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Gas chromatography–mass spectrometry analysis of alkylphenols in produced water from offshore oil installations as pentafluorobenzoate derivatives

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Abstract

A simple, highly selective and sensitive method for the determination of 14 representative alkylphenols from phenol (C_0) to nonylphenol (C_9) in produced water is described. Solid-phase extraction (SPE) by anion-exchange sorbent is used to extract alkylphenols from produced water. The samples are then derivatised by pentafluorobenzoyl chloride and analysed on GC–MS (negative ion chemical ionisation, NCI). The derivatisation procedure has been validated by means of two-level factorial design (2^{7-4}) experiments. Quantification is done with isotope dilution of five internal standards of different alkyl chain length. The detection limits were at low ng/l levels. A comparison with GC–MS analysis of non-derivatised alkylphenol samples revealed the advantage of derivatisation as described in the method.

Keywords: Alkylphenols; GC–MS (NCI); Pentafluorobenzoyl chloride; Produced water; Solid-phase extraction

1. Introduction

Alkylphenols are commonly found in produced water released from offshore oil installations into the marine environment. Due to their solubility in both polar and nonpolar solvents they are highly mobile in aquatic systems, can enter organisms and penetrate lipid membranes. Many alkylphenols are toxic and some of them are suspected endocrine disruptors; earlier work shows that alkylphenols, due to their oestrogen-like structure, may have a considerable effect on the ability of fish to reproduce [1–6]. Almost all research in this field has focused on two long-chained alkylphenols, octyl- and nonylphenol, which are degradation products of alkylphenol ethoxylates (APE), one of the world's most widely used non-ionic surfactants [1].

Produced water is defined as the water that comes up with oil and gas from sea bed reservoirs, separated on the platform from the oil and discharged into the sea. Produced water contains various toxic compounds of natural origin, such as metals, alkylphenols and polycyclic aromatic hydrocarbons (PAH). The contents of these compounds in produced water are relatively low; however, the large volumes of produced water discharged into the ocean result in high total amounts of the compounds discharged. Thus, in 2001 the discharges onto the Norwegian continental shelf constituted 116 million m^3 of produced water containing more than 323 tons of alkylphenols (about 90% of this being the lighter C_1–C_3 phenols) [7,8]. This amount of environmentally dangerous compounds discharged into the sea makes produced water analysis highly relevant and will remain important for years to come since the discharges of produced water into the sea in Norway is a continuous process which is now on the increase [9].

For the purposes of qualitative and quantitative analysis of produced water for alkylphenol contents, it is crucial to have a method that allows detecting and quantifying minute amounts of analyte. The aqueous solubility of alkylphenols

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varies greatly, decreasing with the increase of the alkyl chain length from 82,000 mg/l for phenol to 12.6 mg/l for octylphenol and 5.4 mg/l for nonylphenol at 20 °C and to as low as 4.6 mg/l for nonylphenol at 2 °C [10,11]. The solubility strongly decreases with increasing salinities, easily reaching background levels when traditional analytical methods are used [12]. Produced water has been shown to have little deviation from seawater with respect to salinity [13]. There are not much empirical data on concentrations of alkylphenols in the North Sea around the offshore installations; phenol and lighter alkylphenols (C_1–C_4) were found at the concentrations of 486 and 140 ng/l, respectively [14].

Despite minute concentrations, the components of produced water may still have considerable toxic effects. The phenolic fraction has been identified as one of the main sources of produced water toxicity [13]. Due to rapid dilution of produced water upon discharge into the sea its acute toxic effects on the environment are considered as not severe. However, chronic ecotoxicological effects and long-term problems may arise since for these the "No observed effects concentration" (NOEC) is some 1000 times less than that for acute effects, and may be achieved only at several hundred metres from the platform [15]. Thus, 4-heptylphenol (4-HP) has been found to be acutely toxic to juvenile Atlantic cod (*Gadus morhua*) in concentrations as low as 400 μg/l [16]. This concentration is still higher than what is normally found in produced water, but 4-HP was shown to accumulate in tissues of cod to concentrations far higher than the concentration in seawater [16]. Some studies indicate the possibility of long-chained alkylphenol concentrations as low as 0.032 μg/l to have a significant effect on cod (*G. morhua*) [2].

Of the great variety of chromatographic and other techniques employed for the purpose of analysing water for alkylphenol contents [17–20], gas chromatography–mass spectrometry (GC–MS) is preferable due to its high separation ability and low detection limits. GC–MS analysis is normally preceded by several purification and preparation steps. Since produced water is a complicated mixture of organic compounds and larger suspended particles, filtration is often the first step in the procedure [21]. It is then followed by extraction of alkylphenols, solid-phase extraction (SPE) being preferred to liquid–liquid extraction as the less time consuming one and requiring smaller volumes of organic solvents [21–23]. Alkylphenols can be then analysed by GC–MS without derivatisation [24–29] or as less polar derivatives. Of all the reported derivatisation procedures, such as alkylation [30], silylation [31], acylation [32], preparation of 3,5-bis(trifluoromethyl)benzyl [33] or pentafluorobenzyl ethers [34,35], and others, the conversion to perfluorobenzoyl derivatives [13,36–40] seems to be the more efficient one [13].

Among the available SPE sorbents, the one employed in Oasis® HLB cartridge, [poly(divinylbenzen-co-*N*-vinylpyrrolidone)], has been shown to possess better extraction ability than many other typically used ones (e.g. C_{18}) [41–43]. This is due to its better wetting characteristics and extra possibilities for interactions with functional groups, retaining a wide spectrum of polar and nonpolar compounds. Thus, 46–78% recoveries of 4-nonylphenol were achieved with 10 ng/l detection limit using this SPE cartridge [41]. A somewhat more complicated procedure than the one described above, used for measuring the contents of nonylphenol, octylphenol and bisphenol A in aquifers, provides the recovery of 84–95% and the detection limit of 1–30 ng/l [44]. A procedure similar in general to our method but using a different SPE cartridge and much larger sample volumes, up to 5 l water, resulted in even lower limits of detection (LoDs), down to 50 pg/l for river water [45]; however, these LoD values were set as three-fold height of noise. Other recent works report higher detection limits for phenolic compounds, depending on the technique used [12,46,47]. This sensitivity may be crucial for produced water analyses due to low concentrations of the analytes present.

In this work, we report a method of produced water analysis based on SPE of alkylphenols and GC–MS of their pentafluorobenzoate derivatives. The method employs an SPE sorbent, Oasis MAX, similar to the more common HLB sorbent except for containing quaternary amine groups, thus acquiring a strong anion-exchange ability [48]. This makes these cartridges able to extract both acidic compounds like phenols and neutral and basic compounds like PAH. A weak solution of formic acid in methanol is used for elution of acidic (e.g. phenolic) compounds while pure methanol can be used to elute the neutral and basic compounds. The extraction properties of Oasis MAX sorbent as compared to other, more traditional sorbent materials like C_{18}, Oasis HLB, etc., have been studied earlier [49,50] although not for alkylphenols, the MAX sorbent being a relatively new product on the market.

To adjust and validate the derivatisation part of the method, two different procedures for pentafluorobenzoyl derivatisation were tested, a one-phase system in toluene with pyridine as catalyst [37], and a two-phase system with buffer ($NaOH$–$NaHCO_3$) and hexane [36]. Two factorial experimental designs were used to find the optimal conditions for the derivatisation procedures and to study how different test parameters influenced the efficiency and ruggedness of the procedures. The seven test parameters selected for the factorial experimental design are varied around the values described by Renberg [37] and McCallum and Armstrong [36], respectively: the amount of derivatisation agent, the pH in the two-phase method or amount of pyridine in the one-phase method, the time of shaking the samples after adding the derivatisation agent, the time of hydrolysis of excess derivatisation agent, the effect of adding derivatisation agent before or after the catalytical base, the temperature, the amount of organic solvent when adding the derivatisation agent. A combination of two saturated 2^{7-4} designs were used, giving in 16 experiments the effects of all seven main factors and a combination of two-factor interaction effect. The theoretical background for this design was given by Box and Hunter [51].

2. Experimental

2.1. Chemicals and reagents

Pure standards (95–99.9%) of 17 alkylphenols and five deuterated alkylphenols were from Sigma–Aldrich (Oslo, Norway) and Chiron (Trondheim, Norway). Standard solutions were prepared in methanol. The derivatisation agent, pentafluorobenzoyl chloride (PFBC) was from Sigma–Aldrich. Solvents [methanol, hexane, *tert*-butyl methyl ether (MTBE), formic acid, toluene] were analytical grade from Merck (Oslo, Norway). Sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$) and hydrochloric acid (HCl) were from Merck. The water used was purified with Nanopure Ultrapure Water Systems (USA). Samples of produced water were from the Oseberg C offshore oil installation in the Norwegian sector of the North Sea.

2.2. Instrumentation

The instrumentation used in these experiments is described in Table 1.

2.3. Experimental procedure

2.3.1. Validation of derivatisation procedure

The experimental design and the principal component analysis (PCA) were carried out and evaluated using Sirius 6.0 software package (Pattern Recognition Systems, Bergen, Norway). Table 2 shows the test parameters examined. Table 3 gives the experimental set-up and the results (% recovery data) for three selected alkylphenols (phenol, 2,6-dimethylphenol and 4-*n*-octylphenol).

The derivatisation was carried out in 15 ml test tubes with Teflon-lined screw caps. Standard solution of alkylphenols (100 μl, concentration from 478 to 1195 ng/ml in toluene) was transferred with Hamilton syringe to the test tube, and 2 ml of 1 M $NaHCO_3$ and 1 ml of 1 M NaOH added. After 1/2 min shaking (Retsch mixer), 2 ml of hexane and 50 μl of pentafluorobenzoyl chloride (10% solution in toluene) were added, and the test tube shaken for 1 min. The samples were left for 1/2 h at room temperature before addition of 8 ml of 1 M NaOH (for hydrolysis of excess derivatisation agent), and then kept overnight at +4 °C. The derivatives were extracted with 2 × 2 ml of hexane and 250 μl of the injection standard (821 ng/ml of the pentafluorobenzoate derivative of 4-*n*-nonylphenol) used for quantification was added. The final concentrations of the pentafluorobenzoate derivatives injected on the GC–electron-capture detection (ECD) system varied between 12 and 50 pg/μl. The one-phase work-up procedure was quite similar to the two-phase procedure, except pyridine replacing the aqueous sodium carbonate buffer.

It is only the pentafluorobenzoyl group of the alkylphenol derivative that contributes to the electron-capture detector response. Because of this the calculated amounts are corrected for the difference in molecular weight of the target phenols and 4-*n*-nonylphenol (internal standard). The amount of target phenols are calculated from Eq. (1):

$$\mathrm{Am(X)} = A(x)/A(\mathrm{NP}) \times \mathrm{Am(NP)}/M_\mathrm{r}(\mathrm{NP}) \times M_\mathrm{r}(\mathrm{X}) \quad (1)$$

Table 1
Chromatography parameters

Gas chromatograph	HP 5890-2 with electron-capture detector (GC–ECD) (Agilent)
Column	CP-sil 5 CB 50 m × 0.25 mm i.d., 0.25 μm film thickness (Chrompack)
Injection	HP-7673A autosampler; 1 μl, pulsed splitless (2 min), 280 °C
Oven temperature program	90 °C (2 min)–30 °C/min–155 °C (0 min)–2 °C/min–185 °C (0 min)–7 °C/min–290 °C (5 min)
Carrier gas	Helium, 1.0 ml/min
Detector temperature	320 °C
Detector gas	Nitrogen 60 ml/min
GC–MS system 1	Micromass Autospec equipped with HP 6890
Column	DB5 MS, 50 m × 0.25 mm i.d., 0.25 μm film thickness (J&W)
Injection	HP-7673A autosampler; 1 μl, splitless (2 min), 250 °C
Oven temperature program	40 °C (2 min)–10 °C/min–110 °C (0 min)–3 °C/min–250 °C (0 min)–10 °C/min–300 °C (10 min)
Carrier gas	Helium, 1.0 ml/min
MS temperatures	275 °C (interface), 200 °C (ion-source)
Ionisation	Electron impact (EI) at 70 eV
GC–MS system 2	HP 6890 with 5973 MSD (Agilent)
Column	DB5 MS, 50 m × 0.25 mm i.d., 0.25 μm film thickness (J&W)
Injection	HP-7673A autosampler; 1 μl, pulsed splitless (50 psi 2 min; psi = 6894.76 Pa, 250 °C
Oven temperature program	40 °C (2 min)–10 °C/min–110 °C (0 min)–3 °C/min–250 °C (0 min)–10 °C/min–300 °C (10 min)
Carrier gas	Helium, 1.0 ml/min
MS temperatures	325 °C (interface), 150 °C (ion-source), 150 °C (quadropole)
Chemical ionisation	Methane (40% of maximal HP default value)

Table 2
Experimental variables selected for 2^{7-4} factorial designs

	Factor	1	0	−1
X1	Amount of derivatisation agent (μl)	50	35	20
X2	pH[a,b]	13.2	9.9	9.2
X3	Shaking (min)	2	1	0
X4	Hydrolysis time (h)	2	12	24
X5	Adding derivatisation agent before/after buffer	Before	After	After
X6	Temperature (1 h) °C	60	45	25
X7	Adding derivatisation agent before/after hexane	Before	After	After
X2	pH ≈ amount of pyridine	40 μl		10 μl

[a] For pyridine derivatisation in toluene.
[b] The different pH values were achieved by 1 M buffer of $NaHCO_3$–Na_2CO_3 (pH 9.2), NaOH–$NaHCO_3$ (pH 9.9) and pure 1 M NaOH (pH 13.2).

Table 3
Design matrix for the two 2^{7-4} factorial designs (A and B) and four repeated centre points (C)

	X1	X2	X3	X4	X5	X6	X7	Recovery (%)		
								Phenol	2,6-Dimethylphenol	4-*n*-Octylphenol
A1	−1	−1	−1	1	1	1	−1	40	2	103
A2	1	−1	−1	−1	−1	1	1	84	9	103
A3	−1	1	−1	−1	1	−1	1	48	5	103
A4	1	1	−1	1	−1	−1	−1	72	6	102
A5	−1	−1	1	1	−1	−1	1	42	2	101
A6	1	−1	1	−1	1	−1	−1	69	4	102
A7	−1	1	1	−1	−1	1	−1	102	3	99
A8	1	1	1	1	1	1	1	106	5	100
B1	−1	−1	−1	−1	−1	−1	−1	29	3	99
B2	1	−1	−1	1	1	−1	1	67	6	103
B3	−1	1	−1	1	−1	1	1	63	2	99
B4	1	1	−1	−1	1	1	−1	84	4	101
B5	−1	−1	1	−1	1	1	1	44	2	101
B6	1	−1	1	1	−1	1	−1	77	4	102
B7	−1	1	1	1	1	−1	−1	95	5	101
B8	1	1	1	−1	−1	−1	1	104	4	104
C1	0	0	0	0	−1	0	−1	96	3	102
C2	0	0	0	0	−1	0	−1	98	3	101
C3	0	0	0	0	−1	0	−1	96	3	99
C4	0	0	0	0	−1	0	−1	98	3	100

Recovery values are given for the two-phase experiment for phenol, 2,6-dimethylphenol and 4-*n*-octylphenol.

where *A* is the area of GC–ECD peaks, Am the amount in ng, M_r the molecular weight, NP is 4-*n*-nonylphenol and X is the target alkylphenol.

It was only in this part of the study that the target compounds were derivatised first and the internal standard was derivatised separately and added afterwards before the analysis. This was necessary to be able to separate derivatisation effects on the individual alkylphenols from similar effects on the internal standard. Normally, the internal standard(s) (alkylphenols) would be added before the work-up of the samples and be derivatised together with the target compounds.

2.3.2. Validation of the whole analytical method

Produced water samples from Oseberg C were taken on 03.03.2003. HCl was added for stabilisation immediately and the samples were kept for 10 days at +4 °C until the analyses were carried out. The complete analysis consisted of the following steps:

(I) Filtration. Produced water sample (100 ml) was spiked with 100 μl of alkylphenol standard solution. The sample was filtered by ca. 30 ml/min vacuum suction through a filter into a 100 ml separatory funnel. GF/F Whatman glass fibre filters with pore diameter 0.7 μm were used for filtration. The contents of the filter were extracted with 10 ml dichloromethane (DCM). Alkylphenol internal standard solution (SIS) (50 μl) was added to the filter extract and to the separatory funnel containing the water sample. Two drops of HCl were added to the separatory funnel to achieve the pH of ∼2 for breaking the possible interactions between weakly acidic analytes (alkylphenols) and matrix organic compounds.

(II) Solid-phase extraction with Oasis® MAX extraction cartridges. MAX extraction cartridge (6 ml, 150 mg) was connected to the vacuum flask and conditioned with 6 ml of MeOH–MTBE mixture (1:9, v/v) under vacuum to solvate the sorbent. The cartridge was washed with 6 ml distilled water to equilibrate the sorbent. The sample was loaded on the cartridge by a slow (ca. 10 ml/min) suction of the 100 ml of produced water from the separatory funnel through the cartridge. The empty separatory funnel with all the auxiliary glass equipment was washed with 5% (1.33 M) solution of formic acid in methanol. This is necessary to avoid significant loss of alkylphenols adsorbed to glass walls of the funnel. The used solvent was collected for further use. The cartridge was then washed with 10 ml 30% KOH to remove natural organic matter interference and to lock acidic analytes to sorbent by ion-exchange mechanism. The sample was eluted with 15 ml of 5% (1.33 M) formic acid in methanol, including the solvent used for washing the separatory funnel. The solvent was then evaporated by a gentle N_2 flow at 39 °C on a Turbovap LV evaporator (Zymark, USA) to sample volumes of ca. 1 ml.

(III) Derivatisation. The procedure was generally as described in Section 2.3.1 for the two-phase system, except that 100 μl of 30% PFBC solution in toluene were used for derivatising alkylphenols and that after derivatisation was complete, samples were diluted 100 times before GC–MS analysis. All this was necessary

due to high concentrations of phenol and some lighter alkylphenols in produced water, often at ppm level, i.e. above the linearity range of the detector system of the GC–MS. Both the diluted and the concentrated samples were analysed so that data for both short-chain and long-chain alkylphenols could be obtained despite the large span of concentrations in the actual produced water sample. During drivatisation, the samples were covered with aluminium foil instead of ordinary plastic caps due to alkylphenol additives (see Section 3). Recovery internal standard (RIS; 37.89 ng) (100 μl), pentafluorobenzophenone, was added to all the samples.

(IV) Instrumental analysis. Derivatised samples were analysed on GC–MS with negative ion chemical ionisation (NCI) ion source detector. After that the ion source was changed to EI and non-derivatised samples were analysed with both selected-ion monitoring (SIM) and full scan techniques.

Non-derivatised samples, spiked and non-spiked with standard alkylphenol solution, were divided into two parts after elution from SPE cartridge and volume reduction to ca. 750 μl. Two hundred and fifty microliters was taken directly to GC–MS [electron impact ionisation (EI)] analysis and the remaining ca. 500 μl, with volume measured, were derivatised according to the derivatisation procedure described above.

For method validation, 100 ml of produced water or distilled water samples were spiked with 100 μl of standard alkylphenol solution (Stan AP) containing 17 alkylphenols, and 50 μl of internal standard solution (SIS AP) containing five deuterated alkylphenols. Due to large differences, up to 3 orders of magnitude, between the concentrations of various alkylphenols in produced water (depending on their water solubility), the alkylphenols in Stan AP and SIS AP were also taken in different concentrations. There were five replicates of each run. Chromatographic data for the tested alkylphenols is shown in Table 4.

Table 4
Chromatographic data for the tested alkylphenols: masses of the SIM ions of the derivatised alkylphenols (M_r) and corresponding retention times (t_R)

AP	M_r	t_R (min) (±0.05 min)
Phenol-d5	293	30.48
Phenol	288	30.58
p-Cresol-d8	309	34.57
p-Cresol	302	34.74
4-Ethylphenol-d8	325	37.27
2,4-Dimethylphenol	316	37.38
4-Ethylphenol	316	38.30
4-*n*-Propylphenol-d12	341	41.37
2,3,5-Trimethylphenol	330	41.58
2,4,6-Trimethylphenol	330	40.16
4-Isopropylphenol	330	40.45
2,3,6-Trimethylphenol	330	41.25
4-*tert*-Butylphenol	344	42.88
4-Isopropyl-3-methylphenol	344	44.07
2-*tert*-Butyl-4-methylphenol	358	42.93
4-*n*-Pentylphenol	358	48.58
4-*n*-Nonylphenol-d4	418	59.59
4-*n*-Hexylphenol	372	51.86
4-*n*-Heptylphenol	386	55.01
4-*tert*-Octylphenol	400	53.05
4-*n*-Octylphenol	400	57.68
4-*n*-Nonylphenol	414	59.62

3. Results and discussion

3.1. Validation of the derivatisation step

Fig. 1 gives the average recovery data for the centre points (C) of the two-phase system, i.e. the procedure found to be optimal, from the factorial experimental design study. The recovery for the two-phase experiment for three representative alkylphenols is also shown in Table 3. It was found that both procedures (one-phase or two-phase derivatisation systems) gave quite similar recoveries. However, using the one-phase method led to a large number of unknown peaks in the GC–ECD chromatogram, increasing the recovery of 4-*n*-ethylphenol and 4-*n*-hexylphenol because of interference from the coeluting peaks. The unknown peaks probably originate from impurities in the pyridine. No further effort was taken to identify the compounds causing the problem. The two-phase derivatisation system was therefore selected as the best method for our purpose, and later work described in this paper is performed using this technique.

The results of the factorial experimental design studies were evaluated by principal component analysis (PCA). It has been found that the *ortho*-substituted (*o*-cresol, 2-ethylphenol, 2,6-dimethylphenol and 2,3,6-trimethylphenol) and the smallest and most water-soluble phenols (phenol and cresols) are most affected by variation in the test parameters. The long-chain *para*-substituted phenols are not significantly affected by the variation in the test parameters. This is also evident from Fig. 1 and Table 3. There are big differences between sample recoveries for two of the compounds shown in Table 3: recoveries of phenol varied between 29 and 106%

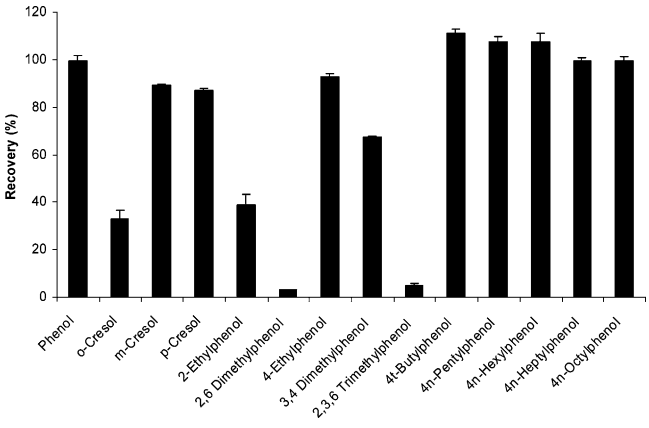

Fig. 1. The average recovery for the centre points (C) of the two-phase system (the optimal procedure). Mean value ± S.D. (n = 4).

(R.S.D. = 36%) and 2,6-dimethylphenol between 2 and 9% (R.S.D. = 43%). However, for 4-*n*-octylphenol the recoveries varied between 99 and 104% with a very low R.S.D. of only 1.4% for the total of 16 samples in the experiment, a most satisfactory reproducibility for this kind of analysis.

None of the variations of the seven parameters tested had any significant influence on the recovery of the long-chain *para*-substituted alkylphenols. However, high amount of derivatisation agent (X_1), high pH (X_2) and long shaking time (X_3) have a positive effect on the recovery of the more water-soluble compounds (phenol and the cresols) and the *ortho*-substituted phenols. Two-factor interactions between these three parameters were also significant for many of the more water-soluble compounds.

The central points (Table 2) gave the best recovery (Table 3, Fig. 1) of most of the alkylphenols tested. These values for the corresponding parameters were therefore selected as the best experimental conditions for the two-phase derivatisation procedure, described in Section 2.3.1.

The time of hydrolysis by 1 M NaOH did not affect the recovery of the tested alkylphenols, indicating that the pentafluorobenzoate derivatives are relatively stable. This was also confirmed by storing a sample (hexane extract) at room temperature for 1 month without detecting any sign of degradations of the alkylphenol derivatives. A sufficiently long hydrolysis time was important to remove excess derivatisation agent, to avoid short lifetime of the glass liner and the GC column, which would gradually result in lower chromatographic resolution. However, it is possible to shorten the time of hydrolysis, an alternative being to shake the samples violently for 1 h.

The extractive two-phase derivatisation is more specific to aromatic hydroxyl (phenolic) groups than the one-phase derivatisation, since it does not attack aliphatic alcohols. Xiao et al. [39] used pentafluorobenzoyl derivatisation in analysing estrogens in human urine and river water. They used a one-phase method for the derivatisation of estradiol with trietylamine as catalyst, and both hydroxyl groups in the molecule were derivated. When the two-phase derivatisation method is used, only the phenolic hydroxyl group in estradiol is esterified, while the non-aromatic hydroxyl group remains intact [37]. This is believed to be a result of shorter lifetime of the acid chloride in an aquatic environment compared with organic solvent and organic base as catalyst.

3.2. Optimalisation of the analytical method

The solid-phase extraction method described above was developed on the basis of methods given by Waters [48] and Kvistad et al. [52]. The procedure given in these sources was modified and further improved for produced water analysis.

The acidic elution agent, 5% formic acid in methanol, was necessary for eluting alkylphenols adsorbed by the anion-exchange groups of the MAX cartridge matrix. Elution with 15 ml 5% HCOOH in MeOH allows recovery of ca. 100% analyte. Samples of up to 2 μg/ml were analysed and no breakthrough of the extraction cartridge was observed, i.e. no alkylphenols were found in the aqueous phase. Increasing the content of formic acid to 10% did not result in an increase of elution efficiency; however, elution by pure methanol without formic acid resulted in up to 45% lower recovery of alkylphenols than with 5% formic acid.

The concentration of the derivatisation agent, PFBC, was adjusted for the high amounts of analytes to be derivatised. Thirty percent solution of PFBC in toluene was found to give highest efficiency of derivatisation, not further improved by higher amounts of PFBC. However, blank tests (see below) revealed presence of *p*-, *m*- and *o*-cresol in commercially obtained toluene. It is therefore necessary to use another suitable solvent, like *iso*-octane, for PFBC solution.

The produced water samples obtained from Oseberg were relatively clean, i.e. with low concentrations of sulphur-containing hydrocarbons and other impurities that could complicate the chromatographic analysis of alkylphenols. It was therefore enough to purify the samples by SPE without additional purification by gel-permeation chromatography, GPC. The samples subjected to GPC following SPE did not show any difference in the chromatographic image. It may however be necessary to use GPC for purification of produced water samples when the latter contain high concentrations of impurities, disturbing the analysis of alkylphenols [53].

3.3. Validation of the analytical method

An example of experimentally measured amounts as compared to the spiked amount with recoveries for eight alkylphenols is given in Table 5.

The efficiency of the method as represented by recovery is good for most compounds, the recovery being as a rule close to 100%, although lower for some of the long-chain alkylphenols which were only taken to the validation experiment at low concentration levels (down to 15 pg/ml; cf. Table 5). However, the method does not give high recoveries for most of the *ortho*-substituted alkylphenols. This is due to steric hindrance of the *ortho*-substituents causing low derivatisation yield as explained in Section 3.1. In particular, di-*ortho*-substituted alkylphenols or those having a bulky substituent in *ortho*-position exhibited low recoveries. Therefore, the method does not allow satisfactory results for the analysis of *ortho*-substituted alkylphenols. However, produced water samples contain a variety of alkylphenol isomers and any detailed analysis of *para*- and *meta*-substituted alkylphenols allows to make an estimate of overall alkylphenol contents in the sample.

Amount of alkylphenols found in filter extracts, in % of total amount, and R.S.D. values for filtrate and filter extract yields (relative to SIS), in %, are given in Table 6.

As shown in Table 6, the filtration affects the procedure very little, allowing ca. 97% of the analytes through (slightly less for long-chain alkylphenols which were taken to the validation experiment in low concentrations).

Table 5
The results of the method validation experiment for some of the derivatised alkylphenols

AP	Spiked amount (μg)	Measured amount (μg)	R.S.D. (%)	Recovery (%)
Phenol	220.02	200.7 ± 4.09	2.0	91
	22.00	20.04 ± 0.71	3.5	93
	2.20	1.85 ± 0.11	5.7	84
p-Cresol	123.82	109.5 ± 3.79	3.5	88
	12.38	12.78 ± 0.85	6.7	103
	1.24	1.20 ± 0.09	7.6	97
2,4-Dimethylphenol	59.14	50.7 ± 2.69	5.3	86
	5.91	5.04 ± 0.71	14.1	85
	0.59	0.51 ± 0.04	7.6	86
2,3,6-Trimethylphenol	10.06	5.46 ± 0.34	6.2	54
	1.01	0.51 ± 0.13	25.6	51
	0.10	0.067 ± 0.01	8.5	67
4-Isopropyl-3-methylphenol	0.91	0.80 ± 0.03	3.3	89
	0.09	0.084 ± 0.001	1.7	92
	0.01	0.009 ± 0.0002	2.5	99
4-*n*-Pentylphenol	1.11	0.91 ± 0.05	5.3	82
	0.11	0.084 ± 0.005	6.1	76
	0.01	0.011 ± 0.0003	2.7	95
4-*n*-Heptylphenol	0.170	0.170 ± 0.014	8.4	100
	0.017	0.013 ± 0.003	23.4	78
	0.002	0.0014 ± 0.0003	25.3	80
4-*n*-Octylphenol	0.152	0.107 ± 0.007	6.6	70
	0.015	0.012 ± 0.002	18.7	78
	0.001	0.0012 ± 0.0003	28.3	79

Table 6
The efficiency of filtration of produced water[a]

Compound	Amount of AP in filter extract (%)	Filter extract R.S.D. (%)	Filtrate R.S.D. (%)
Phenol	2.3	12.1	2.0
p-Cresol	3.1	24.9	3.5
2,4-Dimethylphenol	3.2	37.8	5.3
4-Ethylphenol	4.7	30.4	4.7
4-Isopropylphenol	2.3	28.4	4.5
2,3,5-Trimethylphenol	1.9	29.6	1.6
4-*tert*-Butylphenol	4.0	36.9	3.8
4-Isopropyl-3-methylphenol	2.5	22.1	3.3
4-*n*-Pentylphenol	7.3	30.7	5.3
4-*n*-Hexylphenol	14.5	19.3	8.0
4-*tert*-Octylphenol	20.6	23.5	8.4
4-*n*-Heptylphenol	10.0	25.4	8.4
4-*n*-Octylphenol	13.5	23.1	6.6
4-*n*-Nonylphenol	14.1	18.0	12.0
Mean values	7.43	25.87	5.53

[a] Values for di-*ortho*-alkylphenols and *tert*-*ortho*-alkylphenols are not shown.

Reproducibility of the results is expressed by residual standard deviation, R.S.D., shown in Tables 5 and 6 above. R.S.D. is high for filter extracts due to low concentrations of analytes but is as a rule below 10% for the filtrates. R.S.D. is relatively high for *ortho*-substituted compounds; the mean R.S.D. value for the filtrate data excluding *ortho*-substituted alkylphenols is only 5.9%. Long-chain alkylphenols give slightly higher R.S.D. values due to rather low concentrations.

Response factors (RF) were calculated relative to SIS and to RIS from the current experimental data as well as from independent series of measurements several times during the experiment, particularly when any changes were made to the chromatographic equipment, such as change of GC column. The RF values were first determined from a linearity series of measurements done for standard solution of alkylphenols at different concentrations. RF were also determined for standard solutions of alkylphenols made independently by two different persons. The resulting RF were mostly within 10% R.S.D. between the two sets of data.

Lowest limits of detection (LoD: $Y = 3$ S.D.) and quantification (LoQ: $Y = 10$ S.D.) for the tested alkylphenols, as calculated from spiked produced water samples at the lowest concentration level used in the validation experiment, are given in Table 7.

The chromatographic detection limit for SIM NCI GC–MS analysis was ∼0.05 pg/μl.

Blank samples exhibited a stable profile with largest peaks for phenol and the cresols, as indicated by LoD and LoQ values; cf. Table 7. A number of other alkylphenols, notably 4-*tert*-butylphenol and various nonylphenol isomers, were also found in blank. A possible source for cresol isomers contamination was determined as commercial toluene used as solvent for derivatisation reagent, PFBC. The commercially obtained toluene, 99% analytical grade, was found to contain significant amounts of *o*-, *p*- and possibly *m*-cresol. It is therefore recommended to avoid the use of toluene for alkylphenol analysis using other inert solvents like

Table 7
LoD and LoQ values for the tested alkylphenols

Compound	LoD (μg/l)	LoQ (μg/l)
Phenol	315.39	1051.30
p-Cresol	272.50	908.33
2,4-Dimethylphenol	116.49	388.30
4-Ethylphenol	114.00	380.01
2,4,6-Trimethylphenol	3.91	13.05
4-Isopropylphenol	5.82	19.38
2,3,6-Trimethylphenol	17.16	57.20
2,3,5-Trimethylphenol	6.70	22.34
4-*tert*-Butylphenol	2.97	9.91
4-Isopropyl-3-methylphenol	0.67	2.25
2-*tert*-Butyl-4-methylphenol	2.83	9.44
4-*n*-Pentylphenol	0.85	2.84
4-*n*-Hexylphenol	0.77	2.58
4-*n*-Heptylphenol	0.87	2.90
4-*tert*-Octylphenol	1.03	3.43
4-*n*-Octylphenol	1.03	3.42
4-*n*-Nonylphenol	1.02	3.40

iso-octane. The nonylphenol contaminants found in blank in small amounts are thought to appear from several possible sources since many plastics, such as the one used in caps for glass tubes, contain nonylphenols [53]. Furthermore, it has recently been shown that small amounts of nonylphenol may be found in room air in the laboratory [54]. The contaminant found in largest quantities in blank samples, phenol, is still far below significant levels of concentration since the concentration of phenol in actual produced water samples is several orders of magnitude higher.

The commercially acquired alkylphenol standards were checked for purity. Of the 41 alkylphenol tested, only two are as pure as 99.9% while others have a lower purity, as low as 95% for 2,3,6-trimethylphenol. Various alkylphenols may be present among the impurities. Their presence could alter quantification results for standard alkylphenol solutions, in which different alkylphenols are taken in different concentrations to imitate actual produced water samples. Sixteen alkylphenols were chosen for this experiment and weighed in from commercial stock samples separately. Alkylphenol solutions of ca. 12.5 μg/ml in methanol were prepared, the concentration being the highest possible for using on the GC–MS apparatus without risk of damaging the equipment. The samples were then derivatised as usual. Non-derivatised samples were run on GC–flame ionisation detection (FID) while derivatised ones were run on GC–MS with CI-ion source. GC–FID gave chromatograms of good resolution with a large number of non-identified impurities mostly in low concentrations. No alkylphenols could be detected among the impurity peaks. The more sensitive CI GC–MS, however, gave chromatograms with a number of impurity peaks that were identified as alkylphenols. The concentration for those above blank values varied in the range of 0.01–5% of the amount of the title alkylphenol. The high amounts of some impurities, higher than indicated by the manufacturer, e.g. 1.6% *m*-cresol found in 99% *p*-cresol, can be explained by the lack of response factors for these measurements, since no internal standard could be used. The presence of alkylphenol impurities in alkylphenols used for standard solutions may slightly affect the final recovery values for some of the analysed compounds.

An example of the results of a non-spiked produced water sample analysis is given in Table 8. Only the compounds for which standards had been obtained were identified. The quantification of some of the *ortho*-substituted compounds has been problematic (see above) and the corresponding values are not shown.

A SIM chromatogram of a typical produced water sample is shown in Fig. 2.

3.4. The efficiency of the analytical method for derivatised and non-derivatised alkylphenols

The comparison of the results for some derivatised and non-derivatised alkylphenols is presented in Table 9.

As was pointed out in Section 3.1, the analysis of non-derivatised compounds has several advantages as compared to the method that includes derivatisation. The derivatisation procedure requires a considerable amount of time; samples are kept overnight before GC–MS analysis can be carried out. Furthermore, due to steric hindrance in *ortho*-substituted alkylphenols they are not derivatised efficiently and the recovery of such derivates is lower than for *meta*- and *para*-substituted ones, particularly if the *ortho*-substituent is a bulky one, e.g. 2-*tert*-butylphenol.

Table 8
The results of analysis of a typical sample of produced water from Oseberg C[a]

Compound	Amount measured (μg/l)	R.S.D. (%)
Phenol	6661.8	1.6
o-Cresol	1207.3	5.6
m-Cresol	1799.5	0.4
p-Cresol	951.6	0.9
2-Ethylphenol	30.7	13.9
2,5-Dimethylphenol	109.1	12.7
2,4-Dimethylphenol	149.7	13.5
3-Ethylphenol	194.8	1.1
3,5-Dimethylphenol	232.1	1.8
4-Ethylphenol	62.7	3.7
2,3-Dimethylphenol	52.0	6.1
3,4-Dimethylphenol	129.0	0.6
3-Isopropylphenol	56.8	1.8
4-Isopropylphenol	165.6	0.6
3-*n*-Propylphenol	149.8	0.3
2,3,5-Trimethylphenol	12.6	8.7
4-*n*-Propylphenol	15.3	1.1
3-*tert*-Butylphenol	0.22	2.0
5-Isopropyl-3-methylphenol	22.1	2.7
4-*tert*-Butylphenol	1.07	1.2
4-*sec*-Butylphenol	20.8	0.9
4-Isopropyl-3-methylphenol	3.70	0.1
4-*n*-Butylphenol	2.78	3.9
4-(1,1-Dimethylpropyl)phenol	1.14	3.7
4-*n*-Pentylphenol	0.50	10.9
4-*tert*-Butyl-2-methylphenol	0.60	10.8
4-*n*-Hexylphenol	0.10	9.1
4-*n*-Heptylphenol	0.07	52.8
4-*tert*-Octylphenol	0.04	33.2
4-*n*-Octylphenol	0.02	51.9
4-*n*-Nonylphenol	0.03	60.7

[a] Values for di-*ortho*-alkylphenols and *ortho*-alkylphenols with bulky substituents are not shown.

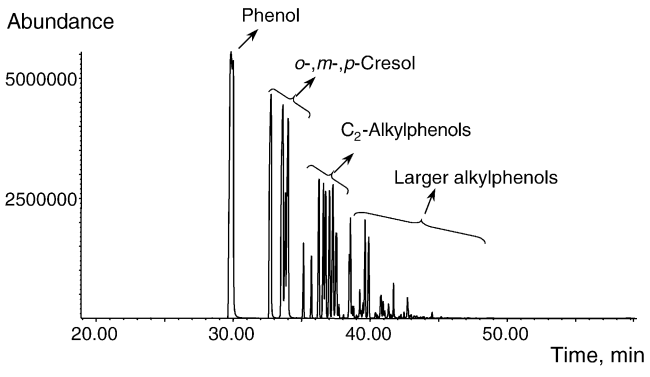

Fig. 2. Total ion spectrum of SIM GC of a typical produced water sample from Oseberg C.

Table 9
The efficiency of the analytical method for some derivatised and non-derivatised alkylphenols[a]

Compound	Amount spiked (μg/l)	Recovery relative to SIS (%)		R.S.D. (%)	
		Derivatised	Not derivatised	Derivatised	Not derivatised
Phenol	1766.00	95.1	121.0	1.3	5.2
o-Cresol	670.00	95.7	145.3	20.7	13.7
m-Cresol	1134.00	109.7	n/a	3.4	n/a
p-Cresol	1784.00	111.4	n/a	1.4	n/a
4-Ethylphenol	296.00	96.9	73.0	1.1	4.1
3,4-Dimethylphenol	380.00	80.6	177.7	0.6	1.1
3-Isopropylphenol	42.40	100.2	109.1	2.5	3.3
4-Isopropylphenol	34.20	87.5	n/a	4.0	n/a
3-*n*-Propylphenol	51.20	94.4	n/a	3.2	n/a
3-*tert*-Butylphenol	8.45	105.7	n/a	1.7	n/a
2,3,5-Trimethylphenol	32.20	87.0	n/a	13.2	n/a
4-*n*-Propylphenol	46.80	108.1	n/a	1.9	n/a
4-*tert*-Butylphenol	13.35	100.9	26.4	1.7	19.7
4-*sec*-Butylphenol	8.65	68.5	n/a	58.5	n/a
4-Isopropyl-3-methylphenol	17.10	102.3	n/a	2.7	n/a
4-*n*-butylphenol	10.95	121.7	70.2	2.0	12.2
4-(1,1-Dimethylpropyl)phenol	16.60	102.3	n/a	1.8	n/a
4-*n*-Pentylphenol	7.70	109.7	n/a	4.6	n/a
4-*n*-Hexylphenol	2.05	88.7	n/a	14.0	n/a
4-*tert*-Octylphenol	3.14	89.1	n/a	18.8	n/a
4-*n*-Heptylphenol	1.99	110.8	n/a	20.1	n/a
4-*n*-Octylphenol	1.70	97.9	n/a	19.6	n/a
4-*n*-Nonylphenol	1.14	76.6	n/a	10.8	n/a

[a] n/a: The peaks in the chromatogram were absent due to low sensitivity or could not be resolved.

However, both quantitatively (recovery) and qualitatively (reproducibility, R.S.D.), data obtained for non-derivatised compounds was of poor quality as compared to the results for derivatised compounds. Fig. 3A and B shows typical EI and NCI mass spectra of the derivatives of a selected alkylphenol (4-*n*-octylphenol). The detection limits and linearity of this compound for different detector systems are shown in Table 10.

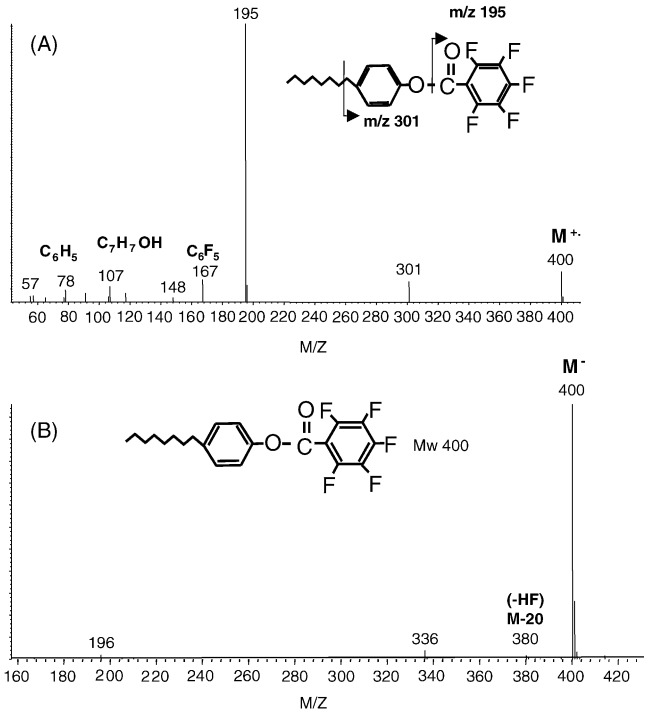

Fig. 3. Mass spectra of pentafluorobenzoate derivative of 4-*n*-octylphenol: (A) EI mass spectra; (B) NCI mass spectra.

Thus, selected-ion monitoring technique with negative ion CI ion source applied to derivatised alkylphenols gives approximately 1000 times better sensitivity than SIM with EI ion source applied to non-derivatised alkylphenols and about 3000 better sensitivity than the same with full scan monitoring. As a result, it is not possible to accurately detect C_5 and larger alkylphenols in produced water samples using non-derivatised compounds by the proposed method. Alternative methods allowing the analysis of non-derivatised long-chain alkylphenols include extraction by large quantities (up to 200 ml) of dichloromethane with rather poor recoveries [55].

The excellent chromatographic performance of the pentafluorobezoyl derivatives makes it possible to separate most of the smaller alkylphenol isomers. The derivatives show much better chromatographic resolution than the non-

Table 10
Linearity ranges for 4-*n*-octylphenol using different detector systems

	Concentration ranges (pg/μl)	Linearity (R^2)
Derivative		
GC–MS (NCI)	0.03–1221	0.9986
GC–MS (EI)	0.9–760	0.9906
GC–ECD	1.3–260	0.9981
Parent compound		
GC–MS (EI)	47–6064	0.9934

derivatised phenols do. Chromatographically the "active" hydrogen atom of the phenol group often results in tailing and poor resolution of the different isomers [56]. Another drawback of analysing free alkylphenols is that fragmentation patterns in mass spectrometry are very much dependent on the branching of the alkyl chain. As an example, the 20 isomers of *para*-substituted nonylphenols identified from technical NP have six different base ions [24]. This makes it difficult to select good and representative ions for SIM analyses of the individual alkylphenol isomers. SIM analysis using typical hydrocarbon ions in the low *m*/*z* area (*m*/*z* 94, 107, 135 and 149) will also give a risk of detecting false positives. Interferences of benzoic acids have been a problem for analysis of alkylphenols in produced water [55]. The NCI analysis of produced water used in this work revealed a number of non-alkylphenol impurities present in SIM and full scan spectra. The sizes of some of the peaks, notably those with *m*/*z* 356, 370, 384 and 398, are of the same order of magnitude as those of many alkylphenols. It may be suggested from the mass spectra that the unknown compounds are pentafluorobenzoate derivatives of aromatic thiols, compounds, commonly found in oil [57]. Thiols from petroleum distillates easily undergo derivatisation by pentafluorobenzoyl chloride [58]. However, in the current analysis the unknown compounds had longer retention times than the alkylphenols of similar masses, thus not obstructing the alkylphenol analysis. The work on identification of the unknown components of produced water is now in progress.

Base ions, molecular ions and retention times for the alkylphenols analysed as non-derivatised compounds by SIM are shown in Table 11.

The pentafluorobenzoate derivatives of alkylphenols have a very homogenous fragmentation pattern on the GC–MS (EI). The molecular ion and the base ion *m*/*z* 195 (originating from the pentafluorobenzoyl group) are present for all alkylphenols. This gives a good basis for SIM analyses; by selecting criteria of stable ratios between the molecular ion and *m*/*z* 195 (the linearity test shows R.S.D. for these ratios <15%), a very selective detection is obtained with low possibility for false positives. Using *m*/*z* 195 for quantification gives a sensitive detection.

In the negative chemical ionisation mode the molecular ion is completely dominating and only very little fragmentation is noted. The NCI analysis has the same high selection in detection as GC–ECD since only halogens and other electrophilic compounds make negative ions. Together with the selection from the SIM, this makes the NCI analysis of pentafluorobenzoate derivatives an extremely sensitive and selective method.

Compared to other commonly used derivatisation methods of phenols (acetylation, methylation and silylation), the halogenated derivatives have the advantage that they can be used together with GC–ECD and GC–MS (NCI) and thereby benefit of the high selectivity and sensitivity of these detection methods. Pentafluorobenzoyl derivatisation has been shown to be more sensitive [35], having less problem with matrix effects [36] and being more specific for phenols [59] than pentafluorobenzyl derivatives. However, both high selectivity and sensitivity has been frequently achieved when using pentafluorobenzyl derivatives and GC–MS (NCI) [34,35]. The fragmentation pattern from pentafluorobenzyl derivatives is very similar to that of pentafluorobenzoate derivatives both on GC–MS (EI) and GC–MS (NCI) [34]. Both methods are therefore most suitable for analysing trace levels of phenols in environmental samples together with GC–MS (NCI), resulting in very low detection limits.

Table 11
MS data for the tested non-derivatised compounds

Compound	t_R (min)	Base ion	Molecular ion
SIS Phenol-d5	11.81	71	99
Phenol	11.84	66	94
SIS *p*-Cresol-d8	14.35	115	116
o-Cresol	13.87	107	108
m-Cresol	14.46	107	108
p-Cresol	14.46	107	108
SIS Ethylphenol-d8	17.22	117	130
2-Ethylphenol	16.40	107	122
4-Ethylphenol	17.37	107	122
3,4-Dimethylphenol	18.38	107	122
SIS 4-*n*-Propylphenol-d12	20.46	113	146
4-*n*-Propylphenol	20.69	107	136
4-*tert*-Butylphenol	22.06	135[a]	150
2-*tert*-Butylphenol	22.82	135[a]	150
4-*n*-Butylphenol	24.61	107	150
SIS 4-*n*-Nonylphenol-d4	43.90	111	224
4-*n*-Nonylphenol	43.94	107	220

[a] Ion 107 used for quantification.

4. Conclusion

The analytical method for the determination of alkylphenols from phenol (C_0) to nonylphenol (C_9) in produced water has been described using GC–MS of pentafluorobenzoate derivatives. This method has some advantages over the more conventional methods. SPE by anion-exchange sorbent followed by pentafluorobenzoyl derivatisation allows facile and efficient analysis of alkylphenols in produced water. The detection limits obtained are at low ng/l levels. It seems reasonable to incorporate the use of derivatisation procedure in the analytical method as resulting in the more efficient recovery of analytes. However, *ortho*-substituted alkylphenols are not successfully analysed due to low derivatisation yield.

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