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Small-scale and rapid quantitative analysis of phenols and carbazoles in sedimentary matter

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Abstract

A rapid small-scale method for the quantitative analysis of alkylphenols, alkylcarbazoles and benzocarbazoles from sedimentary matter is described using silica gel liquid chromatography and GC–MS techniques. Alkylphenol, alkylcarbazole and benzocarbazole components of crude oils can be easily, rapidly and economically separated from saturated and aromatic hydrocarbons using silica gel, as a stationary phase, and disposable glassware such as Pasteur pipettes (sample sizes up to 100 mg). Analysis of these components was performed using GC–MS without any further derivatisation. This method affords rapid sample processing with accurate quantification of carbazoles, benzocarbazoles and alkylphenols suitable for routine use in petroleum geochemistry.

1. Introduction

Polar compounds such as alkylphenols, alkylcarbazoles and benzocarbazoles are predominantly used in petroleum geochemistry for assessing migration of crude oils (Li et al., 1992, 1994, 1997; Dale et al., 1995; Larter et al., 1996; Taylor et al., 1997; Bennett et al., 2002). The separation of these polar compounds from other compound types is required because they usually exist in trace quantities and require concentration prior to further analysis by techniques such as GC–FID and GC–MS.

Most of the published separation methods for alkylphenols in crude oils and sediment extracts involve aqueous alkaline extraction of the matrix followed by acidification and back extraction into an organic phase (MacCrehan and Brown-Thomas, 1987; Pauls et al., 1990; Hertz et al., 1980; Guenther et al., 1981; Ioppolo et al., 1992; Taylor, 1994). Some authors have used reversed phase solid phase extraction (SPE) using C18 alkylbonded silica after alkaline extraction for removal of non-polar material (MacCrehan and Brown-Thomas, 1987; Ioppolo et al., 1992). Later developments used solid phase extraction in "normal-phase mode" to separate alkylphenols directly from the crude oils (Bennett et al., 1996).

The separation of alkylcarbazoles and benzocarbazoles from hydrocarbon matrices is usually performed using silica and/or alumina liquid chromatography columns (Later et al., 1981; Bakel and Philp, 1990; Li et al., 1992). More recently, SPE techniques have also been applied to the analysis of carbazoles and benzocarbazoles (Larter et al., 1996; Bennett et al., 2002).

Galimberti et al. (2000) reported a method allowing for the simultaneous quantification of carboxylic acids, phenols and carbazoles in the whole crude oil sample. These authors derivatised the target compounds in a crude oil matrix using pentafluorobenzylbromide and subsequently analysed the whole sample using GC–MS.

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Unfortunately, because the sample is injected neat, the injection system is rapidly contaminated and injector liners have to be replaced frequently (Galimberti et al., 2000).

In general, commonly used methods for the analysis of alkylphenols and carbazoles are often time consuming, rely on specialty reagents and involve additional steps such as derivatisation. Here we describe a method for the quantitative analysis of alkylphenols, alkylcarbazoles and benzocarbazoles from crude oils and rock extracts using small silica gel columns. The method is simple, rapid, small-scale, economical, reproducible and requires no derivatisation.

2. Experimental

2.1. Samples

Table 1 lists the samples used in this study and their locations, as well as their saturate, aromatic and polar compositions. The Jet Rock-1 sample was obtained from the Norwegian Petroleum Directorate (Dahlgren et al., 1998). Monterey Oil 5 was obtained from the Exxon Production Research Company as part of their oil-set program.

2.2. Materials

2.2.1. Solvents

Analytical grade *n*-pentane and dichloromethane were purified by fraction distillation. Mallinckrodt HPLC grade *n*-hexane, methanol and nanograde ether were used without any further purification. Solvent purity was checked by GC–MS for equivalent amounts used in the separation technique.

2.2.2. Silica Gel

Silica Gel (Merck, 70–230 mesh) was activated at 120 °C for at least 8 h before use.

2.2.3. Alkylphenols

Alkylphenol standards were AR grade with purities in excess of 97% and were obtained from commercial sources: Aldrich Chemical Company, Sigma Chemicals, Fluka Chemie (Switzerland). Totarol was obtained from Industrial Research Limited. Alkylphenol identifications of standards that were not available were based on previous identifications by Ioppolo et al. (1992).

d_3-2,6-Dimethylphenol was prepared from 2,6-dimethylphenol using a method described by Junk and Catallo (1997).

2,3,4-Trimethylphenol, 2,4,5-trimethylphenol and 3-ethyl-5-methylphenol were prepared by hydroxylation of the appropriate alkylbenzene (1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene and 3-ethyltoluene, respectively) using the method described by Kurz and Johnson (1971). These hydroxylations produce a range of alkylphenols with the same methyl substitution pattern as the original alkylbenzene. 1,2,3-Trimethylbenzene thus yielded 2,3,4- and 3,4,5-trimethylphenol. Since the latter's GC retention behaviour is known (Ioppolo et al., 1992), this afforded the identification of both compounds. Similarly, the hydroxylation of 1,2,4-trimethylbenzene produced 2,4,5-, 2,3,5- and 2,3,6-trimethylphenol, of which both 2,3,5- and 2,3,6-trimethylphenol's GC retention behaviour is known (Ioppolo et al., 1992). The hydroxylation of 3-ethyltoluene yielded four ethylmethylphenols, 2-ethyl-6-methyl-, 2-ethyl-4-methyl-, 4-ethyl-2-methyl- and 3-ethyl-5-methylphenol. Based on a comparison with the elution order of the dimethylphenols, 3-ethyl-5-methylphenol was tentatively identified as the last eluting of these ethylmethylphenols.

2.2.4. Carbazoles

The carbazole standard was EP grade with purities in excess of 96% and obtained from Tokyo Kasei Organic Chemicals. Methylcarbazole and dimethylcarbazole identifications were based on comparison of mass spectra and retention times with literature data (Later et al., 1981; Li et al., 1992; Bowler et al., 1997).

d_8-Carbazole was prepared from carbazole using the method described by Junk and Catallo (1997).

2.2.5. Benzocarbazoles

Benzocarbazole standards were prepared using the Fischer indole synthesis described by Kemp (1967).

2.2.6. Mixture of standards

A mixture of standards was prepared consisting of the following compounds (with their relative% w/w in the

Table 1
Sample details and geochemical data

Sample	Country	Basin or location	% Saturates	% Aromatics	% Polars
Barrow	Australia	Carnarvon	77	22	1
Caroline	Australia	Otway	35	56	10
Monterey Oil 5	USA	California	23	32	45
Jet Rock-1	England	Port Mulgrave	28	31	41

Table 2
Concentration of alkylphenol, alkylcarbazole and benzocarbazole for multiple analyses ($n = 5$) of Barrow crude oil

Peak No.	Compound	m/z	Response factors	Barrow crude oil Average concentration ng/g ($n = 5$,%S.D.)	
			(relative to phenol)		
1	Phenol	94	1.00	843	(4.6)
3	*o*-Cresol	108	1.20	3563	(5.1)
4	*p*-Cresol	108	1.20	1326	(2.8)
5	*m*-Cresol	108	1.20	662	(15.3)
6	2,6-Dimethylphenol	122	1.10	6880	(4.1)
7	2-Ethylphenol	122	1.10	755	(6.5)
8	2,4-Dimethylphenol	122	1.10	11914	(5.8)
9	2,5-Dimethylphenol	122	1.10	3768	(4.4)
10	4-Ethylphenol	122	1.10	345	(5.1)
11	3,5-Dimethylphenol + 3-ethylphenol	122	1.10	896	(4.5)
12	2,3-Dimethylphenol	122	1.10	843	(6.9)
13	3,4-Dimethylphenol	122	1.10	690	(7.0)
14	2,4,6-Trimethylphenol	136	1.02	40910	(8.0)
15	2,3,6-Trimethylphenol	136	1.02	4678	7.0)
16	2,4,5-Trimethylphenol	136	1.02	6240	(9.0)
17	2,3,5-Trimethylphenol	136	1.02	2093	(6.8)
18	2,3,4-Trimethylphenol	136	1.02	707	(6.4)
19	3,4,5-Trimethylphenol	136	1.02	448	(5.7)
20	3-Ethyl-5-methylphenol	136	1.02	76	(7.7)
			(relative to carbazole)		
21	Carbazole	167	1.00	2450	(3.6)
22	1-Methylcarbazole	181	1.00	2778	(4.7)
23	3-Methylcarbazole	181	1.00	2564	(3.8)
24	2-Methylcarbazole	181	1.00	2045	(4.5)
25	4-Methylcarbazole	181	1.00	1300	(4.8)
26	1,8-Dimethylcarbazole	195	1.00	2389	(6.7)
27	1-Ethylcarbazole	195	1.00	647	(8.1)
28	1,3-Dimethylcarbazole	195	1.00	2770	(5.6)
29	1,6-Dimethylcarbazole	195	1.00	2544	(4.6)
30	1,7-Dimethylcarbazole	195	1.00	2422	(5.8)
31	1,4-Dimethylcarbazole	195	1.00	2206	(5.2)
32	1,5-Dimethylcarbazole	195	1.00	2265	(6.9)
33	2,6-Dimethylcarbazole	195	1.00	1816	(6.0)
34	2,7-Dimethylcarbazole	195	1.00	1895	(6.9)
35	1,2-Dimethylcarbazole	195	1.00	833	(2.9)
36	2,4-Dimethylcarbazole	195	1.00	1055	(5.3)
37	2,5-Dimethylcarbazole	195	1.00	979	(4.9)
39	Benzo(a)carbazole	217	0.85	698	(6.7)
40	Benzo(b)carbazole	217	0.85	67	(12.0)
41	Benzo(c)carbazole	217	0.85	538	(6.9)

Peak numbers refer to Figs. 1–9.

mixture) in hexane: phenol (8.48%), 2-bromophenol (3.15%), *o*-cresol (5.53%), *p*-cresol (5.59%), *m*-cresol (4.79%), 2,6-dimethylphenol (2.45%), 2,4-dimethylphenol (5.05%), 2,5-dimethylphenol (4.76%), 3,5-dimethylphenol (5.39%), 4-ethylphenol (4.55%), 2,3-dimethylphenol (4.58%), 2,4,6- trimethylphenol (3.77%), 2,3,5-trimethylphenol (3.94%), 3,4,5-trimethylphenol (4.95%), totarol (9.16%), carbazole (9.62%), benzo(a)carbazole (7.54%) and benzo(c)carbazole (6.68%).

2.3. Preparation of samples for separation

2.3.1. Rock extracts

Powdered rock samples were extracted ultrasonically with dichloromethane/methanol (95:5 v/v). The solvent

extract was recovered by filtration and the solvent was carefully removed to yield the soluble organic matter (SOM).

2.3.2. Crude oils and rock extracts

Crude oils and rock extracts (80–100 mg) were dissolved in a small amount of pentane (100 μl). On addition of pentane some samples were observed to precipitate asphaltenes, which were transferred to the silica gel column with additional pentane (2 × 100 μl). Dichloromethane was removed from sediment extracts by addition of hexane (500 μl) and reducing the sample volume (200 μl) in a 2 ml vial on a sand bath at 60 °C.

2.4. Separation

The procedure used a small silica gel column and various solvents to separate phenols, carbazoles and benzocarbazoles from saturate and aromatic components.

2.4.1. Silica gel column

A silica gel column was prepared by taking a glass column (10 cm × 5.7 mm i.d., a Pasteur pipette is used) plugged with a small amount of cotton wool. It was packed dry with activated silica gel (approx. 0.6 g, 55 mm) and was made uniform by passing 3 bed volumes of *n*-pentane under slight pressure (using a pipette teat).

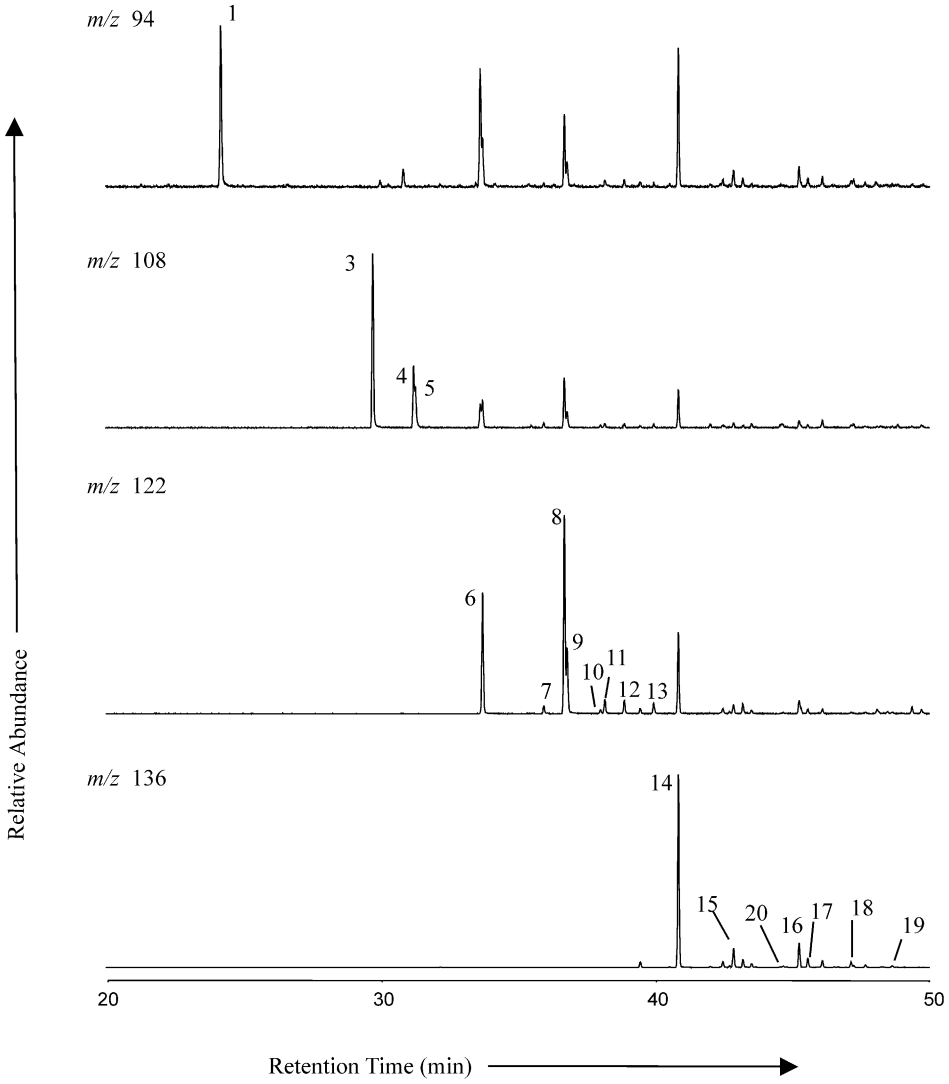


Fig. 1. Partial mass chromatograms showing phenol (*m*/*z* 94), methylphenols (*m*/*z* 108), dimethylphenols (*m*/*z* 122), and trimethylphenols (*m*/*z* 136) for Barrow crude oil phenol/carbazole fraction. For peak identifications refer to Table 2.

The sample (80–100 mg) containing the surrogate standards (d_5-phenol, d_3-2,6-dimethylphenol and d_8-carbazole) in a minimum volume of *n*-pentane (ca. 50 μl), was introduced to the top of the column to produce a concentrated band; additional volumes of pentane (2 × 100 μl) may be used to transfer the sample onto the column.

2.4.2. Saturate and aromatic hydrocarbon fraction (SAA)

Saturate and aromatic hydrocarbons were eluted from the silica gel column under gravity with *n*-pentane/dichloromethane (9:1 v/v, 4 mL).

2.4.3. Phenol/carbazole fraction (PHE)

The phenol/carbazole fraction was collected after elution of the saturate and aromatic fraction from the silica gel column, by eluting under gravity with *n*-pentane/ether (7:3 v/v, 5 mL). To provide a sample ready for GC–MS analysis it is necessary to reduce the amount of ether/pentane without loss of volatiles. This was achieved by adding *n*-hexane (2 ml) to the PHE fraction and carefully reducing the solvent by distillation to approx. 2 ml in a vial (22 ml; 75 mm × 19 mm) using a sand bath set at 60 °C, after which the internal standard was added (2-bromophenol). The fraction obtained in this manner contains alkylphenols and alkylcarbazoles.

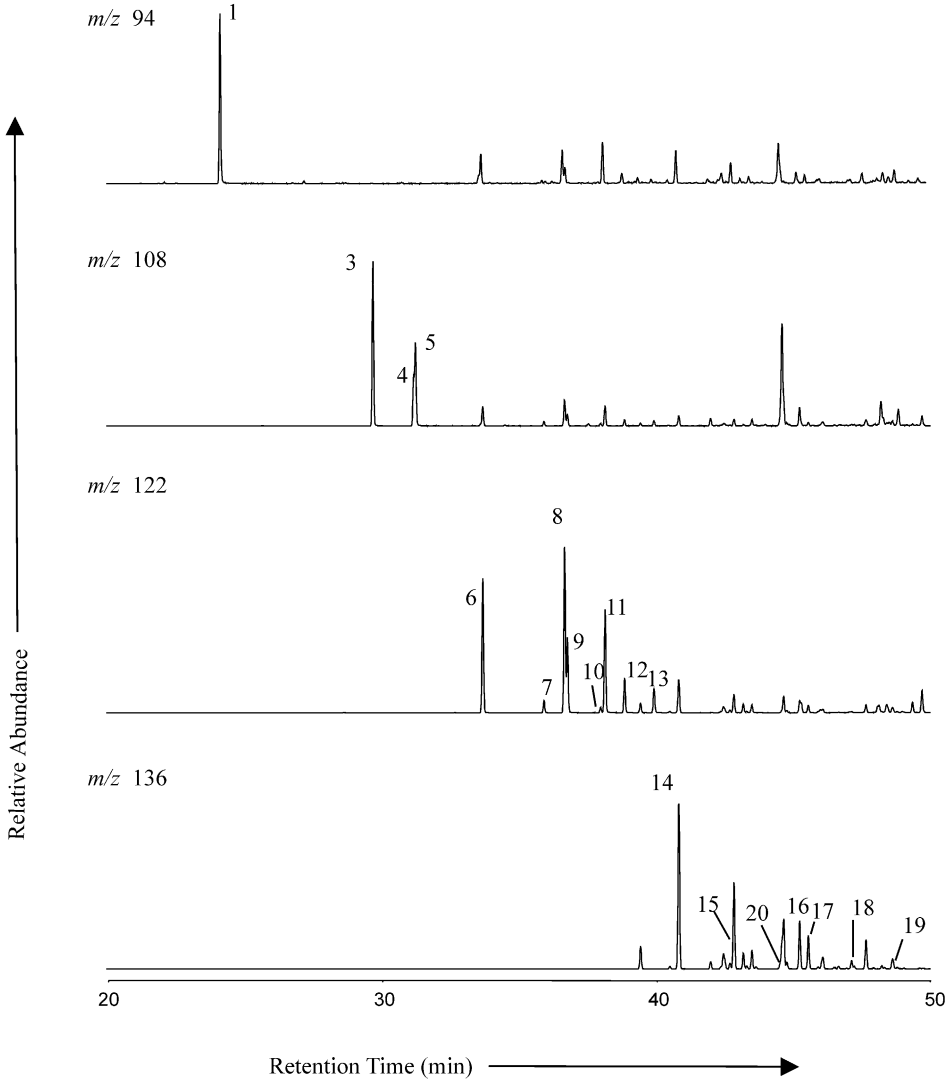


Fig. 2. Partial mass chromatograms showing phenol (*m*/*z* 94), methylphenols (*m*/*z* 108), dimethylphenols (*m*/*z* 122), and trimethylphenols (*m*/*z* 136) for Caroline crude oil phenol/carbazole fraction. For peak identifications refer to Table 2.

2.5. Quantitation and recovery of standards

To enable quantitation the surrogate standards d_5-phenol (530 ng), d_3-2,6-dimethylphenol (532 ng), d_8-carbazole (500 ng) were added to an accurately weighed portion of crude oil (80–100 mg) before separation or addition of any pentane. 2-Bromophenol (660 ng) was added to the phenol/carbazole fraction after solvent reduction just prior to GC–MS analysis.

2.6. Response factors

Response factors for phenols were calculated relative to phenol and for carbazoles and benzocarbazoles, relative to carbazole by dividing the percentage (w/w) of the compounds in the mixture of standards by their appropriate m/z response, which was then divided by phenol's or carbazole's percentage (w/w) to m/z response ratio (Table 2).

Average response factors were used for compound classes, as some standards were not available and to allow for easier comparisons with results where response factors are not used. Methyl- and dimethylcarbazole standards were not available (in this study) and for these compounds the response factor of carbazole was used as a proxy (Table 2). The averaged and estimated relative response factors were used to calculate concentrations from the m/z response of compounds based on the

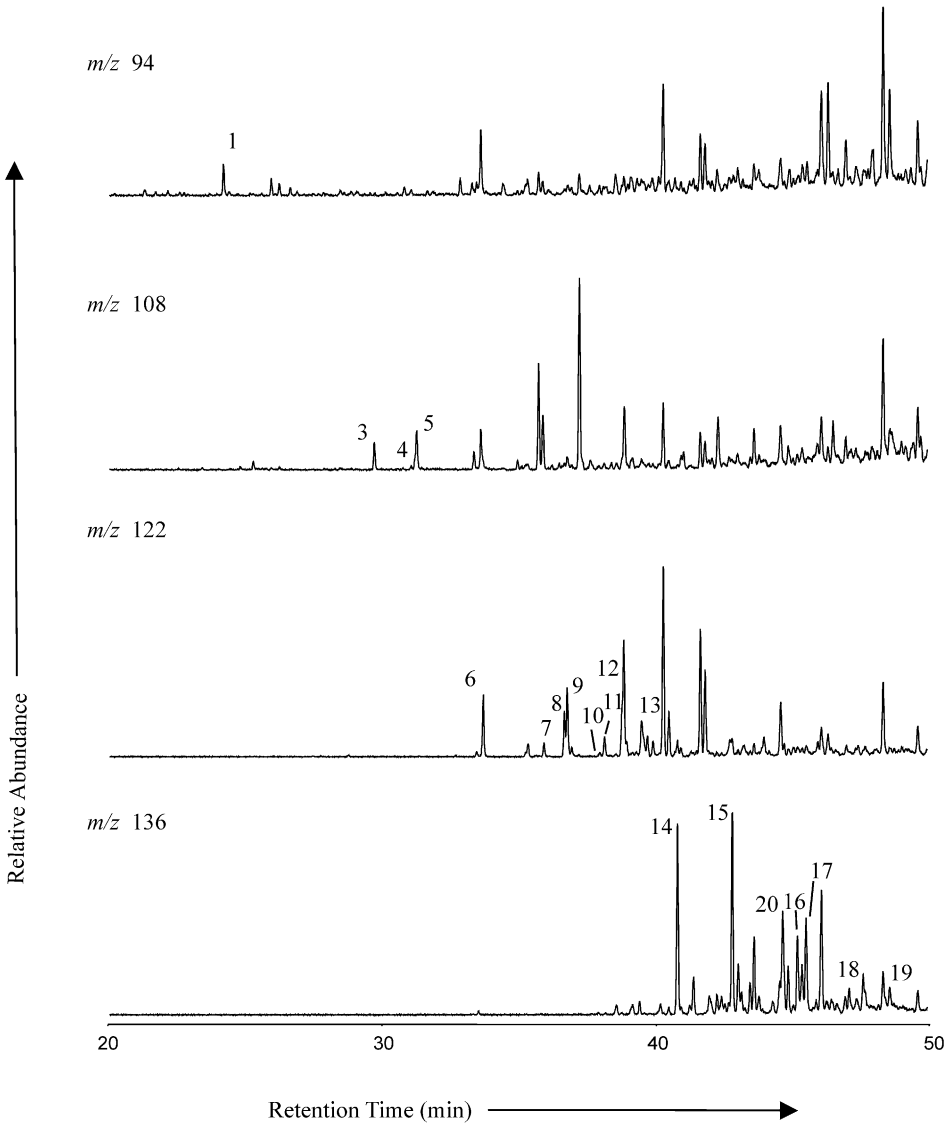


Fig. 3. Partial mass chromatograms showing phenol (m/z 94), methylphenols (m/z 108), dimethylphenols (m/z 122), and trimethylphenols (m/z 136) for Monterey 5 crude oil phenol/carbazole fraction. For peak identifications refer to Table 2.

amount of d_5-phenol and d_8-carbazole added to the crude oils.

2.7. Gas chromatography–mass spectrometry (GC–MS)

A Hewlett-Packard 5973 MSD, interfaced with a HP6890 gas chromatograph was fitted with fused-silica open tubular columns coated with a HP-5MS stationary phase (Agilent, 50 m × 0.20 mm i.d., 0.33 μm film thickness). The GC oven temperature was programmed from 40 °C (1 min) to 310 °C at 3 °C min^{-1} and held at 310 °C for 20 min. Samples for analysis were dissolved in hexane and injected using the vapourising injector and a HP 6890 autosampler. Helium was used as carrier gas at a constant flow of 1.2 ml min^{-1} and the vapourising injector was operated in pulsed splitless mode (40 psi for 0.5 min). The MSD was operated in SIM mode and typical operating conditions were: ionisation energy 70 eV; source temperature 230 °C; electron multiplier voltage 1800 V.

3. Results and discussion

3.1. Phenol/carbazole (PHE) fractions

Phenols, carbazoles and benzocarbazoles are commonly used in organic geochemistry to assess migration, therefore the simultaneous analysis of these compounds in a simple small-scale method is advantageous. Our

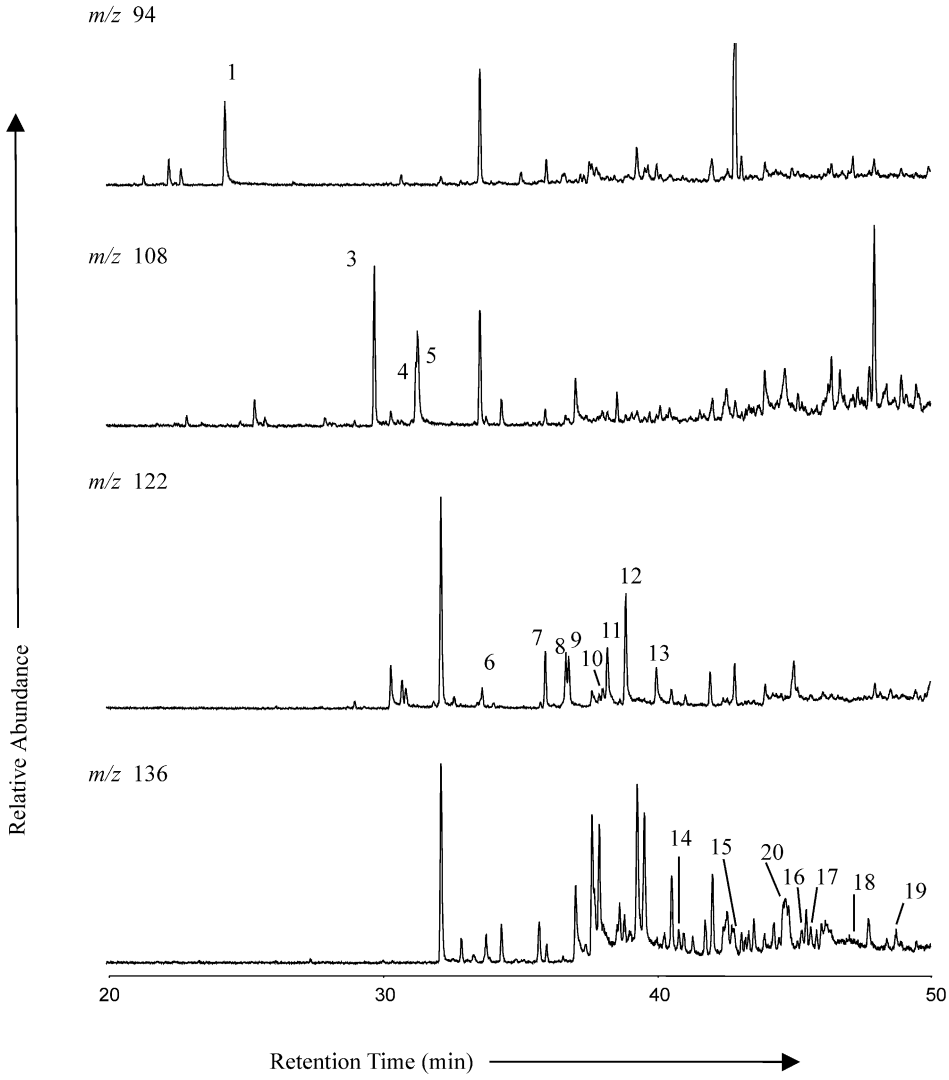


Fig. 4. Partial mass chromatograms showing phenol (*m*/*z* 94), methylphenols (*m*/*z* 108), dimethylphenols (*m*/*z* 122), and trimethylphenols (*m*/*z* 136) for Jet Rock-1 sediment extract phenol/carbazole fraction. For peak identifications refer to Table 2.

Table 3
Recoveries of standards from crude oil phenol/carbazole separations

Sample	% Recovery		
	d_5-Phenol	d_3-2,6-Dimethylphenol	d_8-Carbazole
Barrow	91 ($n=5$,%S.D. 3.7)	95 ($n=5$,%S.D. 2.7)	103 ($n=5$,%S.D. 10.6)
Caroline	105	98	96
Monterey Oil 5	80	91	84
Jet Rock-1	87	102	92

procedure separates phenols, carbazoles and benzocarbazoles in one fraction away from not only saturate and aromatic compounds but also from more polar compounds. The method uses liquid chromatography with high recoveries involving only a small column containing silica gel and mixtures of solvents ranging in polarity. The phenol/carbazole fraction obtained from this method is then analysed using GC–MS techniques. Figs. 1–9 show the partial mass chromatograms obtained for the phenols (Figs. 1–4), carbazoles (Figs. 5–8) and benzocarbazoles (Fig. 9) for the samples used in this study.

The procedure typically requires 80–100 mg of crude oil or sediment extract, but, when there is only little sample available smaller sample sizes can be successfully used with high recoveries. When there is sufficient sample available, the small sample size allows for fresh preparation of the phenol/carbazole fraction when needed, thus removing the need to store fractions. Minimal losses from evaporation during work-up enables accurate analysis of low-molecular weight compounds such as phenol and cresols. The method also affords indoles and fluorenones in the phenol/carbazole fraction. Compound types such as pyridines, quinolines, acids, primary amines, amides, quinones and resorcinols are retained on the column. Because of the absence of these more polar compounds in the PHE fraction, maintenance of injector liners and GC columns is similar to that required for analysing aromatic fractions.

3.2. Recovery

3.2.1. Selection of surrogate standards

Because this separation is based on the polarity of the compounds it was necessary to select surrogate standards that would cover the polarity range of alkylphenols measured in sedimentary material. This was achieved by using d_5-phenol and d_3-2,6-dimethylphenol. Phenol, and thus d_5-phenol, is more polar than methyl phenols as there is no shielding of the hydroxyl group. In addition, because it is the most volatile of all phenols, the standard can be used to account for any losses due to evaporation. In contrast, 2,6-dimethylphenol, and hence d_3-2,6-dimethylphenol, is one of the least polar methyl phenols, due to the fact that the hydroxyl group is shielded on both sides by a methyl group.

The polarities of carbazoles and benzocarbazoles were found to lie within the polarity range of the alkylphenols when subjected to silica gel chromatography and the specified mobile phase. However, because the carbazoles and benzocarbazoles elute much later on a GC column and have higher molecular weights than the phenols, the effectiveness of using the phenolic standards for their quantification would be greatly reduced. Therefore, d_8-carbazole was selected as a surrogate standard for the carbazoles and benzocarbazoles and used to calculate their concentrations.

Table 4
Recoveries of alkylcarbazoles relative to carbazole for Barrow crude oil phenol/carbazole fraction separated a second time

Peak no.	Compound	% Recovery relative
21	Carbazole	100
22	1-Methylcarbazole	97
23	3-Methylcarbazole	98
24	2-methylcarbazole	96
25	4-methylcarbazole	96
26	1,8-Dimethylcarbazole	94
27	1-Ethylcarbazole	98
28	1,3-Dimethylcarbazole	96
29	1,6-Dimethylcarbazole	94
30	1,7-Dimethylcarbazole	99
31	1,4-Dimethylcarbazole	91
32	1,5-Dimethylcarbazole	96
33	2,6-Dimethylcarbazole	100
34	2,7-Dimethylcarbazole	93
35	1,2-Dimethylcarbazole	91
36	2,4-Dimethylcarbazole	93
37	2,5-Dimethylcarbazole	97
39	Benzo(a)carbazole	100
40	Benzo(b)carbazole	97
41	Benzo(c)carbazole	98

Peak numbers refer to Figs. 1–9.

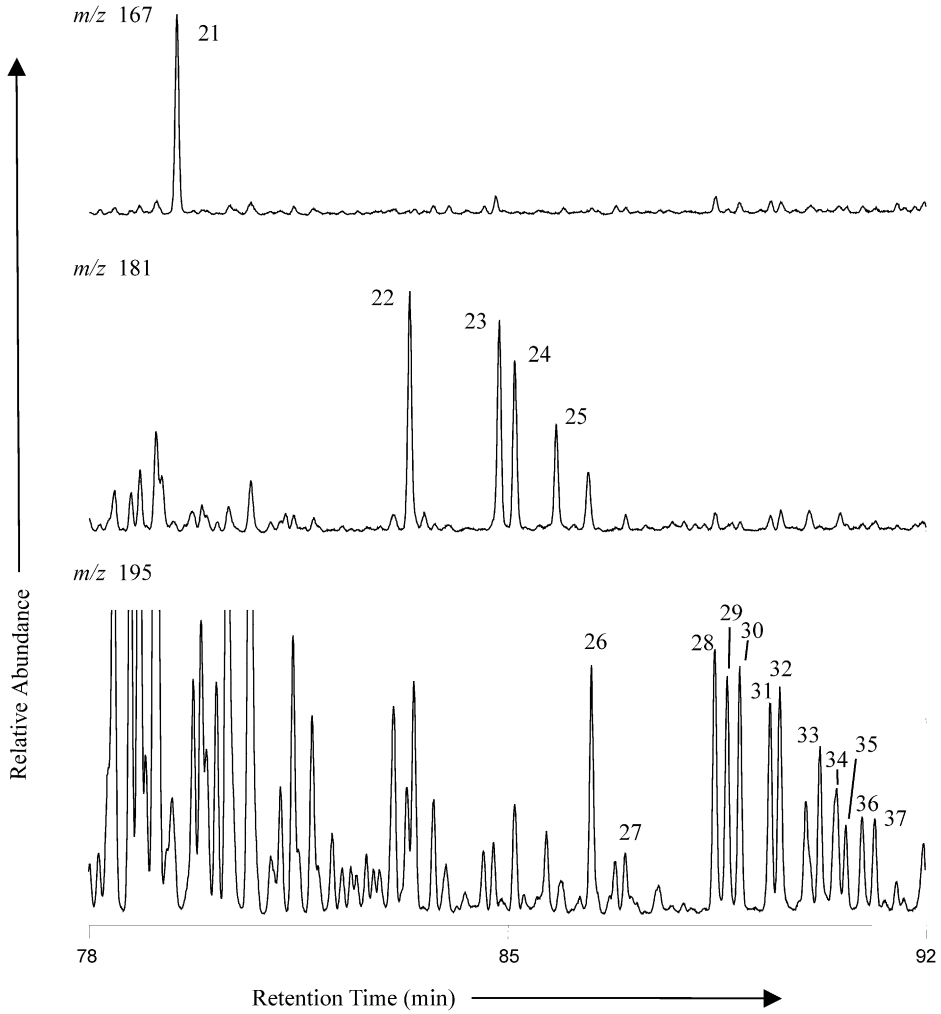


Fig. 5. Partial mass chromatograms showing carbazole (m/z 167), methylcarbazoles (m/z 181), and dimethylcarbazoles (195) for Barrow crude oil phenol/carbazole fraction. For peak identifications refer to Table 2.

3.2.2. Recovery of surrogate standards

Three crude oils and a sediment extract were selected for their different chemical compositions, based on their saturate, aromatic and polar contents to test the procedure for a range of crude oil types (Table 1). Recoveries for surrogate standards from all the samples were high with values ranging from 80 to 105% for d_5-phenol, 91 to 98% for d_3-2,6-dimethylphenol and 84 to 103% for d_8-carbazole (Table 3). Monterey Oil 5 which has the highest polar content of the oils studied (Table 1) and has the lowest recovery for the surrogate standards. For this oil substantial amounts of asphaltenes precipitated on addition of pentane, suggesting that the lower recoveries of the surrogate standards in this sample may be either due to incomplete transfer of the sample on to the silica gel column, or interaction of the polar compounds with the asphaltenes.

3.2.3. Recovery of alkylcarbazoles and benzocarbazoles

Because alkylcarbazole standards were not available it was decided to measure the recovery of the alkylcarbazoles by subjecting a previously obtained phenol/carbazole fraction from a crude oil to the separation procedure. Recoveries were measured by comparing the original alkylcarbazoles relative to carbazole, for which recovery is known. The premise of this experiment was that if the alkylcarbazoles were not discriminated against when separated a second time, then it can be assumed that no fractionation occurs during the separation procedure.

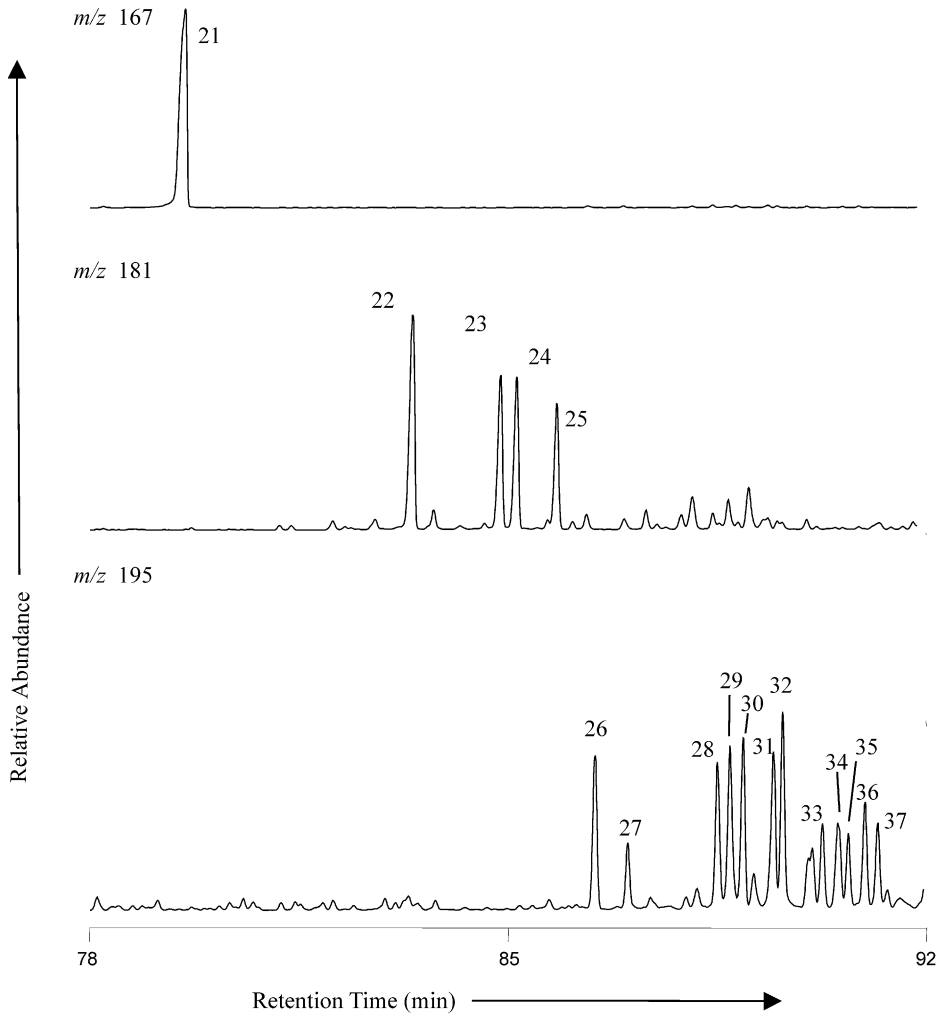


Fig. 6. Partial mass chromatograms showing carbazole (m/z 167), methylcarbazoles (m/z 181), and dimethylcarbazoles (195) for Caroline crude oil phenol/carbazole fraction. For peak identifications refer to Table 2.

Table 4 shows the recoveries of the alkylcarbazoles in Barrow crude oil after a second separation. These recoveries (ranging from 91 to 100%) show that full recovery of the alkylcarbazoles has been achieved.

3.3. Separation efficiency

To test the analytical procedure for its efficiency to separate alkylphenols, carbazole and benzocarbazoles, a standard mixture was prepared and put through the procedure. In addition, to test any possible interference with the separation by saturate and aromatic hydrocarbons in the crude oil, the standard mixture was added to a previously separated saturate and aromatic hydrocarbon fraction of a crude oil (80 mg), separated again and compared with the original standard mixture. Table 5 shows the recoveries of the alkylphenols, carbazole and benzocarbazoles in the mixture of standards, after it was put through the procedure, and the same mixture separated from the Barrow crude oil saturate and aromatic fraction. It is evident from these recoveries (ranging from 91 to 110%) that full recovery of the alkylphenols, carbazole and benzocarbazole could be obtained and that the saturate and aromatic compounds do not interfere with the separation.

These results show that the procedure can be used for the quantitative analysis of alkylphenols, alkylcarbazole and benzocarbazoles in sedimentary matter.

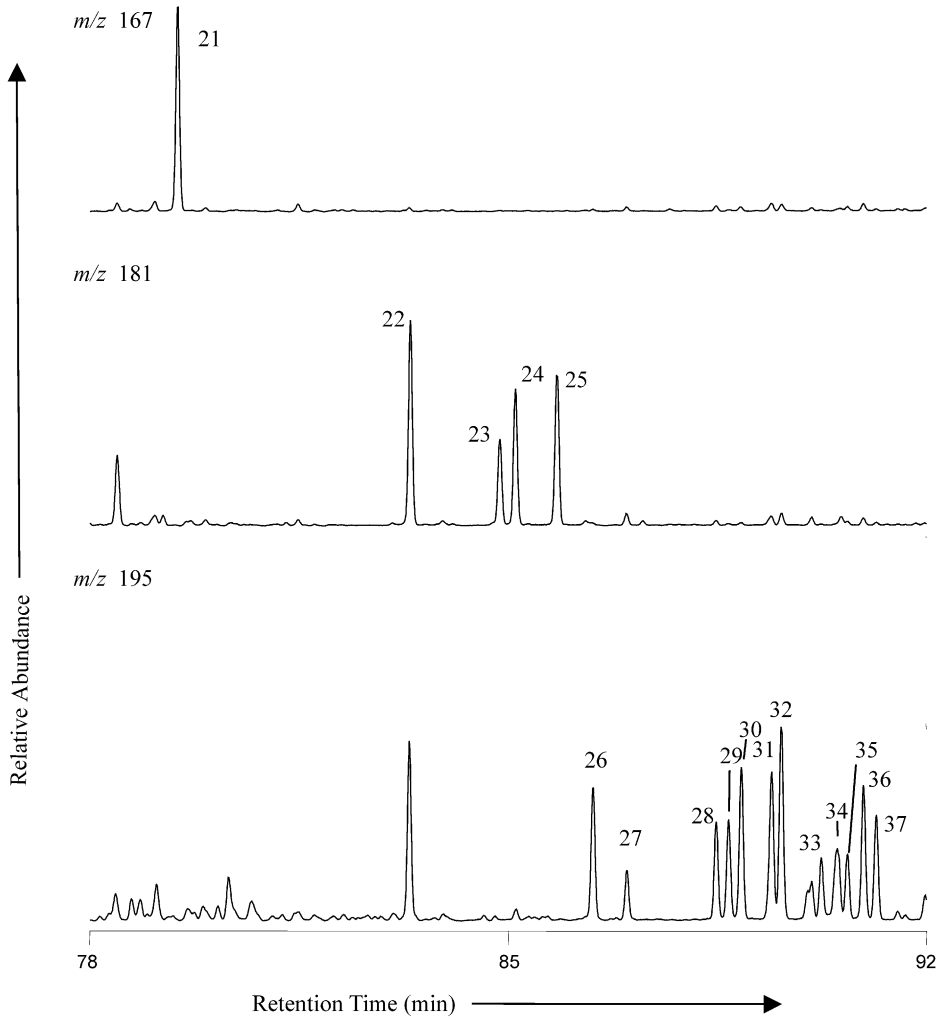
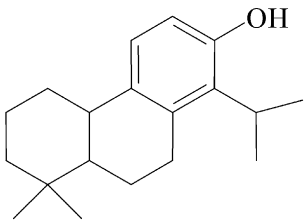


Fig. 7. Partial mass chromatograms showing carbazole (*m*/*z* 167), methylcarbazoles (*m*/*z* 181), and dimethylcarbazoles (195) for Monterey crude oil phenol/carbazole fraction. For peak identifications refer to Table 2.

It is noteworthy that in addition to the low molecular weight alkylphenols that are generally analysed in sedimentary matter, this procedure can also be used for the analysis of high molecular weight alkylphenols such as totarol (I). Totarol is not only a high molecular weight (MW 286) alkylphenol but is also highly shielded (with an isopropyl group *ortho* to the hydroxyl group) which is why these types of compounds have low water solubility. Such attributes make analysis of these compound types difficult using conventional methods that involve water extraction.



Totarol (I)

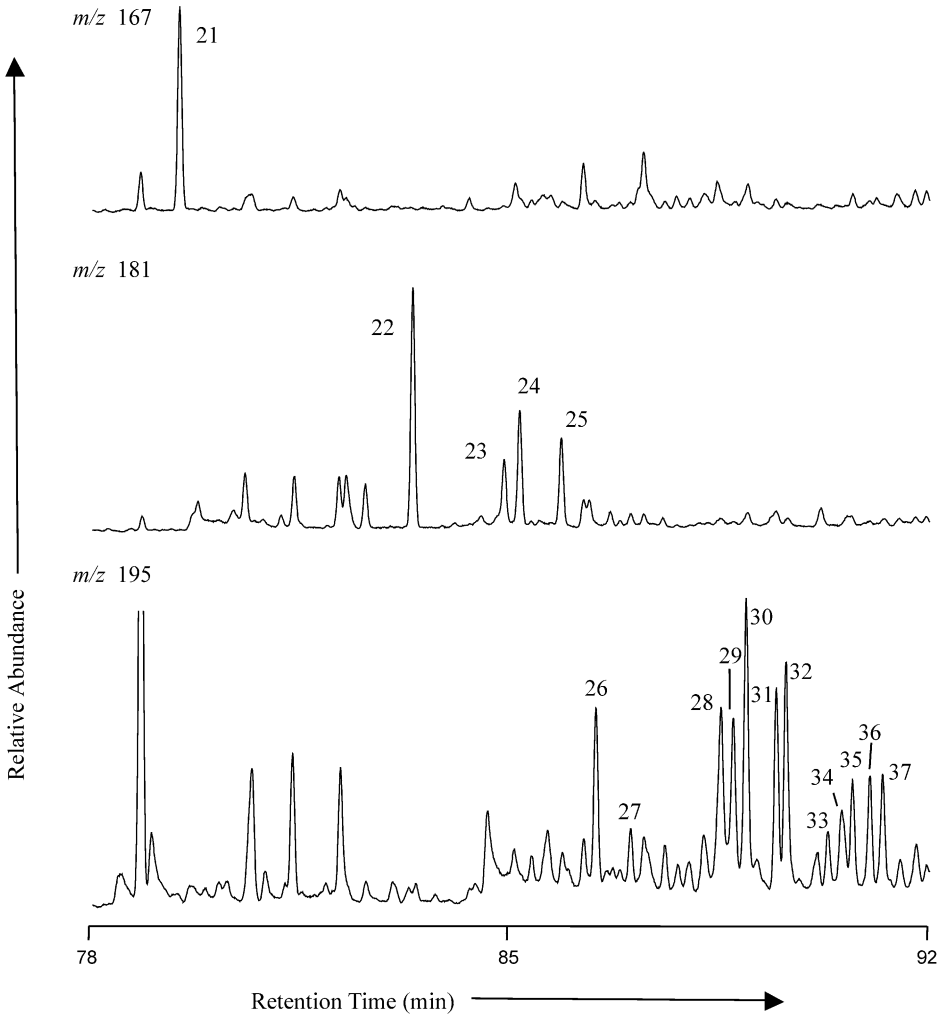


Fig. 8. Partial mass chromatograms showing carbazole (*m*/*z* 167), methylcarbazoles (*m*/*z* 181), and dimethylcarbazoles (195) for Jet Rock-1 sediment extract phenol/carbazole fraction. For peak identifications refer to Table 2.

3.4. Reproducibility

Figs. 1, 5 and 9a show the alkylphenol, alkylcarbazole and benzocarbazole distributions respectively, for Barrow crude oil obtained from a typical separation. This separation afforded high recoveries of d_5-phenol (average 91%, S.D. 3.7%), d_3-2,6-dimethylphenol (average 95%, S.D. 2.7%) and d_8-carbazole (average 103%, S.D. 10.6%).

The alkylphenol, alkylcarbazole and benzocarbazole concentrations measured using this method for Barrow crude oil are shown in Table 2. Replicates of the quantitation ($n=5$ separations) gave average values for the standard deviation of 6.5% for alkylphenols), 5.3% for alkylcarbazoles and 8.6% for benzocarbazoles. Higher standard deviations were observed when the analytes were present in lower concentration, as in the case of the benzocarbazoles, or when incomplete chromatographic resolution was observed for the analytes as with some of the alkylcarbazoles.

4. Conclusions

Silica gel small-scale columns allow for the rapid, cheap, accurate and reproducible recovery of alkylphenols, alkylcarbazoles and benzocarbazoles from

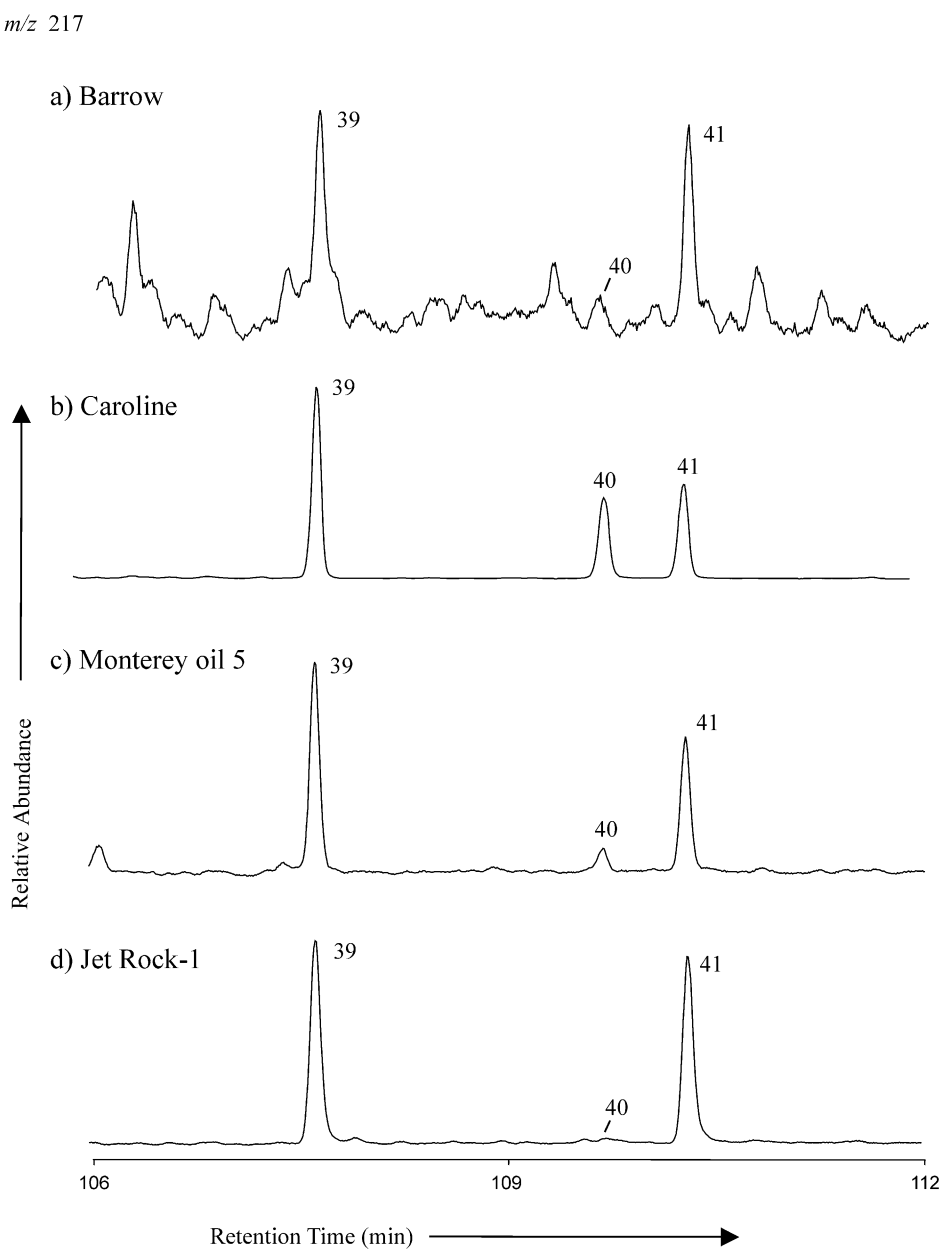


Fig. 9. Partial mass chromatogram (m/z 217) showing the benzocarbazole distribution for (a) Barrow crude oil, (b) Caroline crude oil, (c) Monterey oil 5 crude oil, and (d) Jet Rock-1 sediment extract phenol/carbazole fractions. For peak identifications refer to Table 2.

crude oils and sediment extracts. The successful separation of these compounds from aliphatic and aromatic components was demonstrated for three different crude oils and a sediment extract. During analysis the fraction remains in solvent, therefore quantitatively retaining volatile compounds such as phenol. This method has many practical advantages as all the materials used are disposable, cheap and readily available. The separation requires minimal work-up with no losses to evaporation and is very rapid. For example, a routine batch separation of phenol/carbazole fractions from 10 samples (including preparation) takes less than two hours.

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Table 5
Recoveries of alkylphenol, carbazole and benzocarbazole from the phenol/carbazole fractions of the calibration mixture (stds) and the calibration mixture added to Barrow crude oil (80 mg) saturate and aromatic fraction (SAA)

Peak no.	Compound	% Recovery	
		Stds	Barrow SAA + Stds
1	Phenol	96	98
3	*o*-Cresol	105	102
4	*p*-Cresol	97	99
5	*m*-Cresol	103	99
6	2,6-Dimethylphenol	100	100
8	2,4-Dimethylphenol	98	99
9	2,5-Dimethylphenol	110	109
10	4-Ethylphenol	100	99
11	3,5-Dimethylphenol	105	104
12	2,3-Dimethylphenol	106	105
14	2,4,6-Trimethylphenol	98	105
17	2,3,5-Trimethylphenol	108	103
19	3,4,5-Trimethylphenol	107	101
21	Carbazole	105	109
38	Totarol	96	95
39	Benzo(a)carbazole	93	106
41	Benzo(c)carbazole	91	105

Peak numbers refer to Figs. 1–9.

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