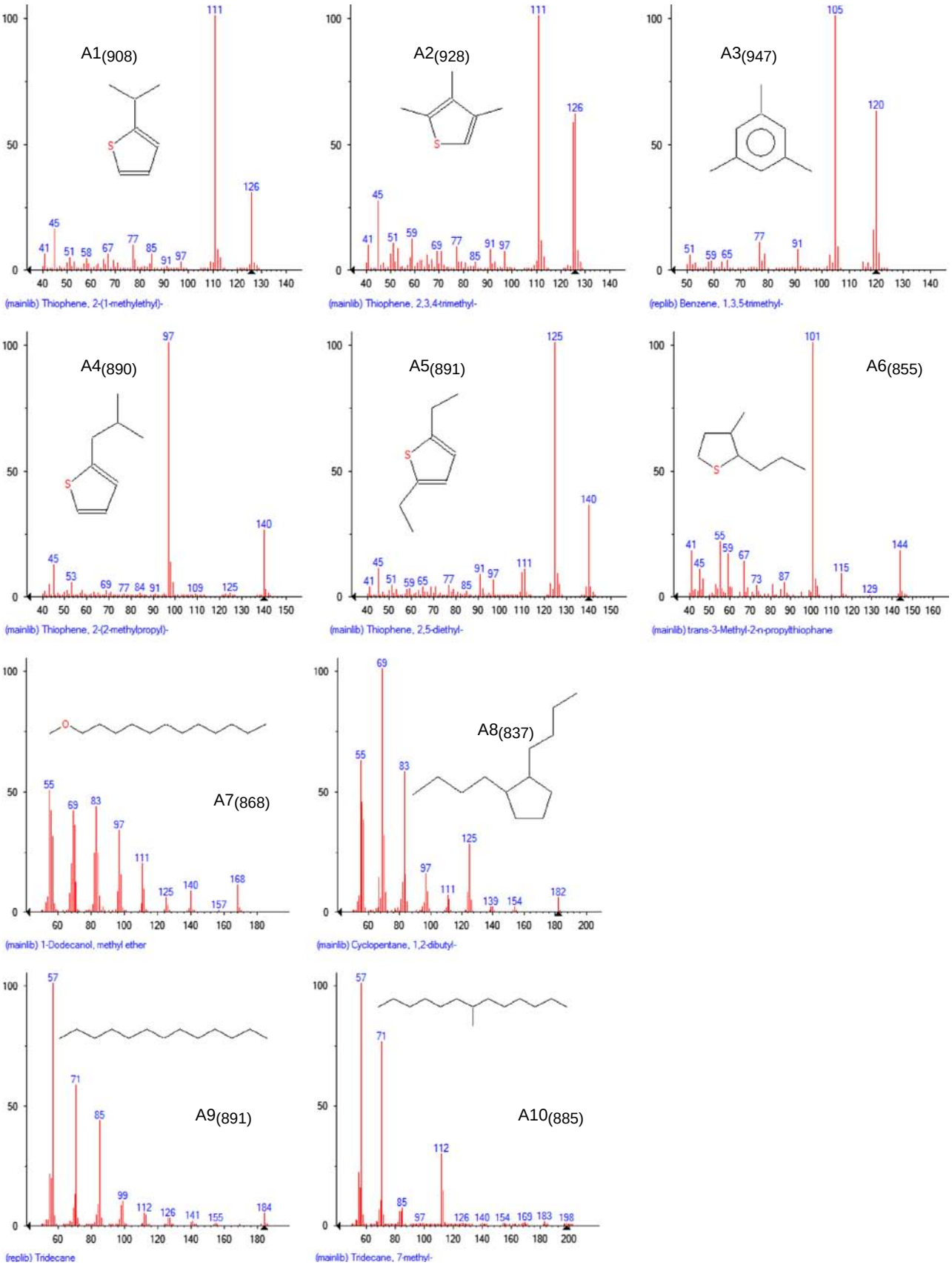

Fig. 6. Mass spectra of 10 components tentatively identified in one H/C of 0.3 min (refer to Fig. 5), together with their structures and match quality against the NIST08 MS library. The decrease in polarity with increase in retention time on the ^{2}D non-polar column is apparent.

Table 2
Components identified in marked region A in Fig. 4 which correspond to the chromatogram in Fig. 5. Their match quality against the NIST08 MS library is included.

Code	Tentatively identified compounds	MS similarity[a]
A1	2-(1-methylethyl) thiophene	908
A2	2,3,4-trimethyl thiophene	928
A3	1,3,5-trimethyl thiophene	947
A4	2-(2-methylpropyl) thiophene	890
A5	2,5-diethyl thiophene	891
A6	trans-3-methyl-2-n-propyl thiophene	855
A7	methyl-1-dodecanol ether	868
A8	1,2-dibutylcyclopentane	837
A9	tridecane	891
A10	7-methyltridecane	885

[a] MS similarity given on a scale 0–999 according to the NIST library match protocol.

Table 3
Components identified in marked region B in Fig. 4 which correspond to the chromatogram in Fig. 7, with their match quality against the NIST08 MS library.

Code	Tentatively identified compounds	MS similarity[a]
B1	2,3-dimethyl phenol	952
B2	4-ethyl-2-methyl phenol	861
B3	2,2′-bithiophene	765
B4	7-ethyl-benzo[b]thiophene	855
B5	2,5,7-trimethyl-benzo[b]thiophene	873
B6	2-ethyl-5,7-dimethyl-benzo[b]thiophene	870
B7	2-ethyl-5-heptyl thiophene	703
B8	2-butyl-5-propyl thiophene	599
B9	2,5-bis[1,1–dimethylethyl] thiophene	606
B10	18-norbietane	708
B11	heptyl cyclohexane	790
B12	methylether-1-docosanol	834
B13	3-methyl-eicosane	790

[a] MS similarity given on a scale 0–999 according to the NIST library match protocol.

sufficiently abundant to give good MS signal (e.g. peak 8–200,000 abundance). The list of compounds identified in Figs. 5 and 6 with their match quality is summarized in Table 2. The thiophenes are C_3 and C_4 substituted species.

It is important to state a disclaimer regarding peak identification and/or assignment in Tables 2–4. At lower retention (Table 2 data) relatively good peak matching is achieved. These would normally correspond to lower mass and higher abundance species (especially for S-containing compounds) which are most likely present in the MS spectral library. Normally accurate attribution of a chromatographic peak relies upon good MS library matching, supported by agreement with retention indices (*I*); best confirmation normally requires available authentic compound data. For ^{2}D separations, *I* data are not generally available due to inability to sample alkanes into the ^{2}D column under equivalent conditions (although novel approaches have been reported for this [20]). In the absence of authentic standards, assignments here are deemed tentative. For peaks eluting later (Tables 3 and 4), which generally are of lower abundance, and with an expected greater degree of branching and longer carbon chains, there is an increasing likelihood that authentic standards will not be available in MS libraries, and so the first match has been reported herein, even if the match quality is low. However, we anticipate that the class of compound will be essentially correct.

The marked region B on the 2D plot in Fig. 4 produces the MDGC result shown in Fig. 7. About 13 discrete peaks were recorded here, but the chromatogram probably comprises at least a further eight peaks, plus zones that are poorly resolved and

Table 4
Components identified in marked region C in Fig. 4 which correspond to the chromatogram in Fig. 8 with their match quality against the NIST08 MS library.

Code	Tentatively identified compounds	MS similarity[a]
C1	2-ethyl-4,5-dimethyl phenol	882
C2	2-[1,1–dimethylethyl]-4-methyl phenol	768
C3	2-allyl-4-methyl phenol	853
C4	2-butyltetrahydro thiophene	809
C5	1,2,3,4-tetrahydro dibenzothiophene	673
C6	2-methyl-1,1′-biphenyl	826
C7	2-ethyl-5,7-dimethyl benzo[b]thiophene	875
C8	7-ethyl-2-propyl benzo[b]thiophene	685
C9	2-ethyl-5,7-dimethyl benzo[b]thiophene	663
C10	2,3-diethyl benzo[b]thiophene	644
C11	6,7-diethyl-1,2,3,4-tetrahydro-1,1,4,4-tetramethyl naphthalene	604
C12	3-methyl-2-pentadecyl thiophene	605
C13	3-methyl-2-tridecyl thiophene	579
C14	2,5-diheptyl thiophene	626
C15	10-heneicosene	783

[a] MS similarity given on a scale 0–999 according to the NIST library match protocol.

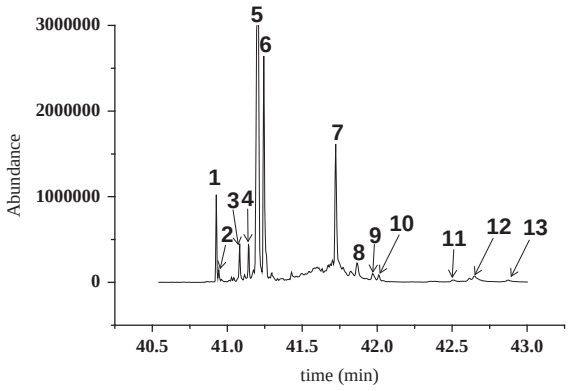

Fig. 7. A typical chromatogram of a single H/C from a mid-region location B of the 1D GC result, obtained by sequential MDGC-MS. Up to 13 components were tentatively identified from a narrow single H/C of 0.3 min. See Table 3 for component identification.

comprise what might resemble an low level unresolved complex mixture (UCM) in the region of peak 7 (the alkyl thiophenes), which has been studied using GC × GC recently [21]. These peaks were identified as listed in Table 3. The polar substituted phenols (B1 and B2) were clearly separated from the C_7 and C_8 thiophenes (B7–B9), and now higher mass benzo[b]thiophenes (B4–B6) with C_2, C_3 and C_4 substituents appear. All the aromatics were clearly separated from later eluting saturates (B10–B13). Thus, from a single 0.3 min H/C, it was possible to separate the mono-, and di-aromatics comprising S atoms from each other, and also from the other saturates, which agrees with the orthogonality of the columns used here.

The marked region C on the 2D plot in Fig. 4 produces the MDGC result shown in Fig. 8, with tentative identifications of 15 compounds listed in Table 4. Again additional minor peaks are present, with an unresolved (UCM) region. The C_4 and C_5 phenols (C1–C2) were clearly separated from the di-aromatics (C6, C11). A range of sulfur compounds were identified in Table 4; a series of substituted C_{14}, C_{15} and C_{16} thiophenes (C4, C12–C14) was separated from C_4 and C_5 benzo[b]thiophene (C7–C10) and from dibenzothiophene (C5). All were separated from the aliphatic compound (C15). The thiophenes and benzo[b]thiophenes comprised larger alkyl substituents than for earlier H/C regions (Figs. 5 and 7), corresponding to their later retention on the ^{1}D column. Thus, from a single

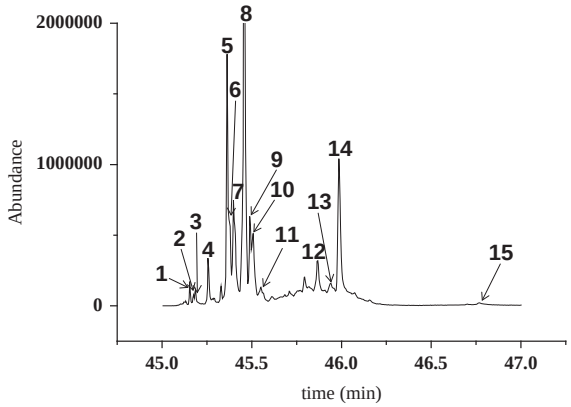

Fig. 8. A typical chromatogram of a single H/C from a late-eluting region C of the 1D GC result obtained by sequential MDGC-MS. Up to 15 components were tentatively identified from a narrow single H/C of 0.3 min. See Table 4 for component identification.

H/C, it was possible to separate several classes of compounds, aromatics from aliphatics, and aromatics from each other (mono-, di- and tri-aromatics). Non-polar saturated compounds are in comparative low abundance in this region. Also compounds in sub-classes may be separated, with the order of elution being the same as on the NP ^{2}D column. So proceeding from A to B to C, generally compounds of increasing molecular mass in a given class were detected. From these three selected examples, a wide range of compounds were detected, illustrating the potential of the method for excellent speciation.

3.4. Comparison between GC–MS and sequential GC × GC-FID / MDGC-MS

The Figures above show all polar components to be clearly separated from the saturated hydrocarbons by using MDGC, with very good peak shape. The selected zone determines if the alkane matrix peak(s) will be major components in the ^{2}D chromatogram. Fig. 2 displays a chromatogram of the 1D GC–MS result, for the EIC *m*/*z* 91 (specific ion for monosubstituted C_n-benzenes). The advantage of MDGC is apparent here. In Fig. 5, NP compounds are well resolved from the mono-ring aromatics, giving narrow and tall peaks due to the combined effects of cryofocusing and resolution on ^{2}D. The mass spectra of alkanes gave negligible *m*/*z* 91 response, but their high abundance led to observable peaks in Fig. 5. In contrast, Fig. 2 1D GC–MS result is indistinct. The GC–MS TIC trace had some measure of overlapping response at almost every position. The location of the substituted benzene component A3 was not as clear in the TIC result, and there is no certainty that each benzene homologue is a pure resolved peak. The monoaromatic responses in Fig. 5 are greater than the small peaks in Fig. 2, since the H/C process is used in Fig. 6 result to just extract a 12 s portion from the ^{1}D separation. Consequently, taking a mass spectrum for the benzene peak in Fig. 5 gave an excellent MS similarity of 947, but the MS result for the scan taken across the suspected benzene peak for Fig. 2 gave a result dominated by the overlapping alkane spectrum. MS similarity search of that peak (marked with asterisk in Fig. 2) did not give a match for benzene but rather was for an overlapping alkane component.

In Fig. 6, the mono-aromatic compounds are well resolved from each other, and the substituted benzene clearly separated from the thiophenes, whereas in the 1D GC–MS result, most of the mono-aromatics appeared to be substituted thiophenes rather than benzenes. A decisive advantage of MDGC-qMS with H/C was its ability to separate the different isomers (sub-class) from each other (Fig. 6), in agreement with what was observed in GC × GC-FID (Fig. 4). A1 – A6 (different thiophene isomers) were individually tentatively identified with good match quality. In 1D GC–MS, it was not possible to identify the different isomers of compounds because of tailing of some components and overlapping of peaks.

Thiophenes often show tailing peak shapes in GC, due to their polarity. Fig. 3 shows the EIC *m*/*z* 97 result for the shale oil obtained using 1D GC–MS. Component identification for each of the thiophenes had low match quality, due to low abundance and matrix overlap. Though the peaks tailed on the ^{1}D column, up to four very sharp peaks, with high match quality (see Fig. 6), were produced in MDGC when the 0.2–0.3 min H/C was cryofocused and released onto the ^{2}D column. The clear separation from NP components is another benefit of the MDGC approach. As a consequence, very good match quality was now obtained (see Table 2).

MS detection in scan mode allows identification of sulfur compounds with good match quality since they are now well resolved from the matrix, especially for the dibenzo[b]thiophene and benzonaphthothiophene. The use of EIC, or selected ion monitoring (SIM) in target analysis, for quantification in MDGC mode is possible provided chemical standards are available, although it is possible that a given peak might be sectioned by the H/C process into two different sampling events.

The distributions of alkanes, aromatics, ethers and sulfur compounds are consistent with other reported analyses of these compounds in shale oil with GC–MS identification [22–24]. Shale oils are extremely complex mixtures consisting of alkanes, naphthalene, monoaromatics, polycyclic aromatic hydrocarbons, steranes, hopanes and some trace components containing S and N compounds, etc. Identification of these classes of compounds in shale oil will allow more understanding about the mechanism of how the oil is produced from the shale bitumen and kerogen, and also knowledge of the components of the shale oil will affect the choice of refining process.

The sulfur content of shale oils varies from 0.05% to 10%, which will affect the refining process since the implementation of new laws on clean air in many countries has brought stricter limitation on sulfur content in petroleum products. The sulfur content in new formula gasoline and clean diesel oil are required to be no higher than 100 mg/kg and 500 mg/kg [25], respectively.

4. Conclusion

The proposed switchable GC × GC /MDGC–qMS with the P/NP column set reported here is better suited for isolation and identification of minor polar components in the presence of high abundance saturates in a complex matrix, as found in algae-derived shale oil, than conventional 1D GC–MS. The instrumental setup is readily converted from GC × GC-FID for general sample profiling to MDGC–qMS for effective target component isolation and identification. The additional cryotrapping of a single H/C, while cooling the oven and then releasing it under a slow temperature program, is also available without any variation to the setup. The width of the sampled H/C can be extended, and the interval between each cut can be reduced (e.g. with a shorter ^{2}D column) for maximum throughput if the GC × GC profile reveals that less than the entire region on ^{1}D is of particular interest.

An initial GC × GC screening of samples aids optimization of conditions for a comprehensive analysis in fewer sample runs than that proposed here (six incremented runs). One of the benefits of this method is that qMS can be applied for reliable identification since the peaks are wider than in GC × GC mode. Cryofocusing at the beginning of the ^{2}D column produced much better peak shapes, enhanced signal, and better separation of target compounds. Several classes of alkanes (normal, branched and cyclic)

were clearly separated from each other, aromatics (mono-, di and tri-rings) and sulfur-compounds (th, bth, dbth and bnth) were identified with much better match similarity than in 1D GC–MS, and furthermore, it was possible to identify the sub-class of compounds, clearly separated in GC × GC-FID and in MDGC-qMS. Some of these classes and sub-classes were detected for the first time in this type of shale oil (e.g. for the sub-classes; C_{11}–C_{16} th isomers, C_1-C_6 bth isomers, C_1–C_3 dbth isomers). A further study will reproduce this study for other oil shales for qualitative comparison with present data, and to elucidate the generality of the finding.

The increasingly stringent limitation on SOx emission imposes an urgent requirement on refineries to reduce the sulfur content in the fuels they produce. Therefore, deep desulfurization of shale oil will remain one of the major problems for the refining industry. Detailed information on the distribution of sulfur-containing compounds in different kind of shale oils can serve as an important basis for improving desulfurization technology. However, to date, due to the complexity of sulfur compounds, it is necessary to adopt laborious and time-consuming combined technologies [25–27] for the analysis of shale oil. Thus there is an urgent need for a method to quickly determine the distribution and quantification of sulfur containing compounds in shale oil, for which the analysis methods reported here provide a starting point.

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