Polar non-hydrocarbon contaminants in reservoir core extracts

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Article

A geochemical investigation of oils in sandstone core plugs and drill stem test oils was carried out on samples from a North Sea reservoir. A sample of diesel used as a constituent of the drilling fluids was also analysed. The aliphatic and aromatic hydrocarbons and polar non-hydrocarbons were isolated using solid phase extraction methods. GC analysis of the hydrocarbon fraction of the core extract indicated that contamination may be diesel derived. From analysis of diesel some compound classes are less likely to be affected by contamination from diesel itself including: steranes, hopanes, aromatic steroid hydrocarbons, benzocarbazoles and C_0–C_3-alkylphenols.

Large quantities of sterols (*ca.* 30 mg g^{-1} total soluble extract) were identified in the polar non-hydrocarbon fractions of the core extract petroleum, presumably resulting from contamination. The origin of sterols is likely to be due to an additive introduced into the drilling fluid. Sterols are surface active compounds and in significant quantities may affect engineering core property measurements including wettability determinations. In addition, bulk petroleum composition screening methods, such as Iatroscan, used for determining saturated and aromatic hydrocarbons, resins and asphaltenes (SARA) content of core extract petroleum may also be affected.

Introduction

One of the fundamental threats confronting geochemists during analysis of reservoir cores and produced petroleum is contamination by drilling mud components.[1] Drilling fluids are made up of a number of components which may include diesel, emulsifying agents, wetting agents, surfactants, scale inhibitors, biocides, kerosene and even crude oils from other producing wells. Contamination of well sample material with water based mud (WBM), oil based mud (OBM) and pseudo-OBM may adversely affect the results of geochemical analysis.[1] While problematic, contamination of oils and cores by OBMs may be easily recognised by reduced concentrations of polyaromatic hydrocarbons or by GC fingerprints.[2] Contamination of non-hydrocarbon fractions may be more difficult to detect.

Since a number of reservoir engineering properties are sensitive to the fluids contained within the reservoir, the contamination problems are a concern for petroleum engineers. Wettability measurements on reservoir cores may be seriously affected by oil-based mud contamination where extreme changes from water-wet cores to strongly oil-wet conditions have been observed.[3] Drilling fluid invasion is more pervasive in permeable sandstones and could result in large scale displacement of *in-situ* fluids. Obtaining cores with low fluid invasion is difficult and while methods have been designed for both oil and water based muds,[4] contamination is still a common problem.

In recent years, there has been an increased interest in the polar components of petroleum such as organic nitrogen, sulfur and oxygen compounds (referred to as NSO compounds). Despite their relatively low abundance, the often polar nature of NSOs means they exert disproportionately large effects on the viscosity and potentially on the phase behaviour of petroleum.[5,6] Adsorption of NSO components onto mineral surfaces may also affect reservoir wettability.[7] Therefore it is increasingly important to obtain compositional data on the polar non-hydrocarbons present in the *in-situ* core extract petroleum.

The aim of this paper is to identify the polar non-hydrocarbon fraction of petroleums susceptible to contamination by drilling fluids. The implications for geochemical investigation of organic nitrogen and oxygen compounds are also discussed.

Experimental

Samples

A great deal of care and attention to sampling was taken during this study to recover "uncontaminated" core material. A 24 ft section of core was recovered from a sandstone reservoir using oil-based drilling mud. The cored section was a typical upper shoreface parasequence with a basal coarsening upwards sequence (5 ft). The permeabilities measured in this section ranged from 500 to 1000 mD, with permeabilities of 5 mD at the base of the coarsening upwards unit. The core (4 in in diameter) was sliced in half using a water cooled saw. A one-inch plug was cut (water as drilling fluid) from the centre of the ½ core and a 5 mm section was removed from the top and bottom of the one-inch plug. Forty one core plug samples were obtained for analysis, in addition to 2 DST oils produced from an equivalent section. A sample of diesel was provided by a drilling company.

Isolation methods

The following schemes describe solid phase extraction (SPE) methods for recovering aliphatic hydrocarbons, aromatic hydrocarbons and polar non-hydrocarbon (containing both nitrogen compounds and C_0–C_3-alkylphenols) fractions from crude oils, diesel and core extracts.

Approximately 30 g of powdered rock sample was extracted with an azeotropic mixture of dichloromethane–methanol (93 : 7) using a soxtherm apparatus (Soxtherm automatic, Gerhardt). Extract weights were determined following concentration and drying under a stream of nitrogen. An aliquot of

the extract (*ca.* 80 mg) was dissolved in CH_2Cl_2 and transferred to a Florisil SPE cartridge (Jones Chromatography, UK). The hydrocarbon and polar non-hydrocarbon containing fractions were recovered in CH_2Cl_2 (5 ml) and the solvent evaporated under a stream of nitrogen gas. The extract was re-dissolved in *n*-hexane (agitated *via* sonication) and transferred to a C18 non-endcapped SPE cartridge (Jones Chromatography, UK). The separation of crude oil and diesel into hydrocarbons and polar non-hydrocarbons is also carried out using C18 non-endcapped SPE. The aliphatic and aromatic hydrocarbon fractions were recovered in *n*-hexane (5 ml). Meanwhile, the polar non-hydrocarbon containing fraction was recovered in CH_2Cl_2 (5 ml). Prior to GC-MS analysis *N*-phenylcarbazole was added to the CH_2Cl_2 fraction to allow quantification of organic nitrogen compounds. The separation of hydrocarbons into aliphatic and aromatic hydrocarbon fractions was carried out using silver nitrate–silica SPE.[8] Prior to separation of the hydrocarbon fraction an appropriate quantity of standard (squalane and 1,1-binaphthyl) was added for quantification purposes. Procedural blanks were also carried out and indicated no potential contamination other than low levels of plasticizers due to the SPE cartridges. The aliphatic and aromatic hydrocarbons and nitrogen compounds were analysed by combined gas chromatography-mass spectrometry (GC-MS) in selected ion monitoring (SIM) mode.

The C_0–C_3-alkylphenols were recovered from the core extracts, oils and diesel by using the same SPE methods as that described above for the recovery of nitrogen compounds. However, 2-naphthol (quantification standard) and deuterated phenol (D6-phenol as a measure for loss of volatile phenol) standards were added to the substrates prior to separation by C18 non-endcapped SPE. The C_0–C_3-alkylphenols were analysed as trimethylsilylated derivatives of phenol hydroxy group following treatment with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) of the polar non-hydrocarbon fraction.[9]

Results and discussion

Hydrocarbons

The GC-MS analysis of aliphatic hydrocarbons isolated by the combined SPE methods from solvent extracts of reservoir sandstones is shown in Fig. 1(a). The chromatogram shows a smooth distribution of *n*-alkanes ranging from *n*-C_{12} to C_{22}, maximising through *n*-C_{15}. The *n*-alkane distribution appears typical of one affected by diesel invasion during coring activities. The *n*-alkane distribution from analysis of diesel is shown for comparison in Fig. 1(b). Usually, petroleum geochemists carry out investigations on biomarkers (steranes and hopanes) which elute beyond the *n*-C_{22} alkane and are less likely to be significantly affected by diesel contamination. Fig. 1(a) also provides a qualitative appreciation of the extent of the contamination problem with respect to the *in-situ* hydrocarbons. The results show that bulk petroleum composition screening methods, *e.g.*, Iatroscan[10] (saturated and aromatic hydrocarbons, resins and asphaltenes (SARA)), are likely to be influenced by contamination.

Fig. 2 shows the GC-MS distribution of aromatic hydrocarbons recovered from diesel. The naphthalenes and phenanthrenes represent abundant components of the aromatic hydrocarbons in the diesel. Concentrations of aromatic hydrocarbon were: naphthalene, 87 µg g^{-1}; dibenzothiophene, 121 µg g^{-1} and phenanthrene, 2246 µg g^{-1} diesel. These compounds are commonly utilised in molecular maturity parameters,[11] therefore in the presence of diesel the maturity values will be affected leading to erroneous maturity assessments. The mono-aromatic steroid hydrocarbons and tri-aromatic steroid hydrocarbons elute beyond the GC retention time interval typical of compounds affected by diesel derived components. Therefore molecular maturity parameters deriving from the
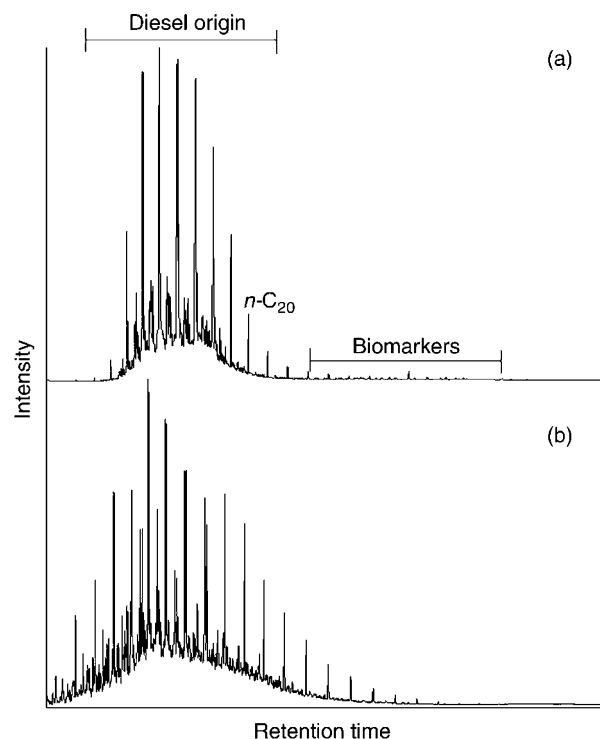
Fig. 1 Partial total ion chromatogram obtained during GC-MS (selected ion monitoring) analysis of the aliphatic hydrocarbons isolated from (a) core extract petroleum and (b) diesel.
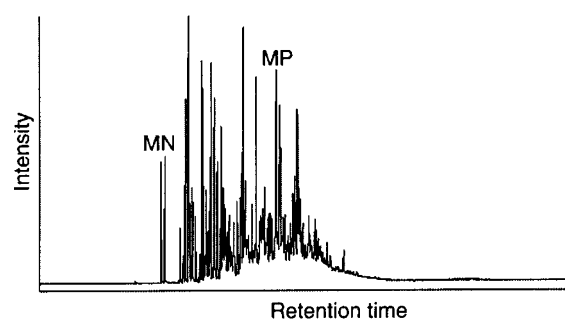

Fig. 2 Partial total ion chromatogram obtained during GC-MS (selected ion monitoring) analysis of the aromatic hydrocarbons isolated from diesel. Key: MN = methylnaphthalenes, MP = methylphenanthrenes.

mono- and tri-aromatic steroid hydrocarbons may be more reliable indicators of the maturity of *in-situ* oils.

Polar non-hydrocarbons in diesel

The polar non-hydrocarbon analysis was carried out on a sample of diesel typically employed as a drilling fluid. Alkylcarbazoles represented a significant portion of the nitrogen compound contribution to the polar fraction isolated from diesel. The GC mass chromatogram of nitrogen compounds is shown in Fig. 3. Concentrations were: carbazole, 10 µg g^{-1}; total methylcarbazoles, 51 µg g^{-1}; and total C_2-carbazoles, 112 µg g^{-1} diesel. This can have a significant impact on geochemical interpretations of alkylcarbazoles in core extracts. However, since no benzocarbazoles were identified in the diesel, these are less likely to suffer from contamination.

GC-MS analysis of the BSTFA treated polar non-hydrocarbon fraction isolated from diesel indicated that no C_0–C_3-alkylphenols were present, suggesting analyses of phenols in core extracts and petroleum are unlikely to be affected by diesel.
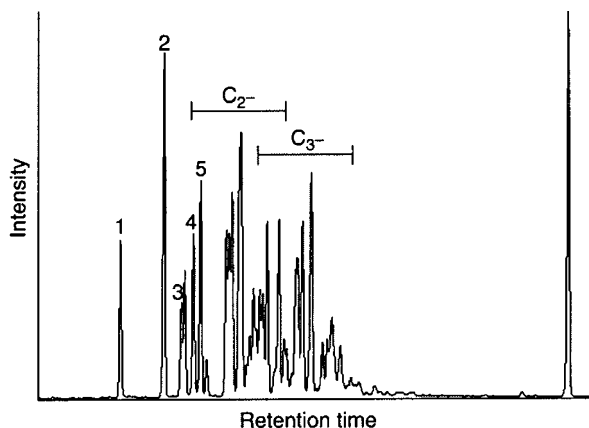
Fig. 3 Partial reconstructed mass chromatogram (summed ions m/z $167 + 181 + 195 + 209 + 217$) representing C_0–C_3-alkylcarbazoles and benzocarbazoles isolated during C18 NEC SPE of diesel. Key: 1, carbazole; 2, 1-methylcarbazole (1-MC); 3, 3-MC; 4, 2-MC; 5, 4-MC; C_2-, C_2-alkylcarbazoles; C_3-, C_3-alkylcarbazoles.

During geochemical appraisals, analysis of drilling fluid components is a pre-requisite to assess which molecular parameters are less likely to be affected by contamination. From this study, polar non-hydrocarbon compound analysis confirmed that benzocarbazoles and C_0–C_3-alkylphenols would not be contaminated, while a cautionary approach to the interpretation of alkylcarbazoles is required as drilling fluid contamination could be severe.

Polar non-hydrocarbons in petroleum

Phenols. The C_0–C_3-alkyphenols in the core extract petroleum were determined following BSTFA derivatisation. Analysis of diesel indicates no alkylphenols present and therefore contamination from this source is low risk. Fig. 4 shows the GC-MS chromatogram corresponding to the analysis of C_0–C_3-alkylphenols in core extract petroleum. The C_0–C_3-alkylphenols were quantified in core samples over a 24 ft section. In general, concentrations ranged from 2 to 1626 µg g^{-1} TSE for phenol and 3.05 to 1115 µg g^{-1} TSE for summed cresols. The corresponding produced DST oils contained 4.5 µg g^{-1} oil of phenol and 22 µg g^{-1} oil of summed cresols. The results indicate that much greater levels of phenol are encountered in the core extracts suggesting
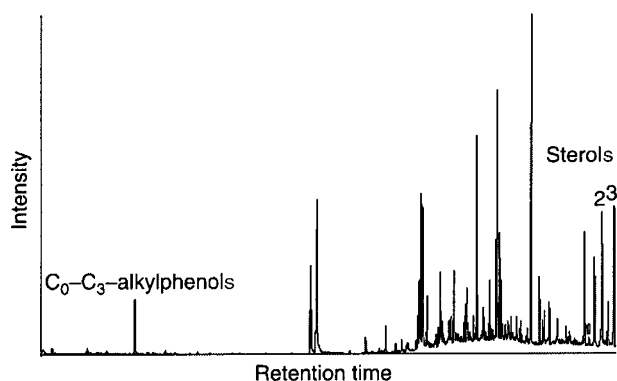

Fig. 4 Partial total ion chromatogram (mass range m/z 50–550) of the BSTFA derivatised polar non-hydrocarbon fraction isolated during C18 NEC SPE of core extract petroleum (see Fig. 5 for corresponding mass spectra of peaks labelled 1–3).
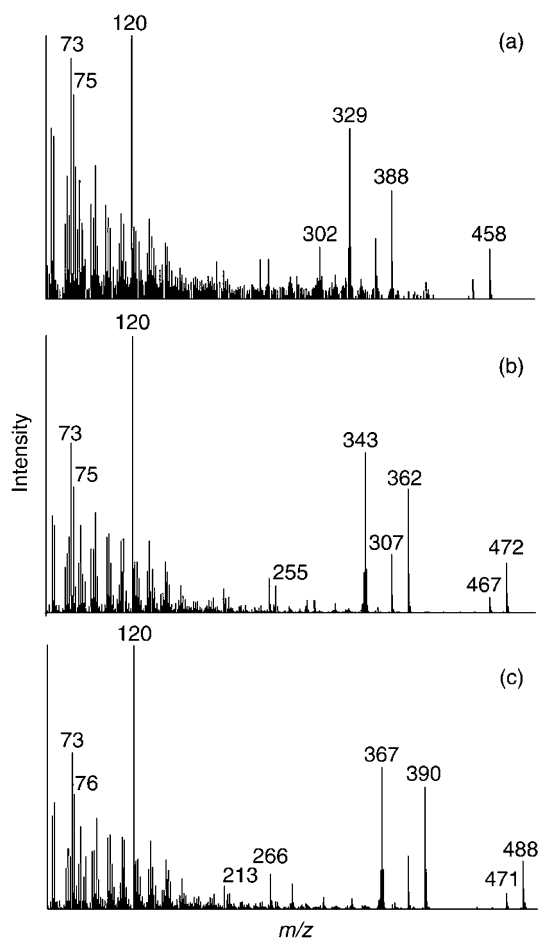

Fig. 5 Mass spectra of (a) C_{27}-cholesterol (labelled peak 1 in Fig. 4), (b) C_{28}-sterol (labelled peak 2 in Fig. 4) and (c) C_{29}-sterol (labelled peak 3 in Fig. 4) isolated during C18 NEC SPE of core extract petroleum.

adsorption onto reservoir minerals and partition into pore waters in the 3 phase crude oil–brine–rock system may be important processes in controlling the distribution of phenols in reservoirs.

Sterols. Further inspection of the full scan GC-MS chromatogram of the BSTFA derivatised polar non-hydrocarbon fractions indicated, however, that the C_0–C_3-alkylphenols are relatively minor components in comparison to compounds eluting towards the high boiling point region of the chromatogram (Fig. 4). The mass spectra of these components (Fig. 5) result in the identification of C_{27} (cholesterol), C_{28} and C_{29} carbon number sterols. Quantification of sterols was performed using the area in the m/z 73 fragmentation ion from sterols relative to the area in the m/z 201 fragmentation ion from 2-naphthol. Vast quantities of sterols were indicated at up to 64 mg g^{-1} TSE in the permeable sandstones. The lowest sterol contents of 0.34 mg g^{-1} TSE were encountered in core samples from the base of the coarsening upwards unit, *i.e.*, the lower permeablility unit. The procedural blanks confirm sterols are not introduced during laboratory work up procedures. Sterols are usually associated with the recent environment since they are lost rapidly during diagenesis,[12] hence their presence in a petroleum reservoir in these samples seems to indicate a source of contamination. The most likely source is a component added to the drilling fluid.

The sterols are surface active compounds and may represent major problems for subsequent physical property measurements such as wettability. In general, the lowest measured levels of sterols were encountered in the lowest permeability unit from the base of the cored section. It seems, coarser

permeable sediments are more likely to be invaded by the drilling fluids, as expected.

Summary

In summary, early recognition of drilling mud contamination may be easily achieved by GC analysis of the aliphatic hydrocarbons. This may provide an indication of potential problems during analysis of the polar non-hydrocarbons. Analysis of a cored section of a sandstone reservoir indicated contamination from oil based drilling fluids was pervasive. Surface-active polar compounds present in the core extract petroleum may be introduced as contamination by invading drilling fluids and may appear in the non-hydrocarbon fraction as well as the hydrocarbon fractions. The interaction of contaminant surface active compounds with core material may have a strong impact on subsequent wettability measurements unless core cleaning is employed. The analysis of drilling fluid components is a pre-requisite for any reservoir geochemical study, particularly during analysis of core samples.

Acknowledgements

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