Acidic polar compounds in petroleum: a new analytical methodology and applications as molecular migration indices

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Abstract

A new method for analysis of acidic polar compounds, is described and discussed. It allows the simultaneous quantification of carboxylic acids, phenols and carbazoles and combines accuracy with a short turnaround time, a requirement strictly necessary for industrial applications. Routinely use of this methodology (more than 50 applications in many different sedimentary basins) has supplied many important pieces of information about oil origin, maturity, biodegradation and, in particular, has allowed to define a molecular migration index (MMI), based on relative abundance of phenol and alkyl phenols. The combination of well-established geochemical tools focused on saturated and aromatic fractions (such as biomarkers, compound specific isotope ratio analysis, and GC fingerprinting) with this methodology results in the definition of an integrated interpretative sequence. This last enhances the quality of interpretations through cross-checks and permits a better exploitation of oil samples by using also their less explored fraction, i.e. the polar compounds. Application results of this methodology are only shortly mentioned in this paper, which is mainly focused on analytical aspects. The results will be more extensively discussed in a future publication. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Carboxylic acids; Alkyl phenols; Alkylcarbazoles; Benzocarbazoles; Molecular migration index; Negative chemical ionisation mass spectrometry

1. Introduction

The geochemical characterisation of polar fractions is not an easy process and the necessary sample pre-treatment is very often time consuming and can introduce errors affecting significantly the accuracy of the final results.

Although polar compounds (NSO compounds) are often a large fraction of oils, geochemists have mainly collected since many years data relevant to saturate and aromatic compounds. The molecular parameters defined by using the analytical data of these two fractions can supply important indications about origin and maturity of oils, but NSO compounds can probably be an important complementary source of information.

In addition to this, the particular properties of polar compounds can supply more specific indications useful to reconstruct processes involving oil–water and oil–rock interactions, such as for example secondary migration.

Considering the largely unexplored potential of geochemical tools based on polar compounds, some research groups have intensified in the last years the investigations about low molecular weight polar compounds.

The types of NSO compounds, which have been characterised in petroleum, are basic nitrogen compounds (quinolines; Yamamoto et al., 1991; Schmitter et al., 1983), non-basic nitrogen compounds (carbazole derivatives; Li et al., 1992; Clegg et al., 1997) and several oxygen compounds (carboxylic acids, phenols and ketones; Douglas and Powell, 1969; Seifert and Teeter, 1970; Ioppolo et al., 1992; Borgund and Barth, 1993; Wilkes et al., 1998a,b).

The complexity of the analytical approach and the related uncertainties have been one of the main limits for a better interpretation of NSO compound occurrence in crude oils. The purification and concentration steps normally used are time consuming and introduce the risk of producing artefacts.

The new proposed method benefits by the experience deriving from the study of acidic metabolites (see for example Galimberti et al., 1992) in the biochemistry
samples at low cost and with a reduced risk of artefact. and carbazoles can consequently be analysed in oil compounds in petroleum can be performed with a similar approach by combining a quick pre-treatment of the sample with a NCI–GC–MS procedure. The new method permits the analysis of three classes of NSO sample with a NCI–GC–MS procedure. The new approach by combining a quick pre-treatment of the compounds in petroleum can be performed with a similar to the clean-up phase of samples. Analysis of acidic NSO specificity of this methodology allow a simplified approach utilised in this specific field. The high sensitivity and ionisation (NCI) mass spectrometry (MS) are widely researched. Gas chromatography (GC) and liquid chromatography (LC) coupled with negative ion chemical ionisation (NCI) mass spectrometry (MS) are widely utilised in this specific field. The high sensitivity and specificity of this methodology allow a simplified approach to the clean-up phase of samples. Analysis of acidic NSO compounds in petroleum can be performed with a similar approach by combining a quick pre-treatment of the sample with a NCI–GC–MS procedure. The new method permits the analysis of three classes of NSO compounds in one GC–MS run; carboxylic acids, phenols and carbazoles can consequently be analysed in oil samples at low cost and with a reduced risk of artefact.

The identification of carboxylic acids up to about C_{22}, alkylphenols in the C_{0–C_{3}} range, alkylcarbazoles in the C_{0–C_{3}} range and benzocarbazoles in oil samples was performed by synthesis and co-injection of standards. The new methodology has been applied in different geochemical studies in order to check its reliability in different geological contexts and with samples characterised by different bulk properties. A few examples of these applications are here summarised, but more complete case histories will be the subject of a further paper.

Oxidation of hydrocarbons to alcohols, ketones and acids is a general mechanism for the bacterial alteration of petroleum. In the first step of the alteration, \textit{n}-paraffins are oxidised at the termini of carbon chains to yield the corresponding acids. For this reason the analysis of carboxylic acids can be a useful indicator of the biodegradation of the oil in the reservoir, in particular during the early stages of the process when the removal of \textit{n}-alkanes could be hard to notice.

Regarding alkylcarbazoles and benzocarbazoles the discussion about the factors controlling their distribution in the petroleum is still open. Interactions with the carrier bed during migration were indicated as the main factor by Larter et al. (1996), but the same authors did not discard the influence of thermal maturation and a possible primary expulsion effect (Li et al., 1997). Later, Clegg et al. (1998) showed by hydrous pyrolysis experiments that maturity is really a key parameter in the control of carbazoles production. In this paper, the new analytical approach has been also used to verify the changes in the profile of the benzo- carbazole isomers in oils showing different maturity levels. However, the main application of the analytical method, achieved so far, is the assessment of a molecular migration index (MMI) obtained by a ratio between molecules of the phenol family characterised by different water solubility. Even if research seems currently more oriented towards nitrogen compounds as “mileometers” (Larter et al., 1996), according to our experience phenols can be very useful and effective in evaluating relative migration distance. The MMI is used in an integrated interpretative sequence considering oil data (organic facies and maturity) together with reservoir continuity considerations. Only oils with the same origin and maturity are compared obtaining the trend in MMI that is indicative of migration pathways and filling points.

2. Experimental

2.1. Materials (chemicals)

All chemicals, solvents, reagents and standards, were of analytical grade and used without further purification. Alkylphenol standards (a 20 compounds kit) were purchased from Theta Corporation (GA) and monocarboxylic acids standard (a 15 compounds kit) were from Alltech (IL).

Microscale syntheses were performed to prepare over 23 carboxylic acids molecules, following Kuroki and Tsunashima (1981) and references cited therein. Reagents for these syntheses were from Aldrich.

Potassium carbonate in grain was from Carlo Erba (Italy). Pentafluorobenzylbromide and 18-crown-6 ether, purchased from Aldrich (WI), were used pure or in dichloromethane (DCM) solution.

For quantitative determination, the following deuterated Internal Standards were used: d_{6}-phenol, d_{8}-carbazole and d_{2}-propionic acid from Aldrich and d_{8-o-cresole}, purchased from Cambridge Isotope Laboratories Inc. (MA).

2.2. Derivatisation

The reaction is carried out directly on crude oil with a minimal manipulation of sample, following the general scheme indicated by Davis (1977) for fatty acids. Oil (100 mg) is introduced into a 1.5 ml volume glass. A mix of internal standards composed by: 0.1 mg of d_{6}-phenol (1 ppm), 0.1 mg of d_{8-o-cresole} (1 ppm), 0.1 mg of d_{8}-carbazole (1 ppm), 1 mg of d_{2}-propionic acid (10 ppm) and 500 mg of DCM are then added. An excess of derivatising agent, PFBBR (4 mg), catalyst, 18-crown-6 ether (1 mg) and some grain of potassium carbonate (less than 1 mg) are finally added. The vials are sealed and heated at 80°C for 3 h. Occasionally the mixture is shaken.

The derivatised sample can be injected directly into GC–MS without any further treatment.

2.3. GC–MS analysis

The injection of 0.5–1 \mu l of derivatised oil was performed in the splitless mode with a temperature of the injector of 290°C. GC separation of derivatised acidic polar compounds was carried out on a HP-1 column (50 m x 0.2 mm x 0.33 \mu m film thickness; Hewlett-Packard). The GC oven was programmed from an initial temperature of 70°C, held for 1 min, to 150°C at a heating rate of 5°C/min, then to 300°C at a rate of 2.5°C/min. Product detection was performed by a MS (Finnigan...
The reagent gas was methane (source pressure 7000 mtorr) with a source temperature of about 135°C.

A list of ions routinely monitored in multiple ion detection (MID) and the corresponding compounds is given in the Appendix.

3. Results and discussion

3.1. Derivatisation

Dilution of the oil sample with a solvent is necessary, in particular when the density of the oil is high. Davis (1977) proposed benzene as the optimal solvent for PFBBr derivatisation of acidic compounds observing poor reactivity of carboxylic and phenolic standards in ethyl acetate, heptane and acetonitrile. Using petroleum as matrix, a low reactivity in toluene and chloroform solution was observed in this study. Dichloromethane seems to be the best alternative to benzene both from a reactivity and toxicological point of view.

The use of a crown ether catalyst for the preparation of pentafluorobenzyl derivatives of fatty acids, mercaptans and phenols was first introduced by Davis (1977). The author reported that the combination of this catalyst with a strong base (K₂CO₃) allows the derivatisation of the compounds having an active hydrogen with nearly quantitative yields.

In this work three classes of molecules able to react have been characterised in the crude oil; carboxylic acids, alkylphenols and carbazole derivatives. An order of reactivity was observed for these classes and it is related to their acidity; the monocarboxylic acids being the most reactive and carbazoles the least. It was estimated that, in the oil matrix, the derivatisation of different carboxylic acids and alkylphenols is complete in less than 1h, at a temperature of 80°C; for carbazole about 2h are required.

The products of the derivatisation reaction show good chromatographic properties and are stable (Kawahara, 1968). It is possible to reanalyse the same oil sample after 1 month without significant changes in the results for alkylphenols and carbazoles. Some problems could arise for short chain (C₁–C₃) carboxylic acids that seem to change their concentration and distribution during storage.

This last fraction is also occasionally affected by contamination, probably coming from reagents. In some batch of samples a high concentration of C₁–C₃ carboxylic acids with a similar profile without any obvious relationship with the nature of the analysed sample was observed.

3.2. GC–MS analysis

The derivatised sample can be injected directly in the GC–MS system without an additional purification step. The excess of PFBBBr and crown ether and the possible formation of PFB polymers in samples containing moisture can be a factor limiting sensitivity, when a GC coupled with an electron capture detector is utilised (Davis, 1977). The high specificity of the GC–MS analysis, conducted in the MID mode, allows the direct analysis of the sample without any interference. More problematic is the degradation of the chromatographic system due to the injection of a “dirty” sample.

A frequent change of the glass liner in the injection port and the use of a retention gap are necessary in order to increase the lifetime of the capillary column. As shown in the example of Fig. 1, PFB esters of carboxylic acids show simple mass spectra in the EC-NCI mode. No molecular ion is evident under these conditions; in fact, the base peak corresponds to the carboxylate ion, which arises from splitting off the PFB group. A similar process occurs also for alkylphenols and carbazoles: any acidic polar compounds derivatised with PFBBBr can be detected by monitoring the m/z ratio corresponding to the molecular weight of the original analyte minus one unit mass.

By choosing an appropriate MID program, it is possible to monitor the three classes of compounds in the same analytical run. As shown in Fig. 2, the carboxylic acids are distributed along the whole chromatogram, alkylphenols elute in the early part and carbazoles at higher retention times. The increase of molecular weight due to the derivatisation establishes a limit for the detection of molecules with a high number of carbon atoms. For example, carboxylic acids with more than 25 carbon atoms cannot be eluted from the GC column under the conditions used in this work.

Only the derivatised molecules form negative ions with high abundance; the more concentrated species in the oil, such as saturate hydrocarbons, are not detected at all by EC-NCI.

For this reason, the chemical background of the analytical method is low and the sensitivity is adequate for most of the analysed samples. A limit of detection lower than 500 fg injected for phenol in the oil matrix was estimated.

The identification of the main peaks in the chromatogram, corresponding to carboxylic acids up to about C₂₂, was performed by synthesis and injection of standards (Fig. 3). In the same way, alkylphenols in the C₉–C₃ range, alkylcarbazoles in the C₀–C₂ range and benzo-carbazoles have been extensively characterised in oil samples (Figs. 4–6).

In the alkylphenol chromatogram, an interference due to the presence of the benzoic acid peak is often observed in particularly high concentration in some biodegraded oils. The difference in the m/z ratio of the ions of C₂ alkylphenols (121.065) and benzoic acid (121.029) is too low to be resolved by a quadrupole or ion trap spectrometer. Moreover, in the conditions used
Fig. 1. EC-NCl mass spectrum of linear C$_{13}$ carboxylic acid. Most of the ion current is concentrated on the ion corresponding to the molecular weight of the original analyte minus one unit mass. No ions with higher m/z values are observed.

Fig. 2. Reconstructed ion chromatogram: the ion current obtained from the selective monitoring of acidic polar molecules is summed in a single signal. Ions generated by C$_2$–C$_{22}$ carboxylic acids (m/z 59 + n*14, n = 0–19), C$_0$–C$_3$ alkylphenols (m/z 93, 107, 121 and 135), C$_0$–C$_3$ alkylcarbazoles (m/z 166, 180, 194 and 208) and C$_0$–C$_2$ alkylbenzocarbazoles (m/z 216, 230 and 244) were acquired in this case and the corresponding retention time ranges are outlined in the chromatogram.
Fig. 3. Reconstructed ion chromatogram: the ion current obtained from the selective monitoring of C_2–C_22 carboxylic acids in a crude oil sample is summed to get a single signal (a). The oil is slightly biodegraded and shows only minor alteration of the saturated hydrocarbons (b).

Fig. 4. Reconstructed ion chromatogram of the phenol family for an oil sample: sum of the signals produced by the detection of ions at m/z 93, 107 and 121, corresponding to C_0–C_2 alkylphenols.
in this work, the GC is not able to separate the peaks of the benzoic acid and of the 2,3-xylenol.

The GC separation has been optimised in this work for phenols that show a good resolution up to C2 alkyl derivatives, resulting in some coelution of the C2 alkylcarbazoles. However, a slower increase in the oven temperature or the use of a slightly more polar column can improve the resolution of the C2 alkylcarbazole fraction.

The quantitation of the analytes is carried out with the internal standard method. Due to the different chemical characteristics of the analytes, a specific deuterated standard is used for each class: d2-propionic acid for the carboxylic acids, d6-phenol for the C0–C2 alkylphenols.

Fig. 5. Example of an oil analysis: carbazole (m/z 166), methylcarbazole (m/z 180) and C2-alkylcarbazole (m/z 194) ion chromatograms are shown.
and $d_8$-carbazole for the $C_0$–$C_2$ alkylcarbazoles and benzocarbazoles. A calibration curve was set up for many carboxylic acids, for most of the isomers of the $C_0$–$C_2$ alkylphenols and for carbazole, showing a linear behaviour. The general shape of the mass spectra, which show the same fragmentation pattern with a predominant (M–1) ion, allows to approximate to the same value the response factor for all the molecules of the same class.

Precision studies show a good reproducibility for the intra-day measurements. The concentrations of some of the most representative compounds have been measured in five sub-samples of the same Italian oil and reported in Table 1. Relative standard deviation (RSD) is usually

Fig. 6. Example of an oil analysis: benzocarbazole ($m/z$ 216) and methylbenzocarbazole ($m/z$ 230) ion chromatograms are shown.
around 5%, increasing only for compounds in the low ppb range. An additional internal standard (d₈-o-cresol) is used to increase the accuracy and precision in the calculation of the MMI.

4. Applications

4.1. Carboxylic acids

In most of the non-degraded oil samples significant concentrations of short chain (C₂–C₆) carboxylic acids, but only minor signals for higher molecular weight compounds were observed. Carboxylic acids are a possible product of the bacterial metabolism during biodegradation processes (Behar and Albrecht, 1984). Meredith et al. (1999) reported a correlation between carboxylic acid content and the level of biodegradation of crude oils. For this reason biodegraded oils were chosen to test the applicability of the new analytical procedure in a larger range of carboxylic acids concentrations.

An example of the analysis of a slightly biodegraded oil is shown in Fig. 3b. In this oil sample the n-alkanes (Fig. 3a) are only slightly decreased with respect to isoprenoids, while minor water-washing affects the light aromatic hydrocarbon fraction. The chromatogram obtained by the specific analysis of the carboxylic acids (Fig. 3b) shows that the whole C₂–C₂₂ range of linear chain acids is present in high concentration (highest peaks are in the order of 8–10 ppm).

The abundant presence of C₁₆ and C₁₈ carboxylic acids and of monounsaturated acids, in particular of the C₁₄, C₁₆ and C₁₈ terms, could be ascribed to the input of the “fresh” biomass acting on the reservoired petroleum (Van Hoeven et al., 1969; Mackenzie et al., 1981).

High concentrations of C₇–C₂₂ carboxylic acids can only be found at the early stages of the biodegradation, as shown by Mackenzie et al. (1981) and confirmed by the application of this methodology in different case histories. These acids are lost in oils suffering heavier bacterial alteration probably by further degradation or water washing.

4.2. Carbazoles

Li et al. (1995) and Larter et al. (1996) showed that alkylcarbazoles and benzocarbazoles undergo a general decrease in concentration and an isomeric fractionation during oil migration. On the same time also thermal maturation plays an important role in controlling the isomeric distribution of the carbazole derivatives (Li et al., 1997; Clegg et al., 1998).

Three oils, sampled in three different wells and generated by the same carbonate source rock at different maturity levels, have been analysed with the methodology here proposed in order to test its applicability in different contexts. Source rock maturation occurred at high heating rate in a highly tectonized geological framework, characterized by compressive phases. A vertical migration style was determined by the presence of faults and fracture systems that connected relatively restricted drainage areas to the reservoir, hindering lateral migration. The source was just below the reservoir and in contact with it; a reduced effect of migration on polar compounds can be reasonably assumed as a consequence of the short distance of hydrocarbon migration, occurring mainly through faults and fractures. Biomarker analyses of these oils show a maturity trend: sterane isomerisation and aromatisation parameters are reported in Table 2 together with the benzocarbazole distribution.

These data seem to confirm the observation of Clegg et al. (1998): the BC ratio (benzo[a]carbazole/benzo[a] carbazole + benzo[c]carbazole as defined by Larter et al., 1996) increases with the maturity.

A comparable maturity effect on benzocarbazoles can be observed in some overmature oils generated by a marly source rock. These oils contain few biomarkers and pentacyclic terpanes are depleted in comparison to more stable structures as 17α-(H)-diahopane and C₂₉Ts (Fig. 7, left).

A modelling exercise showed that the field was charged by different kitchens located at a distance ranging between 3 and 20 Km. In spite of this, no significant changes are observed in the benzocarbazole profile. All
the oil samples show very high BC ratios, being the benzo[c]carbazole nearly absent (Fig. 7, right).

4.3. Alkylphenols

Among NSO compounds, alkylphenols are particularly interesting because they can easily partition out of petroleum into formation water. Their partition coefficients between oil and water (Bennett and Larter, 1997) suggest that alkylphenols may be sensitive indicators of any oil–water interactions in the subsurface.

Taylor et al. (1997) noted that, as expected, during secondary migration the total concentration of the alkylphenols in the oil decreases. On the other hand these authors claimed a consistency of the alkylphenol distribution in oils migrated along different distances. To explain this consistency, chiefly observed on a complex parameter defined as hindered/nonhindered ratio, an oil–water–rock partition process of alkylphenols is required.

In our experience, in contrast, some ratios between the concentration of the most water-soluble phenols show a marked variability in different oils. The ratio between o-cresol and phenol, for example, can show variation up to 7–8 times in the oils produced from different wells in the same field.

When this ratio is measured in oils originated from a source with uniform organic facies and similar maturity and in absence of secondary alterations (as water-washing or biodegradation), its variations can reasonably be ascribed to the oil–water interactions. On the other hand, we have clear evidence of the presence of phenols in subsurface waters as consequence of oil/water interactions occurring in the trap or occurred during migration. The analyses of some water samples of dry wells have shown high phenol content in those wells drilled on the structure flanks in consequence of the presence of a shallower oil–water contact, verified by wells successively testing an up-dip position. On the contrary, a complete absence of phenols was found in produced water of wells properly drilled on the top of the

<table>
<thead>
<tr>
<th>Maturity parameters and benzocarbazole ratio (benzo[a]carbazole/benzo[c]carbazole + benzo[a]carbazole) referred to oil samples in Fig. 7</th>
<th>Oil A</th>
<th>Oil B</th>
<th>Oil C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C29 Sterane isomerisation (20S/20S + 20R)</td>
<td>0.52</td>
<td>0.52</td>
<td>0.56</td>
</tr>
<tr>
<td>Steroid aromatisation (C28TA/C28TA + C29MA)</td>
<td>0.16</td>
<td>0.60</td>
<td>0.82</td>
</tr>
<tr>
<td>BC ratio</td>
<td>0.35</td>
<td>0.43</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Fig. 7. Distribution of benzocarbazole isomers in an oil produced by a marly source rock. The oil is overmature and shows low concentration of biomarkers (a): common maturity parameters are not detectable; hopanes are partially degraded, while more stable structures as 17α(H)-diahopane and C29Ts are present in higher proportion. The profile of the benzocarbazole isomers (b) shows low amount of benzo[c]carbazole.
structures and dry because no oil accumulation occurred. Moreover a distribution of phenols dominated by the more water-soluble phenols, with cresols and C₂ derivatives in relatively low amount was evident in all produced waters.

The water solubility of the alkylphenols was the criteria used in the definition of some possible molecular parameters for migration. Different ratios between some of the alkylphenols and phenol have been successfully utilised in the definition of the main direction of trap filling. The \( o \)-cresol/phenol ratio has been selected because it is easily measured being the two molecules usually relatively abundant and well resolved in the chromatogram. Moreover, the availability of deuterated internal standard for both \( o \)-cresol and phenol makes the measure of the ratio more accurate.

Fig. 8 shows the results regarding a North Sea reservoir, one of the first applications based on this type of molecular ratios. The main problem, in this case history, was to establish the main direction of trap filling by defining the role of the fault systems bordering the structural high, where four wells had been drilled. To define hydrocarbon entry points in the structure it was necessary to assess where faults could act as permeability barriers. Only four oil samples were available and a quick answer was needed before a modelling exercise at regional scale could be performed. First of all, a complete set of geochemical analyses (GC, GC–MS and GC–IRMS) was run to establish the origin of these oils. The analytical results showed a common origin from a marine source rock characterised by uniform distribution of organic facies; moreover no significant maturity differences were detected among the samples. The GC fingerprinting performed according Kaufman methodology (Kaufman et al., 1990) suggested a reservoir continuity among the four wells. Finally the phenol analysis allowed the definition of the MMI values showed in Fig. 8. The increase of MMI values (increase of \( o \)-cresol/phenol ratio) allowed to infer a probable south-eastward migration trend. Four points are really too few to define a trend, but considering the good level of reproducibility of these analyses this risk was taken. After a few months, the modelling exercise provided evidence that the only possible kitchen for this oil accumulation was located in the north-east area, perfectly consistent with the migration trend defined by MMI values.

Many other applications, involving larger number of samples, confirmed successively the reliability of these parameters and more recently the use of MMI was coupled with secondary migration modelling. MMI is used to calibrate secondary migration modelling in an interactive way; the secondary migration simulation code was developed in-house and is a simple model, which uses the ray tracing technique and is based on buoyancy. An average migration distance is estimated in each point where oil samples are collected and plotted versus the corresponding MMI value. In such a way it is
possible to verify the consistency between phenols analyses and modelling results with an interactive approach. This interesting aspect of MMI application cannot be exhaustively discussed in this paper and it will be the subject of a new paper that we intend to publish very soon.

5. Conclusions

The acquisition of many new data relevant to some of the most important polar compound classes is made possible by the proposed methodology at low costs and with short turnaround time. A careful and exhaustive interpretation of this data can add new important parameters on oil origin, migration and preservation. The discussed MMI is probably only one example of many possible further applications of the analytical results obtained through this methodology. Some authors have already explored possible applications of polar compounds and are still working on this subject, but a thorough exploitation of these data is far from being achieved. In particular, we feel that we are still in a pioneer phase, especially taking into consideration the quantity of new available data and the insufficient knowledge about them.

High quality analytical results are, as usual, the fundamental pre-requisite for a correct and effective geochemical interpretation and it seems that the proposed methodology is able to fulfil this important requirement.

The successful applications of MMI in migration studies show its promising potential, although it is particularly important to stress that its interpretation must take into account several other parameters, obtained through a specific analytical sequence and relevant to oil origin, maturity and preservation. However, other ‘migration indexes’ based on different polar compounds, are strictly necessary in order to cover with high reliability all the possible situations both in terms of geological context and of oil sample characteristics.

MMI can be very effective in the calibration of secondary migration models, supplying important constraints such as, for example, the sealing properties of faults. MMI can play for migration models a role similar to that played by vitrinite reflectance in the calibration of the thermal history in sedimentary basins.

Acknowledgements

We gratefully acknowledge Dr. Maowen Li and an anonymous reviewer for their constructive comments.

Appendix. List of compounds (and corresponding \( m/z \) values of the derivatised molecule) routinely monitored during NCI analysis

<table>
<thead>
<tr>
<th>Compounds</th>
<th>R</th>
<th>( m/z )</th>
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<tbody>
<tr>
<td>R-COOH Carboxylic acids</td>
<td>From ( CH_3 ) to ( C_{19}H_{39} )</td>
<td>( 59 + n^*14 ) ( (n=0-19) )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( R' )</th>
<th>( R'' )</th>
<th>( m/z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>H</td>
<td>H</td>
<td>93</td>
</tr>
<tr>
<td>Cresols</td>
<td>( CH_3 )</td>
<td>H</td>
<td>107</td>
</tr>
<tr>
<td>Xilenols</td>
<td>( CH_3 )</td>
<td>( CH_3 )</td>
<td>121</td>
</tr>
<tr>
<td>Ethylphenols</td>
<td>( C_2H_5 )</td>
<td>H</td>
<td>121</td>
</tr>
<tr>
<td>Carbazole</td>
<td>H</td>
<td>H</td>
<td>166</td>
</tr>
<tr>
<td>Methylcarbazoles</td>
<td>( CH_3 )</td>
<td>H</td>
<td>180</td>
</tr>
<tr>
<td>Dimethylcarbazoles</td>
<td>( CH_3 )</td>
<td>( CH_3 )</td>
<td>194</td>
</tr>
<tr>
<td>Ethylcarbazoles</td>
<td>( C_2H_5 )</td>
<td>H</td>
<td>194</td>
</tr>
<tr>
<td>Benzocarbazoles</td>
<td>H</td>
<td></td>
<td>216</td>
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<tr>
<td>Methylbenzocarbazoles</td>
<td>( CH_3 )</td>
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<td>230</td>
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References


