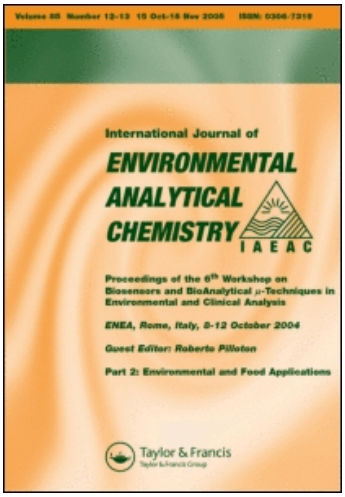

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Bennett, Barry , Noke, Kimberley J. , Bowler, Bernhard F. J. and Larter, Stephen R.(2007) 'The accurate determination of C_0-C_3 alkylphenol concentrations in crude oils', International Journal of Environmental Analytical Chemistry, 87: 5, 307 — 320
To link to this Article: DOI: 10.1080/03067310601151936
URL: http://dx.doi.org/10.1080/03067310601151936

Intern. J. Environ. Anal. Chem.
Vol. 87, No. 5, 20 April 2007, 307–320

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The accurate determination of C_0–C_3 alkylphenol concentrations in crude oils

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(*Received 18 May 2006; in final form 30 November 2006*)

Accurate determination of the concentrations of volatile and semi-volatile phenols in oils is required to reliably quantify the solute levels that are likely to be loaded into oilfield production waters following partition redistribution. We show, from a gas chromatography–mass spectrometry analysis of a North Sea crude oil, that significantly different concentration data for several C_0–C_3 alkylphenols may be obtained, depending upon whether the response of the fragmentation ion or the molecular ion is used, and whether the data are corrected for the relative response factor (RRF) of individual phenols. We also show how a comparison of concentration data for individual phenols obtained both with and without RRF correction can enable the recognition of co-elution. The accurate quantification of phenols in oils can be used to predict more effectively the requirement for production water-treatment facilities and can provide more reliable inventories of these toxic compounds discharged into the environment. The oil–water partition coefficient of *p*-cresol increases in crude oils with increasing nitrogen, sulfur, and oxygen-containing (NSO)-compounds. The occurrence of high phenols concentrations and relatively low NSO contents in some condensates may present particular problems in water treatment and disposal.

Keywords: Alkylphenols; Response factors; Partition coefficient; Production waters

1. Introduction

Alkylphenols occur in variable abundance in many crude oils [1, 2]. They are both toxic and water-soluble, and will distribute into a contacting water phase (e.g. reservoir formation water and production water) according to their partition coefficient. The partition coefficients for phenol and cresols in crude oil + brine systems are influenced by temperature, brine salinity, oil composition [3], and gas saturation [4]. The distributions and concentrations of phenols have been determined in oilfield formation

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International Journal of Environmental and Analytical Chemistry
ISSN 0306-7319 print/ISSN 1029-0397 online © 2007 Taylor & Francis
DOI: 10.1080/03067310601151936

waters [5, 6] and oilfield production waters [7]. Dale *et al*. [6] found concentrations of total C_0–C_2 alkylphenols in the range of 0.8–18 mg L^{-1} in North Sea production waters, with phenol and the cresols accounting for c.50 and 40% of the total, respectively.

Alkylphenol concentrations are often routinely measured as part of environmental monitoring programmes connected with petroleum production, reflecting their relatively high toxicity and water solubility. Operators of offshore petroleum production and processing installations may be required to ensure that the concentrations of these compounds in discharged waters are minimized using the best available technology. Phenol concentration data for a reservoired oil may be used (together with partition coefficients) to guide the selection of appropriate (and costly) processing facilities for the production installation. The abundances of phenol and cresols in production waters also find application in petroleum exploration, where they may give an indication of missed oil banks in watered-out petroleum reservoirs [8]. The involvement of phenols in environmental, technical, and financial aspects of petroleum exploration and production imposes a requirement for robust and rapid analytical methodologies, which provide accurate phenol concentration data for oils and waters.

Several analytical methods for the extraction and analysis of alkylphenols from crude oils, associated waters, and environmental samples have been reported in the literature. Earlier separation methods usually involved aqueous alkaline extraction of the matrix followed by acidification and back-extraction into an organic phase [1, 9–13]. Alkaline extraction, however, may result in the formation of emulsions during the shaking/extraction stage, which may affect the quantitative recovery of compounds [14]. Several authors have used alkaline extraction followed by reverse-phase solid-phase extraction (SPE) on C18 alkyl-bonded silica to remove non-polar material and provide a phenol-enriched fraction for analysis [1, 9]. Galimberti *et al*. [15] and Bastow *et al*. [16] describe methods where both phenols and nitrogen compounds in oils may be analysed simultaneously. Bennett *et al*. [17] developed a method for the rapid analysis of C_0–C_3 alkylphenols in oils which involved SPE using C18 non-endcapped silica (abbreviated to C18 NEC SPE) and gas chromatography–mass spectrometry (GCMS). In the present study, we use a C18 NEC SPE + GCMS method based on that described by Bennett *et al*. [17] to show the variation in phenols concentration data which may occur when different GCMS quantification methods are used, and to highlight the importance of individual relative response factor (RRF) correction in the accurate determination of C_0–C_3 alkylphenols in crude oils.

2. Experimental

2.1 *Samples*

The sample suite for this study comprised five crude oils and three condensates (table 1). The crude oils included two non-biodegraded oils from North Sea reservoirs and three biodegraded oils from North Sea and Monterey, California, oilfields. The condensates were from petroleum reservoirs in Southeast Asia and the North Sea.

Table 1. Sample information and bulk composition as determined by Iatroscan analysis.

Sample code/field	Location	Type	Saturated HCs (%)[a]	Aliphatic HCs (%)[a]	Resins (%)	Asphaltenes (%)
A3	North Sea	Non-biodegraded crude oil	82.1	13.5	1.1	3.3
Nelson	North Sea	Non-biodegraded crude oil	79.7	16.9	1.7	1.7
Heidrun	North Sea	Biodegraded crude oil	69.0	23.6	4.6	2.8
Hobbs 1	Monterey, CA	Biodegraded crude oil	51.6	23.5	6.3	18.6
Hobbs 7	Monterey, CA	Biodegraded crude oil	38.2	24.1	9.8	27.8
Condensate A	Southeast Asia	Condensate	83.6	13.9	0.8	1.6
Condensate B	North Sea	Condensate	95.2	4.3	0.3	0.2
Condensate C	North Sea	Condensate	92.1	6.8	0.3	0.7

[a]HC: hydrocarbon.

2.2 *Materials*

Hexane and dichloromethane (DCM, CH_2Cl_2) were purchased from Fisons. Isolute C18 non-endcapped SPE cartridges were obtained from Jones Chromatography Ltd (UK). Deuterated (d_6) phenol and 2,4-dimethylphenol-d_3 (internal standards) were purchased from Fluka (UK). C_0–C_3 alkylphenol standards were obtained from Aldrich and BDH. BSTFA containing 1% TMCS was obtained from Sigma Chemical Company.

2.3 *Iatroscan analysis*

The content of the aliphatic hydrocarbon, aromatic hydrocarbon, resin, and asphaltene fractions of the crude oils and condensates was determined using the Iatroscan Chromarod technique. The method is described in detail by Karlsen and Larter [18], but essentially the technique combines thin-layer chromatographic fractionation with flame-ionization detection. A known weight of oil was dissolved in DCM (10 mg oil/1 mL DCM) in a glass vial, and a known volume (c. 3 μL) was applied to the Iatroscan rod (Chromarod-S Type III, silica). After allowing the solvent to evaporate, the Chromarods were developed sequentially with hexane, toluene and DCM/methanol (93/7) to separate the aliphatic hydrocarbon, aromatic hydrocarbon, resins, and asphaltenes fractions. The fractions were quantified using a flame-ionization detector and by integration of appropriate peak areas in the resulting chromatogram. Retention-time cutoff points for the various fractions were determined by analysis of suitable standard compounds.

2.4 *SPE of C_0–C_3 alkylphenols*

A fraction containing the C_0–C_3 alkylphenols was isolated from the crude oil by C18 NEC SPE using a modification of the method described in Bennett *et al.* [17]. A known weight (c. 100 mg) of crude oil was adsorbed on to the top of the SPE column. Known amounts of 2,4-dimethylphenol-d_3 (internal standard) and d_6-phenol (to check for losses of volatile compounds) were added to the top of the SPE column after sorption of the oil.

Table 2. Ions monitored in GCMS–SIM analysis of C_0–C_3 alkylphenols (as TMS ether derivatives) in oils.

Compound	Molecular ion (M)	M-15
Phenol	166	151
Cresols	180	165
C_2-Alkylphenols	194	179
C_3-Alkylphenols	208	193
2,3-Dimethylphenol-d_3	197	182
Phenol-d_6	171	156

The hydrocarbon fraction was eluted with 5 mL of *n*-hexane, and a more polar fraction containing the C_0–C_3 alkylphenols was eluted with 5 mL of DCM. The solvent volume was reduced to c. 200 μL by careful evaporation in a stream of nitrogen to reduce loss of volatile phenol. The phenols were derivatized to their trimethylsilyl ethers by adding BSTFA (c. 100–200 μL) to the concentrated phenol-enriched fraction and heating in a sealed vial at 60°C for 2 h prior to GCMS analysis.

2.5 *Gas chromatography–mass spectrometry (GCMS)*

The C_0–C_3 alkylphenols were analysed as the trimethylsilyl ethers using GCMS operated in single-ion monitoring (SIM) mode, monitoring the relevant molecular ion and the M-15 ion (see table 2). GCMS analysis was performed using an HP5890 gas chromatograph (GC) fitted with an HP-5 fused silica capillary column (25 m × 0.25 mm i.d. × 0.17 μm film thickness) and connected to an HP 5973 MSD. The GC oven temperature programme was 35°C (initial hold time 10 min) then 2°C min^{-1} to 150°C then 8°C min^{-1} to 300°C (final hold time 20 min). Helium was used as carrier gas at a (constant) flow rate of 1 mL min^{-1}. The sample was injected in split/splitless mode with an injector temperature of 250°C. Phenol and the C_1–C_3 alkylphenol isomers were identified by comparison of peak retention times with those of authentic standards. Integration of peak areas was performed using the Hewlett–Packard Chemstation RTE integrator.

2.6 *Analytical protocol for the quantification of C_0–C_3 alkylphenols*

An analytical protocol based on commercially available standards (see table 3) was developed for the quantification of the C_0–C_3 alkylphenols in oils. A mixed phenol stock solution containing accurately known amounts (c. 25–50 mg 100 mL^{-1} toluene) of the standard C_0–C_3 alkylphenols was prepared, and a known aliquot was derivatized using BSTFA. Samples for analysis were run as a batch, with the run sequence beginning with the mixed phenols standard, followed by the phenol-enriched fraction from a North Sea oil reference standard (for which individual phenols have been identified by co-injection with authentic standards), followed by the samples to be analysed. The RRF value for the individual C_0–C_3 alkylphenols *versus* 2,4-dimethylphenol-d_3 was calculated using integrated peak area data from the GCMS analysis of the mixed phenol standard and was used in the calculation of C_0–C_3 alkylphenol concentrations in the samples.

Table 3. C_0–C_3 alkylphenols identified in standard mixture (see figure 1a) and in crude oil sample A3 (see figure 1b).

Peak	C_0–C_2 alkylphenols	Peak	C_2–C_3 alkylphenols
1	Phenol	11	2,3-DMP
2	*o*-Cresol	12	3,4-DMP
3	*m*-Cresol	13	2-Isopropylphenol
4	*p*-Cresol	14	2-Propylphenol
5	2-Ethylphenol	15	3-Isopropylphenol
6	2,5-DMP[a]	16	4-Isopropylphenol
7	2,4-DMP + 3-ethylphenol	17	2,4,6-TMP[a]
8	2,6-DMP	18	2,3,5-TMP + 4-propylphenol
9	3,5-DMP	19	2,3,6-TMP
10	4-Ethylphenol	20	3,4,5-TMP

[a]DMP: dimethylphenol; TMP: trimethylphenol.

During a run sequence, some deterioration in chromatographic performance, observed as peak tailing, may appear after 10–15 sample injections. Chromatographic performance was restored by removing approximately 10 cm from the front end of the GC column. The consequent reduction in column length results in a decrease in the retention times of the C_0–C_3 alkylphenols, and it is therefore necessary to include the mixed phenol standard and the reference oil at the beginning of the next sample batch or run. Relative response factor values were determined *for each batch* of samples analysed using the formula in equation (1):

$$\mathrm{RRF} = \frac{\text{Peak area phenol}}{\text{Conc. phenol}} \times \frac{\text{Wt (std)}}{\text{Peak area (std)}} \times \text{Wt (oil)}, \quad (1)$$

where Wt (std) is the weight of 2,4-dimethylphenol-d_3 internal standard added to the sample, and Wt (oil) is the weight of oil sample applied to SPE.

The peak area data were obtained by integration of the appropriate phenol or alkylphenol peaks in both the molecular ion chromatogram and the fragmentation ion (M-15) chromatogram. For example, phenol (C_0) concentrations were determined using the integrated peak areas for phenol from the m/z 151 and 166 (M-15) fragmentogram, and the relevant peak areas for 2,4-dimethylphenol-d_3 from the m/z 182 and 197 fragmentograms.

3. Results and discussion

3.1 *Determination of C_0–C_3 alkylphenol concentrations*

Molecular ion mass chromatograms showing the distributions of C_0–C_3 alkylphenols in the standard mixture and in a typical, non-biodegraded North Sea oil (A3) used as an analytical reference standard are given in figure 1(a) and (b), respectively. The key to the identification of compounds is given in table 3.

The concentrations of C_0–C_3 alkylphenols in North Sea crude oil A3, determined using the molecular ion and the fragmentation ion both with and without individual relative response factor correction, are given in table 4. Figure 2(a) compares

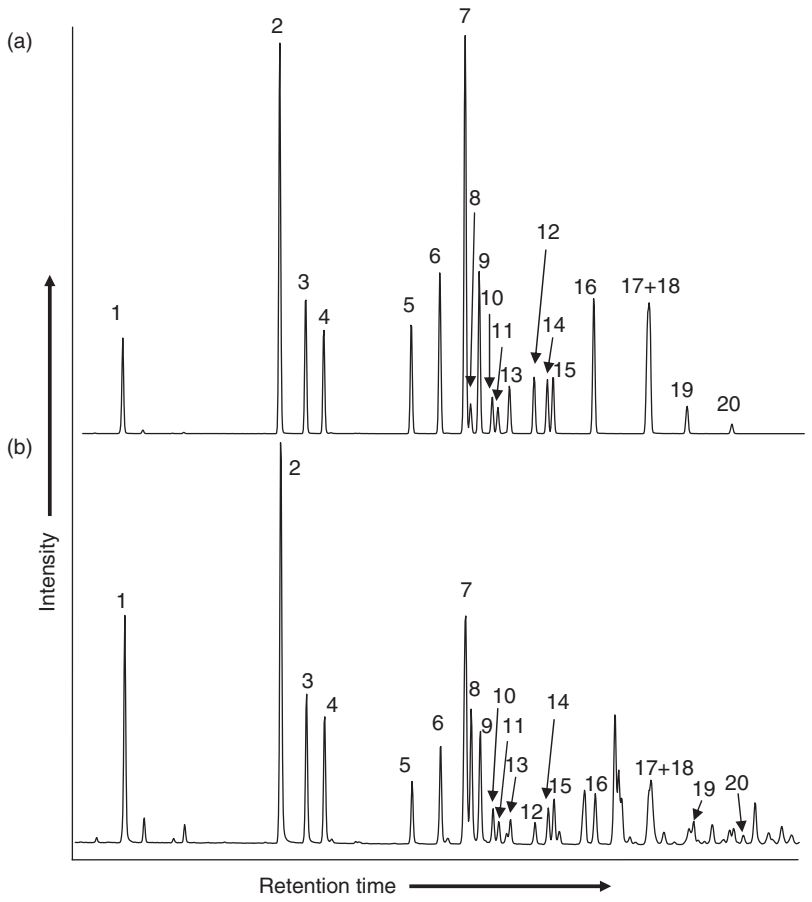

Figure 1. Partial summed ion mass chromatogram (m/z 166 + 180 + 194 + 208) for (a) a standard phenol mixture and (b) North Sea crude oil sample A3. For compound identification, see table 3.

graphically the concentrations of individual phenols in the oil obtained using the molecular ion data with concentrations obtained using the fragmentation ion data. Significant differences are evident in the concentrations derived by the two methods, particularly for phenol and the cresols. For example, the phenol concentration is c. 22.35 $\mu g\,g^{-1}$ oil when peak area data from the fragmentation ion chromatogram are used, and c. 6.46 $\mu g\,g^{-1}$ oil when peak area data from the molecular ion chromatogram are used (without RRF correction, in both cases) (figure 2a and table 4).

The differences in C_0–C_3-alkylphenol concentrations when calculated using peak areas in the molecular ion or fragmentation ion chromatogram are due to the different relative responses compared with 2,4-dimethylphenol-d_3. For example, the RRF for phenol compared with 2,4-dimethylphenol-d_3 based on the fragmentation ion response is 4.96, while for the molecular ion the RRF is 1.44 (table 4). The difference in mass spectral response of individual compounds according to the molecular ion or fragmentation ion is also seen for the C_3 alkylphenols, particularly 2-propylphenol. Figure 3 shows partial mass chromatograms for the molecular ion and the M-15 ion for the C_3-alkylphenols in the standard mixture. In the fragmentation ion chromatogram,

Table 4. Relative response factors determined for C_0–C_3-alkylphenols (*vs.* 2,4-dimethylphenol-d_3) in the standard mixture, and alkylphenol concentrations in a normal crude oil from a North Sea oilfield calculated using the molecular ion and fragmentation ion approach with and without RRF correction.

	RRF		Concentrations ($\mu g\,g^{-1}$ oil)			
Compound	Fragment ion	Molecular ion	Fragment ion	Molecular ion	Fragment ion RRF corrected*	Molecular ion RRF corrected*
Phenol	4.96	1.44	22.35	6.46	4.51 (0.40; 8.9)	4.47 (0.36; 8.0)
o-Cresol	1.37	0.98	11.22	7.90	8.20 (0.34; 4.1)	8.05 (0.30; 3.7)
m-Cresol	3.90	1.46	6.56	2.44	1.68 (0.08; 5.0)	1.64 (0.08; 4.6)
p-Cresol	3.86	1.61	5.44	2.27	1.41 (0.07; 4.9)	1.41 (0.07; 4.7)
2-Ethylphenol	1.08	0.81	1.71	1.24	1.58 (0.07; 4.5)	1.54 (0.06; 3.6)
2,5-DMP	1.20	1.08	2.56	2.21	2.13 (0.07; 3.4)	2.05 (0.05; 2.5)
2,4-DMP	1.67	1.17	6.96	4.91	4.17 (0.08; 2.0)	4.19 (0.08; 2.0)
2,6-DMP	1.12	0.60	5.38	2.65	4.81 (0.24; 5.0)	4.44 (0.23; 5.1)
3,5-DMP	0.93	0.92	2.78	2.32	3.01 (0.11; 3.8)	2.52 (0.08; 1.8)
4-Ethylphenol	3.77	1.48	1.62	0.66	0.43 (0.02; 4.8)	0.44 (0.03; 6.5)
2,3-DMP	1.18	0.94	0.60	0.59	0.51 (0.05; 10.4)	0.63 (0.05; 7.7)
3,4-DMP	2.81	1.64	0.78	0.44	0.28 (0.01; 4.8)	0.27 (0.01; 4.5)
2-Isopropylphenol	0.84	0.39	1.09	0.49	1.30 (0.07; 5.4)	1.26 (0.07; 5.8)
2-Propylphenol	0.10	0.46	0.21	0.91	2.09 (0.15; 7.3)	1.97 (0.07; 3.6)
3-Isopropylphenol	2.21	1.59	1.78	1.18	0.80 (0.06; 7.0)	0.74 (0.04; 5.0)
4-Isopropylphenol	3.81	1.00	2.63	1.23	0.69 (0.02; 3.5)	1.23 (0.02; 1.3)
2,4,6-TMP + 2,3,5-TMP + 4-propylphenol	0.46	0.73	2.49	3.45	5.38 (0.32; 6.0)	4.75 (0.28; 5.8)
2,3,6-TMP	0.10	0.13	0.74	0.40	7.44 (0.37; 4.9)	3.12 (0.46; 14.8)
3,4,5-TMP	1.54	1.64	1.88	0.12	1.22 (0.06; 5.07)	0.08 (0.01; 9.6)

*Average of triplicate analyses; standard deviation and relative percentage standard deviation, respectively, are shown in parentheses.

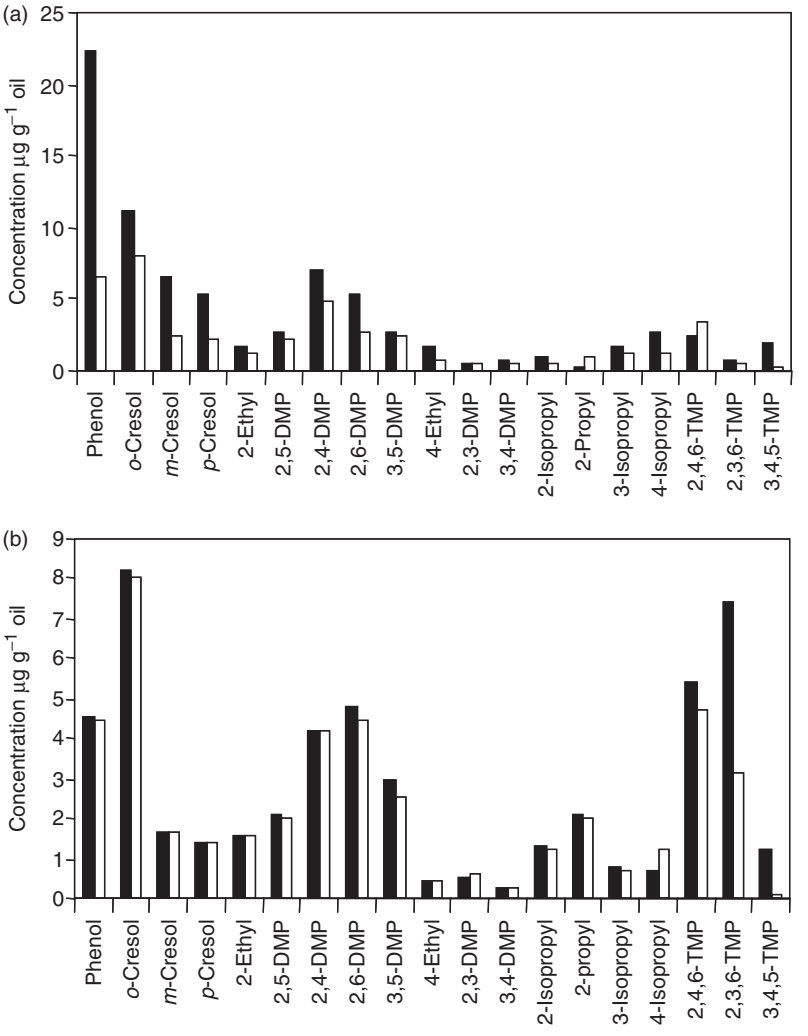

Figure 2. Histograms showing concentrations of C_0–C_3 alkylphenols in a North Sea crude oil (A3) calculated using (a) a relative response factor of 1 for each phenol and (b) individual response factors determined by analysis of a standard phenol mixture using the peak areas in the molecular ion (open bars) and fragmentation ion chromatograms (shaded bars).

the peak area for 2-propylphenol (peak 14) is much less than that of the neighbouring peak, 3-isopropylphenol (peak 15), whereas in the molecular ion chromatogram, similar responses are seen for 2-propylphenol and 3-isopropylphenol. A dramatic difference in response is also seen in the relative abundance of 4-isopropylphenol (peak 16) compared with the other C_3-alkylphenols (figure 3). In view of these significant differences in the mass spectral response of various phenols according to whether the molecular ion or the fragmentation ion is used, it is clearly important that accurate quantification of these compounds should involve response factor correction for individual phenols.

Response factor correction for individual phenols is important for a more accurate determination of phenol concentrations, which is essential when monitoring the

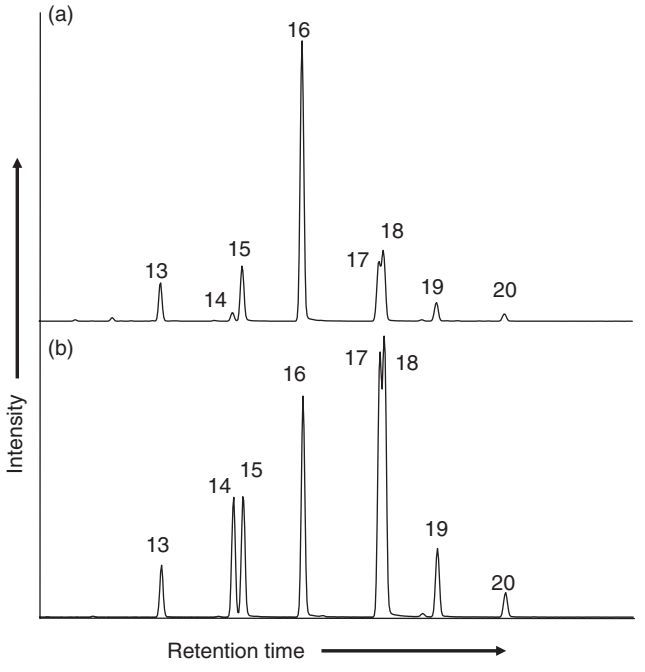

Figure 3. Partial reconstructed mass chromatograms showing distribution of C_3-alkylphenols in the standard phenol mixture based on (a) the fragmentation ion (m/z 179) and (b) the molecular ion (m/z 194). For compound identification, see table 3.

occurrence of toxic compounds in the environment, but it can also indicate possible sources of analytical error. The histogram in figure 2(b) shows the concentrations of C_0–C_3 alkylphenols in North Sea oil A3 calculated from integrated peak areas in the molecular ion and the fragmentation ion chromatograms and using the appropriate individual relative response factors (table 4). In general, there is good agreement between the values obtained for individual phenols using the two procedures, lending confidence to the approach. Several compounds, however, show significant differences in concentration; these may be attributable to co-elution. For example, the significant difference in concentration of 3,4,5-TMP (figure 2b) is due to a co-eluting acid compound which contributes to the fragmentation ion, m/z 193, but not to the molecular ion, m/z 208. In this case, the correct concentration of 3,4,5-TMP is calculated using the molecular ion chromatogram only. The difference in concentration of 2,3,6-TMP (figure 2b) is also attributed to co-elution with an unknown acid compound (tentatively assigned on the basis of the mass spectrum) while that for 4-isopropylphenol is suspected as being due to co-elution with an unknown phenolic compound which contributes to the m/z 208 ion.

The relative response factors for the individual alkylphenols in the standard mixture range from 0.1 (2-propylphenol) to 4.96 (phenol) (table 4); the assumption of a RRF = 1 for all compounds is therefore likely to lead to significant errors in concentration data. For example, the concentrations of phenol calculated using peak areas in the fragmentation ion and molecular ion chromatograms and using RRF correction are, respectively, c. 4.51 and 4.47 $\mu g\,g^{-1}$ oil, i.e. much lower than the

Table 5. Concentrations of C_0–C_3 alkylphenols in a suite of crude oils and condensates based on peak areas in the molecular ion mass chromatograms and applying correction for relative response factor.[a]

	Crude oils					Condensates		
	North Sea			Monterey, USA		Southeast Asia	North Sea	North Sea
Compound	A3	Nelson	Heidrun	Hobbs1	Hobbs 7	A	B	C
Phenol	4.47	6.95	0.81	4.57	3.15	23.51	3.83	16.10
o-Cresol	8.05	5.5	0.54	2.59	0.08	15.27	2.32	13.44
m-Cresol	1.67	6.07	0.37	1.24	0.13	8.90	1.63	5.43
p-Cresol	1.41	2.35	0.50	0.71	0.22	4.72	0.98	3.19
2-Ethylphenol	1.54	0.83	0.17	1.01	0.84	3.12	0.16	2.14
2,5-DMP	2.05	2.25	0.39	2.18	3.46	3.12	0.31	2.41
2,4-DMP	4.19	2.8	0.86	3.37	6.54	5.79	0.90	7.02
2,6-DMP	2.52	0.38	0.26	1.24	1.25	1.86	0.82	2.93
3,5-DMP	4.44	2.51	0.22	0.91	1.00	2.84	0.00	2.95
4-Ethylphenol	0.44	0.52	0.21	0.39	0.86	1.50	0.24	1.74
2,3-DMP	0.63	2.12	0.17	0.56	1.34	1.19	0.00	0.93
3,4-DMP	0.27	0.43	0.15	0.52	0.98	0.94	0.12	0.78
2-Isopropylphenol	1.26	nm	0.14	nm	nm	1.17	0.01	0.28
2-Propylphenol	1.97	0.55	0.08	0.26	0.23	1.53	0.12	0.88
3-Isopropylphenol	0.74	1.36	0.09	0.03	0.03	1.31	0.38	0.94
4-Isopropylphenol	1.23	2.77	0.50	0.55	1.42	2.46	0.06	1.38
2,4,6-TMP + 2,3,5-TMP + 4-propylphenol	4.75	1.56	1.63	2.58	14.86	2.03	0.25	2.41
2,3,6-TMP	3.12	0.70	0.03	0.38	2.45	0.07	0.02	0.19
3,4,5-TMP	0.08	0.80	0.08	0.82	4.83	0.14	0.01	0.08

[a]DMP: dimethylphenol; TMP: trimethylphenol; nm: not measured.

concentrations of 22.35 and 6.46 $\mu g\,g^{-1}$ oil which are obtained when the RRF is assumed to be 1 (table 4). The importance of RRF correction in GCMS analysis was highlighted by Hughes *et al.* [19], who showed that the response factors for pristane and phytane relative to the 5β-cholane internal standard were 6 and 10, respectively, whereas the response factors for aromatic hydrocarbons relative to anthracene-d_{10} internal standard ranged from 0.70 to 0.90.

Although the correction for individual response factors may seem a laborious additional step to the analytical procedure, the similarity in concentrations obtained using peak areas from molecular ion and fragmentation ion chromatograms and RRF correction improves confidence in the data, while significant differences may usefully indicate the presence of co-elution interference.

3.2 *C_0–C_3 alkylphenol composition of crude oils and condensates*

Alkylphenols are common constituents of crude oils, in which they occur in very variable abundance [13]. The concentrations of C_0–C_3 alkylphenols in a suite of crude oils and condensates, shown in table 5, illustrate the degree of variation which may be encountered. The relatively high solubility of phenols (especially phenol and the cresols) in the aqueous phase results in their common occurrence in petroleum reservoir formation waters and production waters, which may be either re-injected into subsurface formations or discharged to sea subsequent to production processing. Owing to the toxicity of the alkylphenols, environmental agencies may impose

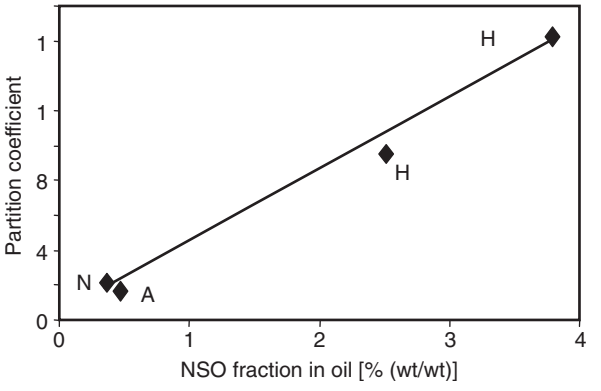

Figure 4. Variation in partition coefficient for *p*-cresol with NSO content (see table 1) in oils from Monterey and the North Sea. The trendline represents the best-fit curve following linear regression analysis. Samples N (Nelson Field) and A3 are from the North Sea; samples H1 (Hobbs 1) and H7 (Hobbs 7) are from Monterey, California.

a requirement on offshore operators to minimize or limit the amounts of phenols which can be discharged to sea from production installations, and compliance usually involves the routine monitoring of phenol concentrations in discharge waters and compilation of pollutant discharge inventories.

Phenol concentrations obtained from the analysis of drill stem test (DST) or repeat formation test (RFT) oils taken during petroleum exploration and field appraisal activities can be used in conjunction with the knowledge of how the partition behaviour of C_0–C_2 phenols is influenced by temperature, brine salinity, and oil composition [3] to predict phenol contents in formation/production waters during the production history of an oilfield. Accurate phenol concentration data provided at the design and planning stage can help ensure that production installations are initially equipped with suitable processing facilities to enable phenol concentrations in discharged waters to be reduced to a minimum or to within 'acceptable limits', and reduce the risk of redundant processing capacity or costly retro-fitting of equipment.

Taylor [13] showed a positive correlation between the partition coefficient of *p*-cresol, measured in a number of crude oil/brine systems under ambient conditions and half seawater salinity, and the NSO content of the crude oil. Figure 4 shows the variation in the partition coefficient of *p*-cresol as a function of the NSO content of oils from Monterey (H1 and H7) and the North Sea (A3 and Nelson). The best-fit curve representing the variation was obtained using linear regression ($y = 0.4128x + 0.4061$) and gave a correlation coefficient $R^2 = 0.9894$. This linear regression function was used to calculate the partition coefficients for *p*-cresol for the Heidrun oil and the condensates (table 6).

The estimated concentration of *p*-cresol in the aqueous phase after equilibration of the crude oils and condensates in the sample suite with an equal volume of water (brine) was calculated using equation (2):

$$C_w = (C_{oi}/K_{ow} + 1), \tag{2}$$

where C_w is the concentration of *p*-cresol in water; C_{oi} is the concentration of *p*-cresol in the original oil; and K_{ow} is the oil–water partition coefficient for *p*-cresol which

Table 6. Concentration (C_{oi}) of *p*-cresol in various crude oils and condensates, and concentration in the oil (C_o) and water (C_w) phases after partition equilibration with water (1 : 1 vol : vol; half seawater salinity (1.75% NaCl)) under ambient conditions.[a]

	Concentration (C) of *p*-cresol				
	Original oil	After partition equilibration			
Sample	C_{oi} ($\mu g\,g^{-1}$)	C_o ($\mu g\,g^{-1}$)	C_w ($\mu g\,g^{-1}$)	Partition coefficient	% NSO fraction[b]
A3	1.41	0.93	0.48	1.92	4.41
Nelson	2.35	1.66	0.69	2.43	3.40
Heidrun	0.50	0.39	0.11	3.46[c]	7.39
Monterey Hobbs 1	0.71	0.64	0.07	9.8	24.83
Monterey Hobbs 7	0.22	0.21	0.01	16.5	37.67
Condensate A	4.72	2.76	1.96	1.41[c]	2.44
Condensate B	0.98	0.38	0.60	0.62[c]	0.51
Condensate C	3.19	1.47	1.72	0.85[c]	1.08

[a]Partition coefficients of *p*-cresol for Hobbs 1 and Hobbs 7 were calculated from oil and water concentration data obtained under ambient conditions and half seawater salinity given by Taylor [13]. The *p*-cresol partition coefficients for the Nelson and A3 oils were obtained under half seawater salinity/ambient conditions by extrapolation of the *p*-cresol partition coefficient obtained from oil–water partition experiments carried out with 5, 10, and 15% NaCl brine salinities.
[b]NSO fraction is the sum of the resins and asphaltene fractions as determined by Iatroscan analysis (see table 1).
[c]Partition coefficients and concentrations of *p*-cresol in water phase for the other oils/condensates calculated from the concentration in original oil and the linear regression function describing variation in partition coefficient with % NSO fraction in oil samples A3, Nelson, Hobbs 1, and Hobbs 7 (see figure 4).

is C_o/C_w = concentration of *p*-cresol in oil (C_o) relative to its concentration in water (C_w) after equilibration.

The concentration of *p*-cresol in the (original, unequilibrated) oil was determined by GCMS analysis using the molecular ion and RRF correction, and the partition coefficient for *p*-cresol was determined either by experiment or by the linear regression/NSO method described above. The equilibrium concentrations of *p*-cresol in the aqueous phase for the suite of crude oils and condensates analysed in this study are given in table 6. If the production operator imposed a maximum concentration of *p*-cresol in discharge waters of $1\,\mu g\,g^{-1}$, then the waters in contact with the crude oils and condensate B in the sample suite would be considered safe for disposal (as regards phenol content), whereas the waters in contact with condensates A and C would require treatment prior to discharge.

Condensates are typically hydrocarbon-rich, and although they generally have a relatively low NSO content, concentrations of C_0–C_3 alkylphenols, particularly phenol and the cresols, may be very high (see, for example, condensates A and C in table 5). Such oils represent a possible cause for concern since the low NSO content is associated with a low oil–water partition coefficient (figure 4), which favours mobilization of phenol and the cresols into the aqueous phase. As indicated in table 6, waters in contact with condensates A and C in the sample suite would contain *p*-cresol concentrations greater than the maximum limit target of $1\,\mu g\,g^{-1}$ imposed in the scenario described earlier and would require additional processing to reduce concentrations before they could be discharged to sea. Bennett and Larter [3] showed that the partition coefficient is influenced by temperature and salinity; a reduction in the oil–water separator temperature combined with an increase in the brine salinity would help to reduce the concentration of *p*-cresol in the production waters from these oils.

The data illustrate the importance of using relative response factors whenever possible in order to provide accurate quantitative data. In the case of phenols, described

here, quantification may have significant economic and planning implications as regards offshore petroleum production and processing installations. There may also be environmental considerations, in that inventories of toxic compounds discharged to the sea may require revision if a suitable relative response factor correction was not used in the calculation of concentration data.

4. Conclusions

The concentrations of C_0–C_3 alkylphenols in crude oils have been determined using the GCMS response in the molecular ion and fragmentation ion chromatograms both with and without individual relative response factor correction. The concentration of a number of phenols differs significantly according to which method of calculation is used. The study highlights the need for individual response factor correction to be used if accurate concentrations are to be determined. In the absence of authentic standard compounds and individual RRF correction, quantification may be significantly less accurate.

The ability to produce accurate phenol concentration data may have commercial and environmental implications. This is illustrated by the quantification of phenol in a North Sea crude oil, where the more accurate, lower value obtained using RRF correction may reduce the need for treatment of discharge waters. The accurate determination of phenol concentrations in oils allows the requirement and specifications for processing plant for the removal of phenols from production water to be more precisely identified prior to production. In environmental monitoring programmes connected with offshore oil production, the accurate determination of phenol concentrations can provide more reliable inventories of the amounts of these toxic compounds entering the sea. In this context, inventories of phenols based on concentration data which have not been appropriately corrected may require revision.

The content of the NSO fraction in oils is an important property controlling the partition distribution of phenols between oil and water. Production waters from petroleum reservoirs containing condensates with low NSO contents and high phenol contents are likely to be more problematic as regards treatment and disposal.

Acknowledgements

We are grateful to the European Commission for funding the Adonis project (Advanced determination of drainage patterns and unswept oil from natural oil components) through grant number OG/277/98/HE/UK/NO/FR. We also thank Unocal, Norsk Hydro and Statoil for generously providing oil samples for analysis. The authors gratefully acknowledge Mr Paul Donohoe (Newcastle) for GCMS analysis of the samples, and Dr Dennis Jiang (Calgary) for the Iatroscan analysis.

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