RAPPORT FRA HAVFORSKNINGEN

Nr. 5-2010

Intercalibration of the analytical method for alkylphenols in produced water

By Stepan Boitsov

HAVFORSKNINGSINSTITUTTET
INSTITUTE OF MARINE RESEARCH

Mai 2010

www.imr.no

PROSJEKTRAPPORT

HAVFORSKNINGSINSTITUTTET
INSTITUTE OF MARINE RESEARCH

Nordnesgaten 50, Postboks 1870 Nordnes, 5817 BERGEN
Tlf. 55 23 85 00, Faks 55 23 85 31, www.imr.no

Tromsø	**Flødevigen**	**Austevoll**	**Matre**
9294 TROMSØ	4817 HIS	5392 STOREBØ	5984 MATREDAL

Rapport fra Havforskningen	**Nr. - År** **5-2010**

Tittel (norsk/engelsk):

Intercalibration of the analytical method for alkylphenols in produced water

Forfatter(e):
Stepan Boitsov

Distribusjon:
Åpen

Prosjektnr.:
100018-04

Oppdragsgiver(e):
OLF

Oppdragsgivers referanse:

Dato:
7. mai 2010

Program:
Olje-fisk

Faggruppe:
Marin miljøkvalitet

Antall sider totalt:
41

Sammendrag (norsk): Fire laboratorier fra Norge og USA deltok i ringtest-undersøkelse av kjemisk analytisk metode for bestemmelse av alkylfenoler i produsert vann. Det var bra samsvar mellom resultatene fra to av laboratoraiene mens metodiske forskjell har ført til noe dårligere overenstemmelse med de to andre. Det anbefales derfor at prosedyren følges nøyaktig for å få sammenlignbare resultater. Det var imidlertid ikke nok deltakere i ringtesten for å kunne dra definitive konklusjoner.

Summary (English): Four laboratories from Norway and USA took part in a ringtest-study of a chemical analytical method for determination of alkylphenols in produced water. There was a good agreement between the results from two of the laboratories, while methodical differences have resulted in a somewhat worse agreement with the two others. It is recommended that the procedure is followed carefully if comparable results are desired. There were, however, not enough participants in the ringtest to draw definitive conclusions.

Emneord (norsk):	Subject heading (English):
1. Alkylfenoler	**1. Alkylphenols**
2. Produsert vann	**2. Produced water**
3. Ringtest	**3. Ringtest**

Prosjektleder

Faggruppeleder

1. Background

The aim of this project was to test the reproducibility of the analytical method used by oil companies in Norway for the determination of alkylphenols in produced water. For this purpose, an interlaboratory study involving 4 laboratories from 2 countries has been arranged by the Institute of Marine Research (IMR) by request of the Norwegian Oil Industry Union (OLF).

The analytical method has been selected for this work based on preliminary tests carried out at IMR in 2007-2008. Three analytical methods for the measurement of alkylphenols in produced water have been tested. After considering the results of the test (given in Appendix A), OLF has chosen one of the methods for intercalibration between several laboratories. The chosen method involves liquid-liquid extraction by dichloromethane, GPC cleanup and GC-MS analysis (a detailed description of the method is given below).

After the method has been selected, a freshly delivered sample of produced water has been distributed between the participant laboratories for analysis according to the suggested plan of work, same for all the participants. Alkylphenol standard solutions, to be used for calibration, identification and quantification, were also distributed by IMR between the laboratories. The following laboratories have agreed to take part in the experiment.

1. IMR (produced water samples were analysed at IMR simultaneously with the other participants)
2. Battelle, USA
3. Intertek West Lab AS
4. NIVA

A fifth laboratory, CEFAS (UK), agreed to participate in the test initially but quit the work later due to impossibility to fulfill it on time.

2. Materials and method description

2.1. Sample collection and handling

Produced water sample was received from Oseberg C oil installation in the North Sea in early November 2008. The sample was split into several parts by transferring it to 5 l glass bottles containing 50 ml (1%) 1:1 mixture of HCl and water and kept in the dark at +2 ^{o}C for approximately 3 weeks. Six extracts of the sample (500 ml produced water each) were prepared at IMR. After that, analytical kits for this work were prepared at IMR and sent out to each participant laboratory together with a description of the procedure to be followed. The samples were received by most participants in late December 2008 (Battelle received their sample a month later due to postal delay) and analyzed by March 2009.

2.2. *Alkylphenol compounds selected for analysis*

Twelve alkylphenols analysed in this work are described in Table 1 together with their chromatographic properties. Six deuterated alkylphenols used as internal standard are shown in bold in the table. Each internal standard is followed by those alkylphenols that are quantified by means of this standard. ”APRI” stands for ”Alkylphenol Retention Indices” and is used as reference instead of retention time as a more stable parameter, according to Mjøs et al., 2006.

Only alkylphenols with up to 6 carbon atoms in the alkyl chain(s) were included in this work, since alkylphenols of higher alkylation degree are not efficiently analysed by this method, as has been confirmed by the test carried out in 2007-2008 (see Appendix A).

Table 1. List of alkylphenols included in the analysis, with their GC-MS parameters.

Compound*	Molecular ion mass	Quantification ion mass	Qualifier ion mass	APRI
SIS Phenol-d5	**99**	**99**	**71**	
Phenol	94	94	66	0,0000
SIS p-Cresol-d8	**116**	**115**	**115**	
o-Cresol	108	108	107	0,7866
SIS 2,4-Dimethylphenol-d3	**125**	**125**	**“**	
2,4-Dimethylphenol	122	122	107	1,8154
2,3-Dimethylphenol	“	“	“	2,1441
SIS 4-Ethylphenol-d10	**132**	**113**	**131**	
2-Ethylphenol	122	122	107	1,6743
3,5-Dimethylphenol	“	“	“	2,0372
SIS 4-n-Propylphenol-d12	**148**	**113**	**147**	
2-Isopropylphenol	136	136	107,121	2,3461
2-n-Propylphenol	“	“	“	2,5997
2,4,6-Trimethylphenol	“	“	“	2,4977
4-tert-Butylphenol	150	135	107, 150	3,3528
4-n-butylphenol	”	”	”	4,0000
SIS 4-n-Pentylphenol-d16	**180**	**113**	**179**	
4-n-Pentylphenol	164	107	164	5,0000
RIS Pentafluorobenzophenone	272	272	107	

* - SIS – surrogate internal standards, RIS – relative internal standard. Alkylphenol analytes are given in chromatographic order, while SIS compounds precede the corresponding groups of alkylphenols that are quantified by these SIS.

2.3. *Materials for the analysis*

The following materials were included in the kit prepared at IMR and sent out to the labs:

1. Produced water sample, approx. 5 l.
2. Produced water extract, approx. 1,5 ml.
3. Alkylphenol surrogate internal standard (SIS) solution, approx. 2 ml.
4. Alkylphenol calibration standard solution, approx. 10 ml.
5. APRI standard solution, approx. 10 ml.

6. Alkylphenol relative internal standard (RIS) solution, approx. 10 ml.

A detailed description of these materials and the suggested procedure for their use were as follows:

1. Produced water sample.

A sample of produced water for analysis, 5 l, was sent out in two 2,5-litre dark-glass bottles. Five replicate samples, 500 ml each, were to be taken from the bottles and analysed according to the single method described below. Own distilled water was to be used for the blank sample.

2. Produced water extract.

A sample of produced water was prepared and cleaned-up at IMR. The hexane extract, approx. 1,5 ml in a GC vial, was sent out for GC-MS analysis. The sample contained 100 µl SIS (see below) and 100 µl RIS (see below), and was ready for analysis.

3. Alkylphenol surrogate internal standard (SIS) solution.

A methanol solution of SIS, approx. 2 ml in an approx. 100 µg/ml concentration, was sent out for use both with the produced water samples and with the calibration standard. One was to add 100 µl SIS to the water samples at the beginning of the sample treatment, as described in the procedure sent out earlier. The calibration standards (see below) were to be added 100 µl SIS each, i.e. equal amount SIS to each calibration solution.

The precise amounts of the internal standards are given in Table 2.

Table 2. The amounts of deuterated alkylphenols in the distributed SIS solution.

Internal standard	**Concentration in the methanol solution µg/ml**	**Amount in 100 µl µg**
Phenol-d5	100	10
Cresol-d8	100	10
2,4-Dimethylphenol-d10	100	10
4-Ethylphenol-d8	100	10
4-Propylphenol-d12	100	10
4-n-Pentylphenol-d16	100	10

4. Alkylphenol calibration standard solution.

A hexane solution of the 15 alkylphenols that were to be analysed in this work, approx. 10 ml in an approx. 300 µg/ml concentration, was sent out for calibration purposes. It was suggested that one makes a dilution series of calibration standards, starting out from this concentrated standard. The precise amounts of the standards are given in Table 2.

Table 3. The amounts of alkylphenols in the calibration standard.

Alkylphenol calibration standard	**Concentration in hexane solution µg/ml**
Phenol	355
o-Cresol	330
2,4-Dimethylphenol	300
2,3-Dimethylphenol	296
2-Ethylphenol	334
3,5-Dimethylphenol	354
2-Isopropylphenol	338
2-n-Propylphenol	256
2,4,6-Trimethylphenol	257
4-tert-Butylphenol	716
4-n-Butylphenol	252
4-n-Pentylphenol	324

5. APRI standard.

A hexane solution og phenol and 6 *para*-substituted alkylphenols, approx. 10 ml in an approx. 200 µg/ml concentration, were sent out for easier identification of alkylphenols in produced water. “APRI” stands for “Alkylphenol retention indices” and substitutes retention times as a more stable parameter, according to Mjøs *et al.* (2006). For each compound of alkylphenol type, APRI may be calculated according to equation (1):

$$\mathrm{APRI}_x = n\,\frac{t_{\mathrm{R}(x)} - t_{\mathrm{R}(z)}}{t_{\mathrm{R}(z+n)} - t_{\mathrm{R}(z)}} + z \qquad (1)$$

where t_R is retention times of the compound of interest, x, and two *para*-substituted *n*-alkylphenols eluting on each side of the compound. z represents the number of carbon atoms in the alkyl chains of the *para*-alkylphenols eluting before x, and n is the difference in the number of carbon atoms between the two references. z is zero if the first reference compound is phenol.

The compounds included in this standard are shown in Table 4. APRI standard was not used for quantitative measurements but the amounts of the components are also given for information.

Table 4. The amounts of alkylphenols in APRI standard.

APRI standard alkylphenols	**Concentration in hexane solution, µg/ml**
Phenol	230
p-Cresol	370
4-Ethylphenol	216
4-Propylphenol	225
4-n-Butylphenol	243
4-n-Pentylphenol	224
4-n-Hexylphenol	145

6. RIS.

Relative internal standard, RIS, used in this work is pentafluorobenzophenone, a compound with molecular weight of 272. A hexane solution, approx. 10 ml in 216 µg/ml concentration precisely, was sent out for use in the end of sample preparation procedure. One was to add 100 µl (21,6 µg) to each sample before the samples are run on GC-MS.

2.4. Analytical method.

The following method was selected for this work, based on the test of 3 methods carried out earlier by IMR, as described in Appendix A. The method is originally developed by Battelle and SINTEF (see SINTEF, 2002). The participant laboratories have been encouraged to adhere to this method as closely as possible. Some participants had, however, certain deviations from the method. These are described as reported by each institution after the main method description below.

Extraction. Samples (500 ml volume) to which 100 µl internal standard has been added are filtered through GF/C glass fiber filters under vacuum. The water sample is the extracted by dichloromethane (DCM), 3 times with correspondingly 100, 50 and 50 ml DCM, while the filters are extracted by DCM by keeping them in this solvent for 1 hour. The water extracts are then reduced in volume by a gentle stream of nitrogen gas at 39°C to ca. 2 ml, and then are merged with the filter extracts and the volume is further reduced to 2 ml. The extracts are then clean-up by GPC.

GPC. The following system is used for GPC: Gilson (Gilson 232 autoinjector, injector Gilson 401 dilutor, Gilson 202 fraction collector, Gilson, France) and Pharmacia (LKB 2150 HPLC pump, LKB 2252 LC controller, LKB 2144 fluorescence detector, Pharmacia LKB, Sweden). Two GPC columns from Waters (Envirogel GPC cleanup 19 mm x 300 mm) are used, coupled together by Gilson 232 autoinjector as switch vent. The procedure is described in more detail in Meier et al., 2005. The elution is done by DCM at flow rate of 5 ml/min. GPC-extracts are then reduced in volume to 2 ml and the solvent is exchanged to hexane. The samples are then ready for GC-MS (EI) analysis. Relative internal standard (RIS) is added to all samples just before GC-analysis.

GC-MS (EI) analysis. The analyses are done with Agilent 6890 GC-system coupled to Agilent 5973 mass-selective detector with electron-impact (EI) ion source, used in ion-selective mode (SIM). The GC-programme is as follows: oven temperature is 50°C at injection and is kept at this level for 2 min. Then the temperature is increased to 100°C at 10°C/min, then to 220°C at 3°C/min, then to 300°C at 15°C/min. The programme ends after that (52,33 min total time). Solvent delay is 10 min, and the total chromatogram is divided into 5 SIM-windows with 7 to 14 ions in each window.

Quantification of the results was done by means of deuterated internal standards given in Table 1. Quantification is corrected for variations in chromatographic response by means of response factors, which are calculated with the help of an independent calibration standard made for this purpose.

Deviations from the method at each laboratory.

Westlab Intertek. The produced water sample was not filtered before the extraction. The sample was extracted once with DCM and not 3 times as suggested by IMR, but it was then stirred for at least 2 hours. The extracts were not cleaned up by GPC or any other technique. Because of this, it was not possible to analyse all the same ions in GC-MS as IMR suggested, since there was too much interference from other compounds. Other ions were therefore used for quantification. Own internal standard (SIS) was used by Westlab, consisting of phenol-d5, p-cresol-d8 and phenanthrene-d10. Alkylphenols were quantified according to this standard, and the extract prepared at IMR and sent to Westlab could only partly be analysed since it lacked one of the internal standards used by Westlab, phenanthrene-d10. Of the 12 alkylphenols suggested for analysis by IMR, 10 were analysed by Westlab. 4-Ethylphenol-d10 was used by Westlab as surrogate internal standard while RIS pentafluorobenzophenone was not used. A detailed description of the method used by Westlab is given in Appendix B.

NIVA. The method used at NIVA was almost exactly as suggested by IMR, except that large amount of SIS, 500 µl instead of 100 µl, was added to the samples, and only about 2/3 of the sample was injected through GPC. Solvent volume was further reduced by nitrogen gas flow instead of rotary evaporation, and the final solvent was DCM and not hexane. There was a long gap (10 weeks) between extraction and GPC+GC-MS analysis at NIVA. GPC recovery was however tested as a separate step at NIVA since the analytical system had been recently changed, and the resulting precision was found appropriate.

Battelle. The method used by Battelle was almost exactly as suggested by IMR. A long delay with the postage of the samples (more than one month) resulted in a much longer time interval between the sampling and the analysis at Battelle.

3 Results and discussion

The results of the interlaboratory study are summarised in Table 5 and are also shown as a plot in Figure 1 (normalised to sum of all results for each compound).

Table 5. Alkylphenol concentrations in Oseberg C produced water sample measured by 4 laboratories.

Compound	Concentration, µg/l				Relative yield, % of the median value			
Institute	IMR	Intertek	NIVA	Battelle	IMR	Intertek	NIVA	Battelle
Phenol	**3001**	**6 816**	**4647**	**4211**	68	154	105	95
o-Cresol	**1259**	**1 683**	**1196**	**2429**	86	114	81	165
2-Ethylphenol	**37**	-	**44**	**73**	84	-	100	166
2,4-Dimethylphenol	**268**	**295**	**315**	**289**	92	101	108	99
3,5-Dimethylphenol	**185**	**261**	**163**	**574**	83	117	73	258
2,3-Dimethylphenol	**56**	-	**63**	**51**	100	-	111	91
2-Isopropylphenol	**30**	-	**41**	**-**	84	-	116	-
2-n-Propylphenol	**7,3**	**9,4**	**7,8**	**8,5**	90	116	96	104
2,4,6-Trimethylphenol	**13**	**14**	**12**	**-**	100	110	95	-
4-tert-Butylphenol	**36**	**6,7**	**43**	**5,2**	169	31	203	24
4-n-butylphenol	**2,8**	**3,1**	**1,9**	**2,3**	111	119	73	89
4-n-Pentylphenol	**0,29**	**0,61**	**0,25**	**0,20**	107	224	93	75
Mean ± SD					*98 ±25*	*121 ± 50*	*104 ± 34*	*117 ± 64*

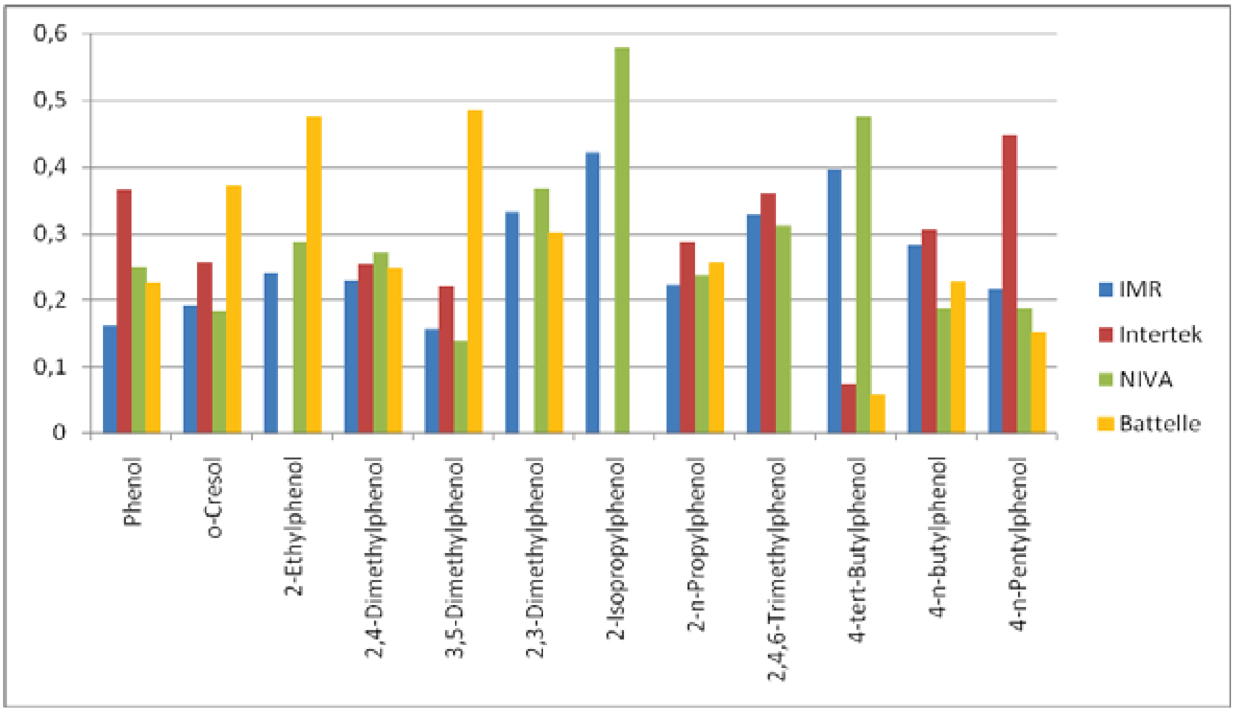

Figure 1. Alkylphenol concentrations in Oseberg C produced water sample measured by 4 laboratories (normalised to the sum of all results for each compound).

The results vary between the laboratories for different compounds from 5% to as much as more than 8-fold. Generally, the results of IMR and NIVA are nearest to the median values, while those of Intertek are consistently higher, with an exception of 4-tert-Butylphenol which is much lower. The results of NIVA are for all but 3 compounds within 20% difference of those of IMR. The results of Battelle are unevenly spread, being close to those of NIVA and IMR for 6 compounds and much higher than any other participant for 3 compounds, while 4-tert-butylphenol is reported by Battelle at approximately the same level as by Intertek.

With regard to specific compounds, phenol seems to have a high variance between the labs, which may be due to problems with correct measurement and quantification of this compound, found in largest amounts in the samples. Only 2,4-dimethylphenol and 2,4,6-trimethylphenol (not measured by Battelle) were found to have similar values by all the laboratories, with less than 20% difference. A curious result obtained for 4-tert-butylphenol, reported at similar low levels by Intrertek and Battelle, and at approximately 10 times higher, but also similar levels by IMR and NIVA, may be explained by difficulties with analyzing this compound due to its presence in many types of plastic, and sometimes contaminating the samples but not the blank.

A similarity of the results of NIVA and IMR and their difference from the results obtained by Intertek may be due to significant differences in the method used by Intertek, in particular the internal standard used for quantification. However, Battelle used the same method as NIVA and IMR, while the results for several compounds reported by Battelle were strongly different from the other laboratories. This could be due to a long time between sampling and analysis taken by Battelle. Thus, it seems problematic to use the results of Intertek for assessing the reproducibility of the method, while it is the results of the other 3 laboratories that should be taken into consideration. One should note, however, that all the results of all the participants, apart from 4-tert-butylphenol, are of the same order of magnitude and are largely comparable, if not always quite agreeing.

Residual standard deviations for each compound are given in Table 6.

Table 6. Residual standard deviations of alkylphenol measurements by the 4 laboratories, %.

Compound	IMR	Intertek	NIVA	Battelle
Phenol	2	3	1	3
o-Cresol	11	2	2	4
2-Ethylphenol	7	-	6	4
2,4-Dimethylphenol	3	5	7	4
3,5-Dimethylphenol	8	2	1	3
2,3-Dimethylphenol	2	-	3	4
2-Isopropylphenol	3	-	13	-
2-n-Propylphenol	4	9	13	3
2,4,6-Trimethylphenol	5	8	12	-
4-tert-Butylphenol	4	7	11	2
4-n-butylphenol	2	12	4	3
4-n-Pentylphenol	15	18	13	7
Mean	5	7	7	4

All the participants achieved good RSD values for the method, 4% to 7% on average and all below 20%, although all the participants had somewhat higher RSD for 4-n-pentylphenol. This is rather typical since this compound is found in lowest concentrations of all, approximately 10 times lower than any other compound analysed in this work. This confirms the previously reported fact that it is problematic to use the studied analytical method for long-chained alkylphenols.

The results of analysis of the extract prepared at IMR by different laboratories are given in Table 7.

Table 7. Concentrations of alkylphenols measured by different laboratories in produced water extract prepared by IMR, µg/l.

Compound	IMR	Intertek	NIVA	Battelle
Phenol	3038	6300	5086	4503
o-Cresol	1510	1700	1160	4016
2-Ethylphenol	39		50	47
2,4-Dimethylphenol	251	280	299	403
3,5-Dimethylphenol	185	260	164	388
2,3-Dimethylphenol	58		115	85
2-Isopropylphenol	31		29	
2-n-Propylphenol	7,5	11	7,0	6,9
2,4,6-Trimethylphenol	12	12	9,0	
4-tert-Butylphenol	37		40	5,5
4-n-butylphenol	2,7		1,6	2,6
4-n-Pentylphenol	0,51		0,24	0,23

All laboratories reported the results for the extract rather close to the results obtained by the same laboratories for the original sample. Thus, one may suggest that the differences in the results between the laboratories is caused by GC-MS analysis and/or quantification method, and not by sample preparation and cleanup. In particular, the difference in the results reported by Intertek as compared to the other laboratories, is probably caused by the difference in the internal standard and possibly also by the difference in the ions used for detecting target compounds in GC-MS. One should note, however, that only half of the compounds has been analysed by Intertek in the extract, with no C4- or C5-phenols.

4 Conclusion

There is a good agreement between two of the laboratories on the results, and a slightly worse, though not an altogether wrong one, for the two others. Methodical differences, such as differences in quantification technique, seem to explain some of the difference in the results. A long time between sampling and analysis may also lead to poor reproducibility. The method may be well reproducible and deliver comparable results at different laboratories, on the condition that the procedure is followed closely at each laboratory and that the time between sampling and analysis is not longer than 2 months. At the same time, one has to note that only 4 laboratories have taken part in this study, which is far from enough for drawing any statistically confirmed conclusions.

5 References

1. S.A. Mjøs, S. Meier, S. Boitsov (2006). Alkylphenol retention indices. *Journal of Chromatography A*, 1123, 98-105.
2. SINTEF Rapport (2002). Forfattere: G. Durell, B. Liu, and L.-G. Faksness, Produced Water Phenol Analysis. Summary report from the Round Robin Study. SINTEF Applied Chemistry, Trondheim.
3. S. Meier, J. Klungsøyr, S. Boitsov, T. Eide, A. Svardal (2005). Gas chromatography–mass spectrometry analysis of alkylphenols in cod (*Gadus morhua*) tissues as pentafluorobenzoate derivatives. *Journal of Chromatography A*, 1062, 255-268.

Appendix A. The results of the test of 3 analytical methods for the determination of alkylphenols in produced water. Report on the work carried out by IMR in 2007-2008. (In Norwegian)

Uttesting av alkylfenol analysemetoder.

Arbeidet utført av: Marin Miljøkvalitet gruppe, Havforskningsinstituttet

Tid: november-desember 2007

Rapportert: 03.01.2008

Ansvarlig: S. Boitsov

Innledning

Formålet med dette arbeidet var å finne den optimale analytiske metoden for alkylfenol analyse i vann som kunne videre bli brukt til interkalibrering av flere laboratorier knyttet til oljeindustri og organisert av OLF.

Tre følgende metoder for alkylfenol analyse ble undersøkt i denne omgang:

pentafluorobenzoyl-derivatisering av prøvene ekstrahert med fastfase ekstraksjon (solid-phase extraction, SPE) og videre analysert med GC-MS med negativ kjemisk ionisering, NCI (Metode I),

en variasjon av den første som forutsetter samme type derivatisering direkte på SPE-kolonne (Metode II),

væske-væske ekstraksjon med diklormetan (DCM), uten derivatisering, med GC-MS analyse med elektron-impakt, EI (Metode III).

Metodisk prosedyre brukt i dette arbeidet var basert på tidligere publisert beskrivelser gitt for Metode I i Boitsov et al., (2004, 2007); for Metode II i Jonsson (2004) og Jonnson et al. (2008); og for Metode III i SINTEF (2002); med små endringer som er beskrevet i detalj nedover.

Metoder og forsøksbeskrivelse

Plan for forsøket

Standardløsning av 48 alkylfenoler (C0-C9) og intern standard oppløsning (7 deutererte alkylfenoler) ble laget for videre bruk gjennom hele forsøket (for listen over komponentene se Tabell 1). Alkylfenoler ble kjøpt fra Chiron (Trondheim, Norway) eller Aldrich (Oslo, Norway), eller tidligere syntetisert på HI, som beskrevet av Boitsov et al. (2007). Pentafluorobenzofenon (Chiron, Trondheim, Norway) ble brukt som relativ intern standard for bestemmelse av absolutt mengde alkylfenoler.

Produsert vann til analyse ble levert fra Oseberg C installasjon i Nordsjøen, 5 l med tilsatt 50 ml HCl:vann 1:1 blanding for stabilisering. Produsert vann var oppbevart i mørke ved +2°C i 2 uker før analysestart.

Følgende prøver ble analysert med hver av de 3 metodene:

1. destillert vann prøver spiket med alkylfenol-standardoppløsning ved konsentrasjonsnivå som ligner på en reell prøve, 5 paralleller og en blankprøve, 100 ml hver (500 ml hver ved Metode III). De nøyaktige mengdene er gitt i Appendiks A.

2. produsert vann fra Oseberg C oljeplattforme, 5 paralleller og en blankprøve, 100 ml hver (500 ml hver ved Metode III).

Resultatene fra hver metode blir sammenlignet for

Nøyaktighet (avvik fra riktige verdier)

Presisjon (repeterbarhet)

Selektivitet (kromatografisk oppløsning)

Følsomhet (LOD og LOQ verdier til metoden)

Metode I

Ekstraksjon. 100 ml produsert vann prøve er tilsatt 100 µl deuterert internstandard. Prøven filtreres gjennom glassfiber GF/C filtrer med bruk av vakuum. Filtrene lagres etterpå i diklormetan (DCM) i ca. 1 time for å ekstrahere partikkel-bundete alkylfenoler. Filtraten (100 ml vannløsning) surgjøres med HCl (ca. 100 µl) og kjøres videre med svak vakuum gjennom Oasis® MAX fastfase-ekstraksjon kolonner, kondisjonert med 6 ml tert-butyl-metyl eter og vasket med 6 ml dest.vann. Prøven påsatt MAX-kolonne vaskes med 10 ml KOH (30%) og elueres sakte med 15 ml 5% maursyre i metanol. Etter det slås prøvene sammen med DCM-ekstraktet av filteret og neddampes til ca. 1 ml volum med hjelp av nitrogen strøm ved 39oC. Det er viktig å ikke tillate prøvene bli dampet ned til tørrhet.

Derivatisering. Prøvene derivatiseres med pentafluorobenzoyl klorid (100 µl 30% PFBC i isooktan) i et 2-fase system med 1 ml NaOH og 2 ml Na2CO3 som uorganisk fase og 2 ml heksan som organisk fase. Etter kraftig risting i ett minutt står prøvene i en halv time ved rom temperatur. Rester av derivatiseringsmiddelet fjernes med overskudd NaOH (ca 15 ml) i løpet av natten, prøvene lagres ved +4 oC overnatt. Neste dag er heksan-fasen tatt ut fra derivatiseringsblanding (2x2 ml heksan, til endelig prøvevolum 4 ml). Deretter tar man ut 1 ml og fortynner 10 ganger i heksan for å analysere de høyt-konsentrerte alkylfenoler, og både den fortynnete og den konsentrerte fraksjon analyseres på GC-MS (NCI SIM). Relativ intern standard (RIS, 100 µl) tilsettes alle prøver like før GC-MS-analyse.

GC-MS (NCI) analyse. Analysene utføres på Agilent 6890 GC-system koblet til Agilent 5973 masse-selektiv detektor med negativ kjemisk ionisering (NCI), i full-skan modus (skan fra *m/z* 50 til 500) eller i ion-selektiv modus (SIM). Analytisk GC-kolonne brukt til hele arbeidet var Varian FactorFour VF-5ms (Varian, Lake Forest, CA, USA), *L* = 50 m, I.D. = 0.25 mm, *d*f = 0.25 μm. Helium (99.9%) ble brukt som bærer-gas i et 30 cm/s constant-flow modus. Prøver (1 μl i heksan oppløsning) ble injisert i splitless modus og split-valve ble åpnet etter 2 min. GC-programmet var som følger: ovnens temperatur var 90^{o}C ved injeksjon og ble holdt slik i 2 min etterpå. Så var temperaturen økt til 110^{o}C ved 10^{o}C/min, så til 250^{o}C ved 3^{o}C/min, så til 300^{o}C ved 10^{o}C/min og holdt ved denne temperaturen i 10 min (65,67 min total tid). Solvent delay var 14 min, og den totale kromatogrammen ble delt i 5 SIM-vinduer med mellom 4 og 9 ioner i hvert vindu.

Metode II

Ekstraksjon. Denne delen av Metode II er lik samme delen i Metode I fram til påføring av prøven på fastfase-ekstraksjon kolonne (MAX), bortsett fra at filtrene kunne ikke analyseres i denne metoden siden derivatiseringen skjer direkte på MAX-kolonne.

Derivatisering. Før derivatisering, tørkes MAX-kolonner med påsatt prøve med svak strøm av nitrogen i ca. 30 min. Etter det derivatiseres prøvene med pentafluorobenzoyl klorid (750 μl 4% PFBC i isooktan) direkte på MAX-kolonnen. Kolonnene står så ved +60^{o}C i 2 timer med Al kork på, og så elueres med heksan (15 ml). Etter det er prøvene dampet ned til 2 ml volum med strøm av nitrogen ved 50^{o}C. Rester av derivatiseringsmiddelet fjernes med tilsatt overskudd NaOH (ca 15 ml) - prøvene ristes kraftig og står i ca. 1 time ved romtemperatur, før heksan-fasen tas ut (2x2 ml heksan). Prøvene er da klare for GC-MS. Relativ intern standard (RIS) tilsettes alle prøver like før GC-analyse. Det var ikke nødvendig å fortynne disse prøver siden absolutt gjenvinning av lav-kokende alkylfenoler er lavere med denne metoden.

GC-MS (NCI) analyse. GC-MS-analyse for denne metoden er nøyaktig lik Metode I.

Metode III.

Ekstraksjon. Prøver (500 ml volum) tilsettes 500 μl intern standard, filtreres på samme måte som i Metode I. Vannprøven ekstraheres så med diklormetan (DCM), 3 ganger med henholdsvis 100, 50 og 50 ml DCM, mens filtrene ekstraheres med DCM på samme måte som i Metode I. Vannprøve-ekstraktene er så redusert i volum mha. inndamping med nitrogen gass ved 39^{o}C til ca. 2 ml, slått sammen med filter-ekstraktene og neddampet videre til 2 ml. Så renses prøvene opp med GPC.

GPC. Til GPC ble det brukt følgende system: Gilson (Gilson 232 autoinjector, injector Gilson 401 dilutor, Gilson 202 fraction collector, Gilson, France) and Pharmacia (LKB 2150 HPLC pump, LKB 2252 LC controller, LKB 2144 fluorescence detector, Pharmacia LKB, Sweden). To GPC kolonner fra Waters (Envirogel GPC cleanup 19 mm x 300 mm) ble brukt, koblet sammen med hjelp av Gilson 232 autoinjector som switch vent. Prosedyren er beskrevet i mer detalj av Meier *et al.*, 2005. Elueringen ble gjort med DCM ved flow rate av 5 ml/min. GPC-ekstrakten neddampes så til 2 ml med løsemiddelet byttet til heksan, og prøvene analyseres med GC-MS (EI). Relativ intern standard (RIS) tilsettes alle prøver like før GC-analyse.

GC-MS (EI) analyse. Samme GC-MS-apparattet og GC-kolonne som i Metode I ble brukt til denne analyse. Elektron-impakt (EI) ionisering ble brukt i full-skan modus (skan fra *m/z* 50 til 500) eller i ion-selektiv modus (SIM). GC-programmet var som følger: ovnens temperatur var 50^{o}C ved injeksjon og ble holdt slik i 2 min etterpå. Så var temperaturen økt til 100^{o}C ved 10^{o}C/min, så til 220^{o}C ved 3^{o}C/min, så til 300^{o}C ved 15^{o}C/min. Programmet ble avsluttet med en gang etter det (52,33 min total tid). Solvent delay var 10 min, og den totale kromatogrammen ble delt i 5 SIM-vinduer med mellom 7 og 14 ioner i hvert vindu.

Alkylfenoler analysert i dette arbeidet, samt deres kromatografiske egenskaper er gitt i Tabell 1. ”APRI” står for ”Alkylphenol Retention Indices” og erstatter retensjonstider som et mer stabilt parameter, ifølge Mjøs et al. (2006). Deutererte alkylfenoler brukt som interne standarder er vist med hevet skrift i tabellen. Hver intern standrad er fulgt med de alkylfenoler som er kvantifisert etter denne standard. Kvantifisering er korrigert for variasjoner i kromatografisk respons med hjelp av respons fatkorer, som ble regnet ut med uavhengig alkylfenol standard laget til dette formål, både for derivatiserte og uderivatiserte alkylfenoler.

Tabell 1. Liste av alkylfenoler i standardoppløsning, med deres GC-MS-parametrer.

Forbindelse	Molekular ionmasse	Kvantifiserings ionmasse, frie fenoler	Qualifier ionmasser, frie fenoler	PFBC derivat ionmasse	APRI, frie fenoler	APRI, PFBC derivat
IS Phenol-d5	**99**	**99**	**71**	**293**		
Phenol	94	94	66	288	0,0000	0,0000
IS p-Cresol-d8	**116**	**115**	**115**	**309**		
o-Cresol	108	108	107	302	0,7866	0,6847
m-Cresol	“	“	“	“	1,0000	0,8990
p-Cresol	“	“	“	“	1,0000	1,0000
IS 2,4-Dimethylphenol-d3	**125**	**125**	**“**	**319**		
IS 4-Ethylphenol-d10	**132**	**113**	**131**	**325**		
2-Ethylphenol	122	122	107	316	1,6743	1,3203
2,6-Dimethylphenol	“	“	“	“	1,4318	1,4847
2,5-Dimethylphenol	“	“	“	“	1,8401	1,6379
2,4-Dimethylphenol	“	“	“	“	1,8154	1,7354
3-Ethylphenol	“	“	“	“	2,0038	1,7772
3,5-Dimethylphenol	“	“	“	“	2,0372	1,8774
4-Ethylphenol	“	“	“	“	2,0000	2,0000
2,3-Dimethylphenol	“	“	“	“	2,1441	2,0214
3,4-Dimethylphenol	“	“	“	“	2,3166	2,3089
IS 4-n-Propylphenol-d12	**148**	**113**	**147**	**341**		
2-Isopropylphenol	136	136	107,121	330	2,3461	1,6379
2-n-Propylphenol	“	“	“	“	2,5997	2,0550
3-Isopropylphenol	“	“	“	“	2,6614	2,2813
2,4,6-Trimethylphenol	“	“	“	“	2,4977	2,5474
4-Isopropylphenol	“	“	“	“	2,6580	2,6361
3-n-Propylphenol + 3-ethyl-5-methylphenol	“	“	“	“	3,0000; 3,0072	2,7187

2,3,6-Trimethylphenol	“	“	“	“	2,8106	2,8720
2,3,5-Trimethylphenol	”	”	”	”	3,1619	2,9908
4-n-Propylphenol	”	”	”	”	3,0000	3,0000
2-tert-Butylphenol	150	135	107, 150	344	3,1241	2,4683
5-Methyl-4-isopropylphenol	”	”	”	”	3,7385	2,5872
3-tert-Butylphenol	”	”	”	”	3,3388	2,8624
3-Methyl-5-isopropylphenol	”	150	”	”	3,5541	3,1440
4-tert-Butylphenol	”	135	”	”	3,3528	3,3435
4-sec-Butylphenol	”	150	”	”	3,5541	3,5263
4-Isopropyl-3-methylphenol	”	135	”	”	3,7385	3,6870
4-n-butylphenol	”	”	”	”	4,0000	4,0000
2,3,5,6-Tetramethylphenol	”	”	107	”		4,0934
IS 4-n-Pentylphenol-d16	**180**	**113**	**179**	**373**		
2-tert-Butyl-4-methylphenol	164	164	107, 135	358	4,6403	3,3130
2-tert-Butyl-5-methylphenol	”	”	”	”	4,0429	3,3296
2-tert-Butyl-6-methylphenol	”	”	”	”	4,0431	3,3573
4-tert-Butyl-2-methylphenol	”	”	”	”	3,9819	3,4432
4-(1,1-Dimethylpropyl)phenol	”	107	164	”	4,3823	4,3855
4-n-Pentylphenol	”	”	”	”	5,0000	5,0000
2,6-Diisopropylphenol	178	163	178	372		3,7119
2-tert-Butyl-4-ethylphenol	”	”	”	”	4,6403	3,8615
4-(1,1-Dimethylbutyl)phenol	”	135	178, 107	”	5,1490	5,1009
4-(1,2,2-Trimethylpropyl)phenol	”	135	”	”	5,3420	5,3609
4-n-Hexylphenol	”	107	178	”	6,0000	6,0000
4-(1-Ehtyl-1-methylpropyl)-2-methylphenol	192	163	192, 107	386	5,8761	5,7248
4-(1,1-Dimethylpentyl)phenol	”	135	”	”	6,0371	5,9419
4-n-Heptylphenol	”	107	192	”	7,0000	7,0000
4-tert-Octylphenol	206	107	206	400	6,4168	6,3786
IS 4-n-Nonylphenol-d4	**224**	**111**	**224**	**418**		
4-n-Octylphenol	”	”	”	”	8,0000	8,0000
4-n-Nonylphenol		”	220		9,0000	9,0000

Resultater

Detaljerte resultater er gitt i Appendikser A (spiket destillert vann) og B (produsert vann).

Nøyaktighet. Nøyaktigheten til hver av metodene ble vurdert som gjennomsnittlig % gjenvinning av alkylfenoler målt i 5 parallelle prøver av destillert vann spiket med standard-oppløsning av alkylfenoler.

Gjenvinning for et utvalg av alkylfenoler er gitt i Tabell 2 (gjennomsnitt for 5 paralleller, korrigert for bidrag fra blanke prøver).

Tabell 2. Gjenvinning av enkelte alkylfenoler analysert med 3 forskjellige metoder.

Forbindelse	Gjenvinning, %		
	Metode I	Metode II	Metode III
Fenol	89	97	83
p-Kresol	91	82	-
4-Etylfenol	99	148	-
2,6-dimethylphenol	85	491	81
4-Isopropylfenol	97	116	-
4-tert-Butylfenol	89	85	86
2-tert-Butyl-4-Ethylphenol	0	0	95
4-n-Heptylfenol	91	140	79
4-tert-Oktylfenol	104	162	103
4-n-Nonylfenol	90	75	219
Gjennomsnitt over alle 48 alkylfenoler	356	2512	120
Gjennomsnitt over alle alkylfenoler, ekskludert *orto*-substituerte alkylfenoler*	99	127	117

*o-Kresol er tatt med siden den gir god respons

Ingen metode gir perfekt gjenvinning for alle 48 alkylfenoler. Metoder I og II, som innebærer derivatisering av OH-gruppe, gir dårlig gjenvinning for orto-substituerte alkylfenoler, på grunn av sterisk hindring av OH-gruppen (dette gjelder imidlertid ikke orto-kresol og enkelte andre forbindelser med liten substiuent i orto-posisjon). Dette kan rettes på ved å bruke en separat intern standard for disse forbindelser som har samme struktur, dvs. en deuterert orto-substituert alkylfenol. Dette ble gjort for C2-alkylfenoler (2,4-dimetylfenol-d_3 brukt som intern standard for dimetyl-fenoler mens 4-etylfenol-d_{10} brukt for etylfenoler), og man får dermed god resultat for disse forbindelser. For alkylfenoler med lengre alkylkjede var orto-substituerte interne standarder ikke tilgjengelige, og resultatene er mye verre, mellom 0 og ca. 10 000% gjenvinning (så høy gjenvinning kan forklares av svært lave responsfaktorene for noen forbindelser av denne type).

Når alkylfenoler med store grupper i orto-posisjon er ekskludert fra listen, gir metode I best gjennomsnittlig gjenvinning, mellom 80 og 100% for aller fleste forbindelser. Årsaken til at metode II gir noe verre resultater kan skyldes utilstrekkelig tilpassing av metoden til denne type analyse. Den publiserte versjonen av metoden (Jonsson et al., 2008) bruker en annen derivatiseringsmiddel, TMS, mens gjeldende arbeide på HI disponerte ikke nok tid for optimalisering av betingelser. Verre resultater fått med metoden kan være forårsaket av en sterk økning i reaktiviteten i derivatiseringen under metodens forhold: 60°C i 2 timer.

Metode III tillater analyse av orto-substituerte alkylfenoler, og det er ingen vesentlig forskjell i gjennomsnittlig gjenvinning med denne metoden, når disse forbindelser er tatt til hensyn eller ikke. Men mange alkylfenoler kan ikke analyseres med Metode III på grunn av dårlig selektivitet (se nedover).

Presisjon (repeterbarhet). Presisjonen til hver av metodene ble vurdert som gjennomsnittlig relativ standardavvik av alkylfenolers mengde målt i 5 parallelle prøver av destillert vann spiket med standard-oppløsning av alkylfenoler.

Relativ standardavvik (i prosent) for et utvalg av alkylfenoler er gitt i Tabell 3 (gjennomsnitt for 5 paralleller, korrigert for bidrag fra blanke prøver).

Tabell 3. Relativ standardavvik av enkelte alkylfenoler analysert med 3 forskjellige metoder.

Forbindelse	Relativ standardavvik, %		
	Metode I	Metode II	Metode III
Fenol	6	5	8
p-Kresol	5	8	-
4-Etylfenol	2	12	-
2,6-dimethylphenol	14	40	4
4-Isopropylfenol	5	17	-
4-tert-Butylfenol	7	11	8
2-tert-Butyl-4-Ethylphenol	-	-	9
4-n-Heptylfenol	5	60	8
4-tert-Oktylfenol	8	10	18
4-n-Nonylfenol	15	61	24
Gjennomsnitt over alle 48 alkylfenoler	10	26	8
Gjennomsnitt over alle alkylfenoler, ekskludert *orto*-substituerte alkylfenoler*	6	17	9

*o-Kresol er tatt med siden den gir god respons

Av samme årsaker som nevnt for gjenvinning, gir Metode I best presisjon for alle alkylfenoler unntatt orto-substituerte C3-C9-fenoler, mens Metode III gir like god presisjon for de forbindelser som kan analyseres kromatografisk med denne metoden.

Selektivitet (kromatografisk oppløsning). GC-MS med negativ kjemisk ionisering (NCI) gir mye bedre selektivitet enn elektron-impakt (EI). Detaljert diskusjon av årsakene når det gjelder alkylfenoler kan finnes i Boitsov et al. (2004).

I tabell 4 er det gitt resultater for noen forbindelser som illustrerer forskjell i selektiviteten mellom de to kromatografiske teknikkene.

Tabell 4. Gjenvinning og relativ standardavvik av enkelte alkylfenoler analysert med 3 forskjellige metoder. Forbindelser etter skråstrekk står for frie fenoler som er ikke kromatografisk adskilt og gir summert verdi.

Forbindelse	Gjenvinning, %			Relativ standardavvik, %		
	I	II	III	I	II	III
m-Cresol / m-Cresol + p-Cresol	80	68	81	6	8	13
p-Cresol	91	82	-	5	8	-
3-Ethylphenol / 3-Ethylphenol + 4-ethylphenol	101	114	127	1	9	5
4-Ethylphenol	99	148	-	2	12	-
2,3,5-Trimethylphenol + 4-n-Propylphenol	128	207	131	7	28	4

Både metode I og II gir mulighet å analysere langt flere alkylfenoler enn Metode III. Som eksempel, gitt i Tabell 4, er det mulig å kvantifisere både p-Kresol og 4-Etylfenol med de to første metodene men ikke med metode 3. Det er også enkelte forbindelser som blir ikke adskilt kromatokrafisk ved bruk av de to første metoder, som for eksempel 2,3,5-timetylfenol og 4-n-propylfenol, men disse er heller ikke adskilt ved metode III. Blant de studerte 48 alkylfenoler, er det bare 2 par som kan ikke skilles med Metoder I og II (andre paren er 3-n-Propylphenol og 3-Ethyl-5-Methylphenol), mens det er 17 alkylfenoler som er ikke adskilt med Metode III (se resultatene i Appendiks).

Det er derfor ikke ønskelig å bruke Metode III hvis man vil finne konsentrasjoner til enkelte alkylfenoler. Som det fremgår fra eksempel i Tabell 4, man kan likevel oppnå relativt gode resultater for disse forbindelser med denne metoden hvis man ønsker å måle summen av alkylfenoler.

Følsomhet (LOQ og LOD verdier til metoden). Kvantifiserings- og deteksjonsgrense for metoden (hh. LOQ og LOD) gis vanligvis som mengde forbindelse funnet i blank prøve pluss 3 ganger standardavvik for denne forbindelse (LOD) eller 10 ganger standardavviket (LOQ).

Som man kan se i Appendiks Tabell A, det er ikke funnet forstyrrelser i blank prøver for de fleste av 48 alkylfenoler; der hvor det er funnet noe (typisk for fenol og kort-kjedete fenoler som finnes i størst mengde både i produsert vann, men også for nonylfenol som er funnet i mange typer plast og gummi brukt på laboratoriet), er nivåene svært lave sammenlignet med nivåer i produsert vann.

Det er derfor andre parametrer som definerer LOD og LOQ for alkylfenoler i de studerte prøvene, som linearitetsområde for måling av alkylfenoler med denne kromatografiske teknikken. Denne er svært lav for NCI, for eksempel 0,03 pg/µl for 4-n-oktylfenol pentafluorobenzoat, og er ca. 10 ganger høyere for EI, for eksempel 0,9 pg/µl for samme forbindelse.

Det er likevel en annen faktor som forstyrrer effektiv analyse ved uderivatiserte alkylfenoler når det gjelder produsert vann. Siden slike prøver inneholder en svær mengde organiske forbindelser av forskjellig type, opprensningsteknikken brukt med Metoden III (GPC) er ikke tilstrekkelig for å fjerne noen av disse forbindelser fullstendig. Dette tillater ikke å analysere de alkylfenoler som finnes i lavest mengde i produsert vann, nemlig langkjedete alkylfenoler (omtrent C6- og oppover). Massespektrometrisk analyse av forbindelser funnet ved samme retensjonstider som tilsvarende alkylfenoler (bestemt fra en standard) peker på at det er andre forbindelser av samme masse som er tilstedet. Et eksempel er gitt i Tabell 5 mens fullstendige data er gitt i Appendiks B.

Tabell 5. Resultater av produsert vann analyse med de tre analytiske metoder, for et utvalg alkylfenoler (gjennomsnitt av 5 paralleller korrigert for blank verdi). Ikke kvantifiserbare resultater er merket med ”nq”.

Forbindelse	Konsentrasjon, µg/L			Relativ standardavvik, %		
	I	II	III	I	II	III
Phenol	2501	5706	3105	12	6	6
p-Cresol	756	849	-	3	3	-
4-tert-Butyl-2-methylphenol	0,12	9,6	1,6	38	13	56
4-(1,1-Dimethylpropyl)phenol	1,5	1,1	1,7	7	35	59
4-n-Pentylphenol	0,56	0,35	0,53	8	20	31
2-tert-Butyl-4-Ethylphenol	1,9	2,2	nq	8	10	107
4-n-Hexylphenol	0,08	0,08	nq	27	24	35
4-(1-Ethyl-1-Methylpropyl)-2-methylphenol	0,08	0,11	nq	24	12	36
4-n-Heptylphenol	0,03	0,03	nq	9	28	94
4-n-Octylphenol	0,00	0,00	nq	-	-	8
4-n-Nonylphenol	0,03	0,16	nq	256	164	75

Som man ser fra eksemplet i Tabell 5, det er ikke mulig å kvantifisere langkjedete alkylfenoler med Metode III, selv om for alkylfenoler av lavere molekylarmasse, som finnes i større mengde i produsert vann, får man like resultater med de to andre metoder, eller bedre for orto-substituerte forbindelser (hvor de er kromatografisk adskilt).

Konklusjon

Valg av beste metoden er avhengig av formålet med forsøket. Ønsker man å få en estimat av total mengde alkylfenoler, med fokus på kortkjedete alkylfenoler som finnes i høyest konsentrasjon i produsert vann, kan man gjerne bruke Metode III som trenger verken derivatisering eller NCI-ionekilde på masse-spektrometeret. Summerte resultater oppnådd med denne metoden er like presise som det man får med de to andre metoder, og bedre i tilfelle orto-substituerte alkylfenoler. Men det går ikke an å analysere mange enkelte alkylfenoler med denne metoden, og ikke langkjedete alkylfenoler heller. Man kan også bemerke at Metode III krever relativt stor forbruk av dyrt og helseskadelig organisk løsemiddel, diklormetan, og gir ingen gevinst i tiden pga. behov for GPC-oppresning.

Hvis man ønsker et detaljert bilde av mange enkelte alkylfenoler, og spesielt langkjedete meta- og para-substituerte alkylfenoler (men også mange kortkjedete fenoler, inkludert alle C0-C2 fenoler), er metode I best. Metoden er robust og svært følsom, men krever NCI ionekilde installert på mass-spektrometeret.

Metode II kan være aktuell for videre uttesting, siden dette kan føre til sparing av tid. Foreløpig er den ikke anbefalt til bruk for denne type analyser.

Referanser

S. Boitsov, S. Meier, J. Klungsøyr, A. Svardal (2004). Gas chromatography–mass spectrometry analysis of alkylphenols in produced water from offshore oil installations as pentafluorobenzoate derivatives. Journal of Chromatography A, 1059, 131-141.

S.Boitsov, S.A. Mjøs, S. Meier (2007). Identification of estrogen-like alkylphenols in produced water from offshore oil installations. Marine Environmental Research, 64, 651-665.

G. Jonsson (2004). Personal communication.

G. Jonsson, A. Cavcic, T. U. Stokke, J. Beyer, R. C. Sundt, C. Brede (2008). Solid-phase analytical derivatization of alkylphenols in fish bile for gas chromatography-mass spectrometry analysis. Accepted for publication by Journal of Chromatography A in December 2007.

S. Meier, J. Klungsøyr, S. Boitsov, T. Eide, A. Svardal (2005). Gas chromatography–mass spectrometry analysis of alkylphenols in cod (*Gadus morhua*) tissues as pentafluorobenzoate derivatives. Journal of Chromatography A, 1062, 255-268.

S.A. Mjøs, S. Meier, S. Boitsov (2006). Alkylphenol retention indices. Journal of Chromatography A, 1123, 98-105.

SINTEF Rapport (2002). Forfattere: G. Durell, B. Liu, and L.-G. Faksness, Produced Water Phenol Analysis. Summary report from the Round Robin Study. SINTEF Applied Chemistry, Trondheim.

Appendiks A. Resultater av spikeforsøket, alkylfenoler i destillert vann analysert med metodene I, II, III. Forbindelser etter skråstrekk står for frie fenoler som er ikke kromatografisk adskilt og gir summert verdi.

Forbindelse	Mengde tilsatt, ng *(per 100 ml vann)*	Mengde funnet, ng *(gjennomsnitt 5 paralleller, korrigert for blank)*			Mengde funnet i blank, ng			Gjenvinning, %			Relativ standardavvik, %		
		I	II	III	I	II	III	I	II	III	I	II	III
Phenol	79200	70596	76652	65886	360	611	249	89	97	83	6	5	8
o-Cresol	74880	64009	79261	65245	103	26	57	85	106	87	5	12	5
m-Cresol / m-Cresol + p-Cresol	85600	68600	58480	122761	51	15	217	80	68	81	6	8	13
p-Cresol	65440	59302	53875	-	63	15	-	91	82	-	5	8	-
2-Ethylphenol	4975	7910	11595	4146	0,6	1,6	8,0	159	233	83	2	14	1
2,6-dimethylphenol	6775	5765	33259	5481	0	6,0	11	85	491	81	14	40	4
2,5-Dimethylphenol	9250	8212	8115	9521	1,0	3,0	11	89	88	103	2	8	6
2,4-Dimethylphenol	9350	7398	8360	10408	1,0	0	17	79	89	111	2	6	8
3-Ethylphenol / 3-Ethylphenol + 4-ethylphenol	6875	6968	7864	21049	18	6,6	18	101	114	127	1	9	5
3,5-Dimethylphenol	13600	9817	6400	16477	365	9,7	12	72	47	121	4	9	6
4-Ethylphenol	9700	9623	14356	-	27	17	-	99	148	-	2	12	-
2,3-Dimethylphenol	8850	10063	11407	11151	0	2,5	15	114	129	126	3	8	6
3,4-Dimethylphenol	6550	4413	1718	8067	0,7	0	7,0	67	26	123	7	13	2
2-Isopropylphenol	1405	1131	3985	3152	2,5	6,3	0	80	284	224	11	24	5
2-n-Propylphenol	1170	1593	3645	2049	0	0	0	136	312	175	6	17	4
3-Isopropylphenol / 3-Isopropylphenol + 4-isopropylphenol	1255	1176	1376	5103	1,3	0	0	94	110	193	6	12	3
2,4,6-Trimethylphenol	840	1104	36454	1375	0	0	0	131	4340	164	28	87	6
4-Isopropylphenol	1390	1344	1616	-	1,3	0	-	97	116	-	5	17	-
3-n-Propylphenol + 3-Ethyl-5-Methylphenol /	1870	2019	2505	6923	2,8	0	0	108	134	192	6	17	3

3-n-Propylphenol+3-ethyl-5-methylphenol+4-n-propylphenol													
2,3,6-Trimethylphenol	1185	2271	44672	2085	25	0	0	192	3770	176	26	86	7
2,3,5-Trimethylphenol + 4-n-Propylphenol	2475	3176	5115	964	1,9	2,6	0	128	207	131	7	28	4
2-tert-Butylphenol	122	858	4965	139	25	92	0	704	4070	114	13	31	3
5-Methyl-4-isopropylphenol / 5-Methyl-4-isopropylphenol+3-methyl-4-isopropylphenol	104	173	545	209	0	0	0	166	524	72	8	49	1
3-tert-Butylphenol	206	175	196	217	0	0	0	85	95	105	2	11	5
5-Isopropyl-3-methylphenol	86	98	160	-	0	0	-	113	185	-	2	14	-
4-tert-Butylphenol	255	226	217	219	29	88	0	89	85	86	7	11	8
4-sec-Butylphenol / 4-sec-Butylphenol+3-methyl-5-isopropylphenol	103	88	114	149	0	0	0	86	111	79	2	13	2
4-Isopropyl-3-metylphenol	185	164	180	-	0	0	-	88	97	-	2	20	-
4-n-butylphenol	108	93	121	67	0	0,8	0	87	113	62	3	10	3
2,3,5,6-Tetramethylphenol	66	190	3379	46	0	0	0	291	5159	70	35	93	9
2-tert-Butyl-4-methylphenol	49	0,0	9121	60	2508	0	0	0	18768	122	-	30	10
2-tert-Butyl-5-methylphenol / 2-tert-Butyl-5-methylphenol+2-tert-butyl-6-methylphenol	72	2074	9866	184	0	0	31	2873	13664	153	24	27	10
2-tert-Butyl-6-methylphenol	48	277	24186	-	0	0	-	577	50387	-	99	91	-
4-tert-Butyl-2-methylphenol	37	70	110	39	0	0	0	191	299	108	6	17	8
4-(1,1-	31	39	38	33	0	0,4	0	126	123	107	6	10	5

Dimethylpropyl)phenol													
4-n-Pentylphenol	44	48	47	42	0	0	0	110	108	96	4	7	5
2,6-Diisopropylphenol	8,6	682	1016	12	0	0	0	7972	11887	137	8	93	9
2-tert-Butyl-4-Ethylphenol	5,8	0,0	0,0	5,5	4,4	0	0	0	0	95	-	-	9
4-(1,1-Dimethylbutyl)phenol	4,2	4,6	5,0	5,6	0	0	0	111	119	134	5	10	5
4-(1,2,2-Trimethylpropyl)phenol	4,9	5,8	5,9	4,9	0	0	0	119	122	101	4	10	8
4-n-Hexylphenol	4,5	3,2	6,5	5,6	1,4	0	0	71	145	124	10	6	14
4-(1-Ethyl-1-Methylpropyl)-2-methylphenol	13,2	20	43	10	0	0	0	150	326	77	3	37	5
4-(1,1-Dimethylpentyl)phenol	6,5	6,7	9,5	6,3	0	0	0	102	146	96	5	19	8
4-n-Heptylphenol	6,3	5,7	8,8	4,9	0	0	0	91	140	79	5	60	8
4-tert-Octylphenol	8,9	9,3	14	9,2	0,9	0	0	104	162	103	8	10	18
4-n-Octylphenol	4,9	7,1	8,4	10	0	0	0	146	171	212	25	35	36
4-n-Nonylphenol	5,1	4,6	3,8	11	0	1,0	0	90	75	219	15	61	24
Gjennomsnitt uten ortho-substituerte								99	127	117	6	17	9
Gjennomsnitt alle								356	2512	120	10	26	8

Appendiks B. Resultater av analyse av produsert-vann prøver med metodene I, II, III. Forbindelser etter skråstrekk står for frie fenoler som er ikke kromatografisk adskilt og gir summert verdi. Ikke kvantifiserbare resultater er merket med ”nq”.

Forbindelse	Konsentrasjon, µg/L *(gjennomsnitt 5 paralleller, korrigert for blank)*			Relativ standardavvik, %		
	I	II	III	I	II	III
Phenol	2501	5706	3105	12	6	6
o-Cresol	1266	1809	1117	9	2	47
m-Cresol / m-Cresol + p-Cresol	1020	1099	1401	3	4	43

p-Cresol	756	849	-	3	3	-
2-Ethylphenol	129	169	327	12	5	48
2,6-dimethylphenol	85	410	318	32	16	46
2,5-Dimethylphenol	109	132	426	3	6	98
2,4-Dimethylphenol	159	176	1414	3	2	49
3-Ethylphenol / 3-Ethylphenol + 4-ethylphenol	201	239	1358	9	4	46
3,5-Dimethylphenol	88	86	862	2	6	66
4-Ethylphenol	63	101	-	13	5	-
2,3-Dimethylphenol	54	39	645	6	7	83
3,4-Dimethylphenol	42	24	972	1	9	53
2-Isopropylphenol	27	152	29	16	14	64
2-n-Propylphenol	21	37	23	5	7	130
3-Isopropylphenol / 3-Isopropylphenol + 4-isopropylphenol	29	66	121	6	14	88
2,4,6-Trimethylphenol	154	905	12	48	34	93
4-Isopropylphenol	40	127	-	6	12	-
3-n-Propylphenol + 3-Ethyl-5-Methylphenol / 3-n-Propylphenol + 3-ethyl-5-methylphenol + 4-n-propylphenol	63	193	106	4	20	90
2,3,6-Trimethylphenol	32	307	13	44	37	61
2,3,5-Trimethylphenol + 4-n-Propylphenol	24	66	45	9	22	134
2-tert-Butylphenol	114	1099	4,6	35	27	71
5-Methyl-4-isopropylphenol / 5-Methyl-4-isopropylphenol+3-methyl-4-isopropylphenol	30	86	5,9	5	8	91
3-tert-Butylphenol	0,13	0,38	23	45	16	136
5-Isopropyl-3-methylphenol	15	40	-	3	18	-
4-tert-Butylphenol	0,35	0,33	10	29	108	115
4-sec-Butylphenol / 4-sec-Butylphenol+3-methyl-5-isopropylphenol	16	23	46	24	6	89
4-Isopropyl-3-metylphenol	3,7	6,8	-	24	30	-
4-n-butylphenol	2,1	3,3	1,3	5	10	79
2,3,5,6-Tetramethylphenol	2,2	15	5,1	32	46	78
2-tert-Butyl-4-methylphenol	30	155	2,2	75	24	34

2-tert-Butyl-5-methylphenol / 2-tert-Butyl-5-methylphenol+2-tert-butyl-6-methylphenol	328	283	1,2	10	22	89
2-tert-Butyl-6-methylphenol	138	45	-	8	59	-
4-tert-Butyl-2-methylphenol	0,12	9,6	1,6	38	13	56
4-(1,1-Dimethylpropyl)phenol	1,5	1,1	1,7	7	35	59
4-n-Pentylphenol	0,56	0,35	0,53	8	20	31
2,6-Diisopropylphenol	90	16	nq	13	167	29
2-tert-Butyl-4-Ethylphenol	1,9	2,2	nq	8	10	107
4-(1,1-Dimethylbutyl)phenol	0,08	0,10	nq	13	11	34
4-(1,2,2-Trimethylpropyl)phenol	0,02	0,00	nq	7	224	18
4-n-Hexylphenol	0,08	0,08	nq	27	24	35
4-(1-Ethyl-1-Methylpropyl)-2-methylphenol	0,08	0,11	nq	24	12	36
4-(1,1-Dimethylpentyl)phenol	0,01	0,00	nq	18	-	27
4-n-Heptylphenol	0,03	0,03	nq	9	28	94
4-tert-Octylphenol	0,00	0,00	nq	-	-	24
4-n-Octylphenol	0,00	0,00	nq	-	-	8
4-n-Nonylphenol	0,03	0,16	nq	256	164	75
Gjennomsnitt uten ortho-substituerte				21	32	59
Gjennomsnitt alle				22	30	65

Table 2. Amount of alkylphenols found in produced water with the relevant analytical method. Compounds after slash are the phenols which are not chromatographically separated and are given as sum value. Non-quantifiable results are marked with “nq”.

Forbindelse	Konsentrasjon, µg/L *(gjennomsnitt 5 paralleller, korrigert for blank)*	Relativ standardavvik, %
Phenol	3105	6
o-Cresol	1117	47
m-Cresol / m-Cresol + p-Cresol	1401	43
p-Cresol	-	-
2-Ethylphenol	327	48
2,6-dimethylphenol	318	46
2,5-Dimethylphenol	426	98
2,4-Dimethylphenol	1414	49
3-Ethylphenol / 3-Ethylphenol + 4-ethylphenol	1358	46
3,5-Dimethylphenol	862	66
4-Ethylphenol	-	-
2,3-Dimethylphenol	645	83
3,4-Dimethylphenol	972	53
2-Isopropylphenol	29	64
2-n-Propylphenol	23	130
3-Isopropylphenol / 3-Isopropylphenol + 4-isopropylphenol	121	88
2,4,6-Trimethylphenol	12	93
4-Isopropylphenol	-	-
3-n-Propylphenol + 3-Ethyl-5-Methylphenol / 3-n-Propylphenol + 3-ethyl-5-methylphenol + 4-n-propylphenol	106	90
2,3,6-Trimethylphenol	13	61
2,3,5-Trimethylphenol + 4-n-Propylphenol	45	134
2-tert-Butylphenol	4,6	71
5-Methyl-4-isopropylphenol / 5-Methyl-4-isopropylphenol+3-methyl-4-isopropylphenol	5,9	91
3-tert-Butylphenol	23	136
5-Isopropyl-3-methylphenol	-	-
4-tert-Butylphenol	10	115
4-sec-Butylphenol / 4-sec-Butylphenol+3-methyl-5-isopropylphenol	46	89
4-Isopropyl-3-metylphenol	-	-
4-n-butylphenol	1,3	79
2,3,5,6-Tetramethylphenol	5,1	78
2-tert-Butyl-4-methylphenol	2,2	34
2-tert-Butyl-5-methylphenol / 2-tert-Butyl-5-methylphenol+2-tert-butyl-6-methylphenol	1,2	89
2-tert-Butyl-6-methylphenol	-	-
4-tert-Butyl-2-methylphenol	1,6	56
4-(1,1-Dimethylpropyl)phenol	1,7	59
4-n-Pentylphenol	0,53	31

2,6-Diisopropylphenol	nq	29
2-tert-Butyl-4-Ethylphenol	nq	107
4-(1,1-Dimethylbutyl)phenol	nq	34
4-(1,2,2-Trimethylpropyl)phenol	nq	18
4-n-Hexylphenol	nq	35
4-(1-Ethyl-1-Methylpropyl)-2-methylphenol	nq	36
4-(1,1-Dimethylpentyl)phenol	nq	27
4-n-Heptylphenol	nq	94
4-tert-Octylphenol	nq	24
4-n-Octylphenol	nq	8
4-n-Nonylphenol	nq	75
Gjennomsnitt uten ortho-substituerte		59
Gjennomsnitt alle		65

Appendix B. Description of the analytical method used by Westlab Intertek AS in this work for the determination of alkylphenols in produced water. (In Norwegian)

Havforskningsinstituttet

Nykirkekaien 1

5004 Bergen|

Kontaktperson: Stephan Boitsov

Rapport: 2008-07974

Dato: 10.05.2010

Side: 1 av 3

Utgave: 1

Vedlegg til rapport nr 2008-07974, Ringtest alkylfenoler

Analysene er utført i henhold til Intertek Westlab's interne Metode, M-038, Alkylfenoler i vann. Vår metode er laget med referanse til "OLF's retningslinjer for prøvetaking og analyse av produsertvann". Metode M-038avviker fra ringtestens metodebeskrivelse og avvik er vist i tabell 1.

Kort metodebeskrivelse av M-038

Vannprøven, som er surgjort ved prøvetaking, tilsettes deutererte intern- og surrogat-standarder og ekstraheres over i DCM ved hjelp av magnetrører og skilletrakt. Ekstraktet dampes inn vha inndampningsenhet og analyseres ved GC/MS-SIM-analyse. Som intern standarder benyttes Phenol-d5, Cresol-d8 og Phenanthrene-d10. Som surrogat standarder benyttes naphtalene-d8, biphenyl-d10, 4-eyhylphenol-s10, 4-tert-butylphenol-d13, 4-n-octylphenol-d17 og 2,6-ditertbutyl-4-methylphenol-d20.

Komponenter som ikke inngår i vår metode er ikke rapportert i ringtesten.

Det ferdige ekstraktet er analysert på samme måte som prøvene. Ekstraktet mangler en av våre internstandarder, Phenanthrene-d10. Komponenter som vi kvantifiserer med Phenanthrene-d10 som internstandarder er derfor ikke rapportert for ekstraktet. Dette gjelder for 4-tert-Butylphenol, 4-n-butylphenol og 4-n-Pentylphenol.

En sammenligning melom metode beskrevet av Havforskningsinstituttet, Intertek Westlab's interne Metode M-038 og OLF's retningslinjer er gitt i tabell 1.

Tabell 1. Sammenligning av alkylfenol-metoder

	Havforskningsinstituttet	**Intertek Westlab**	**OLF's retningslinjer**
Filtrering	Filtrering av prøven før ekstraksjon	Prøven filtreres ikke	Prøven filtreres ikke
Ekstraksjon	3 ganger ekstraksjon med DCM	1 ekstraksjon med DCM, røring i minimum 2 timer	3 ganger ekstraksjon med DCM
Opprensning	Opprensning vha GPC	Ingen opprensning av ekstraktet	Opprensning vha GPC
Komponenter rapportert og deres ISTD	**IS Phenol-d5**	**IS Phenol-d5**	**IS Phenol-d5**
	Phenol	Phenol	Phenol
	IS p-Cresol-d8	**IS p-Cresol-d8**	**IS p-Cresol-d8**
	o-Cresol	o-Cresol	o-Cresol
	IS 2,4-Dimethylphenol-d3		**IS 2,4-Dimethylphenol-d3**
	2,4-Dimethylphenol	2,4-Dimethylphenol	2,4-Dimethylphenol
	2,3-Dimethylphenol	Rapporteres ikke som enkelt komponent	Rapporteres ikke som enkelt komponent
	IS 4-Ethylphenol-d10	4-Ethylphenol-d10 benyttes som surrogate std	Komponent inngår ikke i metoden
	2-Ethylphenol	Rapporteres ikke som enkelt komponent	Rapporteres ikke som enkelt komponent
	3,5-Dimethylphenol	3,5-Dimethylphenol	3,5-Dimethylphenol
	IS 4-n-Propylphenol-d12	Komponent inngår ikke i metoden	**IS 4-n-Propylphenol-d12**
	2-Isopropylphenol	2-Isopropylphenol	2-Isopropylphenol
	2-n-Propylphenol	2-n-Propylphenol	2-n-Propylphenol
	2,4,6-Trimethylphenol	2,4,6-Trimethylphenol	2,4,6-Trimethylphenol
	Komponent inngår ikke i metoden	**Phenanthrene-d10**	**Phenanthrene-d10**
	4-tert-Butylphenol	4-tert-Butylphenol	4-tert-Butylphenol
	4-n-butylphenol	4-n-butylphenol	4-n-butylphenol
	IS 4-n-Pentylphenol-d16	Komponent inngår ikke i metoden	Komponent inngår ikke i metoden
	4-n-Pentylphenol	4-n-Pentylphenol	4-n-Pentylphenol
	RIS Pentafluorobenzophenone	Komponent inngår ikke i metoden	Komponent inngår ikke i metoden

Tabell 2. Komponenter som inngår i M-038

Komponent	Intern-standard	Surrogat-standard
fenol	fenol-D5	naftalen-D8 bifenyl-D10
2-metylfenol 3-metylfenol 4-metylfenol	2-metylfenol-D8	4-etylfenol-D10 naftalen-D8 bifenyl-D10
2,4-dimetylfenol 2,5-dimetylfenol 4-etylfenol 3,5-dimetylfenol 2-n-propylfenol 2,4,6-trimetylfenol 2-n-propylfenol 4-n-propylfenol 2,3,5-trimetylfenol 4-tert-butylfenol 4-iso-propyl-3-metylfenol 4-n-butylfenol 2-tert-butyl-4-metylfenol 4-tert-butyl-2-metylfenol 4-n-pentylfenol	fenantren-D10	4-etylfenol-D10 naftalen-D8 bifenyl-D10
2,6-di-iso-propylfenol 6-tert-butyl-2,4-dimetylfenol 2-tert-butyl-4-etylfenol 2,5-di-iso-propylfenol 4-n-hexylfenol 4-n-heptylfenol 2,6-di-tert-butylfenol 2,4-di-sec-butylfenol 4-tert-octylfenol 4-n-octylfenol 2,6-di-tert-butyl-4-metylfenol 4,6-di-tert-butyl-2-metylfenol 2-metyl-4-tert-octylfenol 4-n-nonylfenol	fenantren-D10	4-tert-butylfenol-D13 2,6-di-tertbutyl-4-metylfenol-D20

Med vennlig hilsen

Unn Endresen

Senior kjemiker Miljø

E-post: unn.endresen@intertek.com

Appendix C. The results of NIVA (raw data).

	Blank	1	2	3	4	5	IMR		GPC test
	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/extract	μg/L ???	%
Phenol	Below Cal	4667,93	4718,74	4612,08	4552,08	4681,89	2543,22	5086,44	107
o-cresol	Below Cal	1182,98	1205,25	1178	1228,77	1187,45	579,86	1159,72	91
2,4-Dimethylphenol	Below Cal	312,64	308,83	294,98	314,6	346,18	149,48	298,96	90
2,3-Dimethylphenol	Below Cal	60,28	61,06	58,25	64,85	68,86	57,28	114,56	88
2-Ethylphenol	Below Cal	43,94	44,72	43,92	44,22	45,05	25,13	50,26	88
3,5-Dimethylphenol	Below Cal	156,6	163,8	162,05	171,02	162	81,99	163,98	89
2-Isopropylphenol	0,02	37,4	38,26	36,59	42,73	48,84	14,34	28,68	89
2,4,6-Trimethylphenol	n.d	11,1	11,33	10,84	12,73	14,54	4,48	8,96	83
2-n-propylphenol	n.d	7,17	7,29	6,98	8,09	9,29	3,49	6,98	86
4-tert-butylphenol	0,03	40,5	41,5	39,07	43,77	51,54	20,05	40,1	104
4-n-Butylphenol	0,01	1,91	1,89	1,75	1,91	1,93	0,81	1,62	89
4-n-Pentylphenol	0,02	0,3	0,27	0,23	0,25	0,31	0,12	0,24	91

1. 500μL SIS was added to samples, not 100μL
2. Approximately 2/3 of sample is injected through GPC.
3. Some of extract from samples 4 and 5 were lost during solvent reduction.
4. Solvent reduction by nitrogen not rotary evaporation.
5. Final solvent DCM not hexane.
6. Long gap (10 weeks) between extraction and GPC/ analysis
7. GPC recovery tested as a separate step as we have recently changed our system. Seems ok.
8. IMR sample reported as μg/extract as the extraction volume is unknown?

chain-of-custody documentation was received. Battelle prepared the chain-of-custody documentation as part of the log-in procedure.

nmary of the materials provided by the Institute of Marine Research is listed below.

ratory

ient ID Volume Date Received

7 Produced Water 2 @ 2.5 L January 29, 2009

8 Produced Water Extract in Hexane 1.5 mL January 29, 2009

29-01 Alkylphenol Calibration Solution 20 mL January 29, 2009

29-02

phenol Surrogate Internal

ard (SIS) Solution 8 mL January 29, 2009

29-03

phenol Relative Internal

ard (RIS) Solution 20 mL January 29, 2009

29-04 APRI Standard Solution 20 mL January 29, 2009

ods

le Extraction: Five sub-samples, 500 mL each, of the produced water sample were processed by liquid/liquid extraction. Initially, the pH was ch djusted, if need, to < 2 with the addition of 10 % HCL. The samples were filtered through GF/C glass fiber filter under vacuum. The water was s 100 µL of alkyphenol surrogate internal standards (SIS) and serially extracted three times with dichloromethane (DCM). The filter was extracted using an orbital shaker table for 1 hour. The water extracts and the filter extracts were combined and concentrated to 1 mL using a combinati rna Danish and nitrogen evaporation techniques. The extracts were cleaned-up through HPLC equipped with a size exclusion column to isolate analy st. The extracts were solvent exchanged to hexane and spiked with recovery internal standards (RIS) and submitted for the analysis of alkylphenols b natography/mass spectrometry (GC/MS) in the selected ion monitoring (SIM) mode. The following quality control (QC) samples were processed he batch of produced water samples: a procedural blank (PB) and a laboratory control sample (LCS). The IMR extract was analyzed with the ba cted samples.

le Analysis: The produced water samples and extract provided by IMR were analyzed for l and selected alkylated phenol compounds by GC/MS operating in the SIM mode. An ized, highly compound-specific, mass spectrometric acquisition method was used to ensure le quantitation of the specific compounds of interest and to avoid potential interferences. to sample analysis the GC/MS was tuned with perfluorotributylamine (PFTBA) and calibrated wo initial calibrations to demonstrate the linear range of the analysis: a low level 6-point ation which contains all individual target analytes ranging from .06 ng/µL to 2 ng/µL; and a evel 6-point calibration which contains all individual target analytes ranging from 4 ng/µL to g/µL. Continuing calibration check standards were analyzed at least every 10 samples. The as equipped with a 60-m DB-5 column (0.25 mm ID, 0.25µm film thickness), and a plitless injector (with electronic pressure control) operated in the splitless mode was used. oncentrations of the individual target compounds were calculated by the internal standard od. The individual low level compound concentrations were quantified using average nse factors (RF) generated from the low level initial calibration linear. The high level ound concentrations were quantified using the RF from the high level curve. As a result, each e was quantified using both initial calibrations. Final concentrations were determined versus propriate surrogate compound.

rtical reporting limits and estimated limits of detections were determined for each sample. The ting limits are defined as the sample concentration equivalent to the low level standard. The ated limits of detection are based on a sample concentration equivalent to a signal:noise ratio . The data were qualified with a “J” if the measured concentration was below the reporting Each non-detect was qualified with a “ND”.

ty Assurance/Quality Control

boratory and data assessment and reporting activities were conducted under a Quality System ed in the Quality Assurance Manual for the BDO Laboratory. Project activities were defined aboratory quality assurance project plan (QAPP) that was prepared by the Project Manager and ved by management. The QAPP specified the work to be performed, the analytical methods followed, the measurement quality objectives (MQOs) to be achieved, and level of data v. All sample receipt, storage, preparation, analysis, and reporting procedures followed n Standard Operating Procedures (SOPs). Project staff members were responsible for ving these procedures and ensuring that MQOs were achieved. In the event that an MQO was et, the analytical staff documented all corrective actions taken related to that exceedance. The ct manager reviewed and approved corrective actions. An independent QC Chemist reviewed mple preparation and analytical documentation for completeness and accuracy and conducted rror checking of reported project data. The project manager was responsible for ensuring that ct objectives were met and that the data were traceable and defensible.

ty Control Issues

C data for the produced water analysis were overall good, particularly considering the complex e matrix, low detection limits, and the variable target compound concentrations. The procedural extracted with the batch of samples did not indicate any notable laboratory contamination. alkylphenols were detected, but at concentrations at or below the RL and generally orders of itude lower than what was detected in the field samples.

urrogate recoveries for all of the field and QC samples met the MQO criteria (40 – 120%, l 30 – 120%) with a few exceptions. The surrogate recovery of phenol-d5 in the PB and LCS 3% and 20%, respectively. Also the surrogate recovery of 4-methylphenol-d8 was low in all roduced water samples. The majority of the surrogate recoveries were in the 40 to 115% range.

ecovery of spiked analytes for the laboratory control spike (LCS) results met the MQO criteria – 130%) with a couple of exceptions. The recovery of 2-methylphenol and 2,4,6-hylphenol were lower than expected (64% and 61%, respectively).

PMENT

od of Delivery: Commercial Carrier **Tracking Number:** 4787079205

orms: Shipped with samples No Forms

ler(s)/Box(es)

nples

ype Tracking No. Seal Seal Condition Container Condition Temp C Smps

Cardboard Box 4787079205 Tape Intact Intact 17.3 7

Cardboard Box 4787079205 Tape Intact Intact 13.2 0

le Labels: Sample labels agree with COC forms

pancies (see Sample Custody Corrective Action Form)

iner Seals: Tape Custody Seals Other Seals (See sample Log)

ntact for each shipping container

broken (See sample log for impacted samples)

tion of Samples: Sample containers intact

e containers broken/leaking (See Custody Corrective Action Form)

erature upon receipt (°C): 17.3 Temperature Blank used Yes No

If temperature upon receipt differs from required conditions, see sample log comment field)

les Acidified: Yes No Unknown

pH 5-9?: Yes No NA

individual sample adjustments on the Auxiliary Sample Receipt Form

Residual Chlorine Present?: Yes No NA

individual sample adjustments on the Auxiliary Sample Receipt Form

Space <1% in samples for water VOC analysis: Yes No NA

dual sample deviations noted on sample log

les Containers:

es returned in PC-grade jars: Yes No Unknown /Lot No.: UnKnown

les logged in by: Seyfert, Jeannine **Date/Time:** 01/29/2009 12:00 AM

ge Location: Chem South: Refrigerator - R0003 (Upper Cold **BDO IDs Assigned:** Q6277 - Q6348

oved By: Approved On:

orized By: Authorized On:

d on 4/1/2009 Page 1 of 1

nple Receipt Form Details

No SHP-090203-01

oved: Authorized

ct Number: Client: Institute of Marine Research

ved by: Seyfert, Jeannine **Date/Time Received:** Thursday, January 29, 2009 12:00 AM

f Shipping Containers: 2

d: Client Sample ID: Collection Date: Login Date: Ctrs: Matrix: Temp: pH: TRC: VOC: Stored In: Loc: No: Comments:

telle Project No:1013183-AP

7 Produced water 10/30/08 0:00 02/03/09 10:27 6 WATER 17.3 NA NA NA R0003 (Upper C

8 Produced water extract in hexane 01/26/09 0:00 02/03/09 10:30 1 WATER 17.3 NA NA NA R0003 (Upper C extract

4 Produced Water-1 10/30/08 0:00 02/10/09 13:13 1 WATER 17.3 NA NA NA R0003 (Upper C Q6277

5 Produced Water-2 10/30/08 0:00 02/10/09 13:13 1 WATER 17.3 NA NA NA R0003 (Upper C Q6277

6 Produced Water-3 10/30/08 0:00 02/10/09 13:13 1 WATER 17.3 NA NA NA R0003 (Upper C Q6277

7 Produced Water-4 10/30/08 0:00 02/10/09 13:14 1 WATER 17.3 NA NA NA R0003 (Upper C Q6277

8 Produced Water-5 10/30/08 0:00 02/10/09 13:14 1 WATER 17.3 NA NA NA R0003 (Upper C Q6277

Samples: 7

d on 4/1/2009 Page 1 of 1

ort Corrective Actions

orized Approved:

ective Action No: 1 of

No: SHP-090203-01

telle Project No:1013183-AP

Client: Institute of Marine Research

Project: Institute of Marine Research

Date: 2/3/2009 10:02:00 AM

mentation of project manager notification

: 2/3/2009 10:32:00 AM

:

: 2/10/2009 11:53:00 A

mentation of client notification (should be completed by project manager within 24 hrs):

contacted at

ts of communication with client (Describe any corrective action directed by the client):

d with analysis.

this form was received back to the custodian:

rence Number:

ple Custodian Seyfert, Jeannine

oratory Manager:

ect Manager: Krahforst, Kerylynn

ription of Problem: Explanation:

e samples arrived without a COC. A

was created in-house by the sample

dian.

ody Incomplete sample custody forms

e samples were received at ambient

erature.

erature Receipt temperature outside of acceptability

ID	Q6347-P	Q6348-P
Type	SA	SA
on Date	10/30/2008	10/30/2008
on Date	02/17/2009	02/17/2009
s Date	03/05/2009	03/05/2009
al Instrument	MS	MS
ture	NA	NA
	NA	NA
	WATER	WATER
Size	0.50	0.50
t-Basis	L_LIQUID	L_LIQUID
	UG/L_LIQUID	UG/L_LIQUID

405.32 D 4205.59 D
lphenol 2548.28 D 2305.07 D
ethylphenol 301.08 D 274.23 D
thylphenol 52.59 D 52.60 D
henol 73.28 69.00
ethylphenol 578.85 D 552.75 D
pylphenol U U
ylphenol 8.40 8.33
nethylphenol U U
tylphenol 5.19 5.15
lphenol 2.32 2.24
ylphenol 0.20 J 0.19 J

te Recoveries (%)

5 43 44
lphenol-d8 37 N 42
ethylphenol-d10 68 71
henol-d10 51 56
ylphenol-d12 87 93
ylphenol-d16 111 115

By Thorn, Jonathan

09-0029MS-New_Phenols:FINAL

e Corrected

ID	BM858PB-P
Type	PB
on Date	02/17/2009
on Date	02/17/2009
s Date	03/04/2009
al Instrument	MS
ture	NA
	NA
	WATER
Size	0.50
t-Basis	L_LIQUID
	UG/L_LIQUID

U
lphenol 0.04 J
ethylphenol 0.03 J
thylphenol 0.01 J
henol U
ethylphenol 0.02 J
pylphenol U
ylphenol U
nethylphenol U
tylphenol 0.05 J
lphenol U
ylphenol U

te Recoveries (%)

5 23 N
lphenol-d8 43
ethylphenol-d10 49
henol-d10 51
ylphenol-d12 51
ylphenol-d16 42

Analyzed By Thorn, Jonathan

Project Client: Institute of Marine Research
Project Name: Intercalibration for Alkylphenols
Project Number: C1013183-AP

Client ID Laboratory Control Sample

Battelle ID BM859LCS-P
Sample Type LCS
Collection Date 02/17/2009
Extraction Date 02/17/2009
Analysis Date 03/04/2009
Analytical Instrument MS
% Moisture NA
% Lipid NA
Matrix WATER
Sample Size 0.50
Size Unit-Basis L_LIQUID
Units UG/L_LIQUID **Target % REC Qual**

Phenol 39.11 50.04 78
2-Methylphenol 17.11 26.84 64 N
2,4-Dimethylphenol 25.99 20.04 130
2,3-dimethylphenol U
2-ethylphenol U
3,5-Dimethylphenol 18.26 26.08 70
2-isopropylphenol U
2-n-Propylphenol U
2,4,6-trimethylphenol 16.07 26.16 61 N
4-tert-Butylphenol 3.27 4.68 70
4-n-butylphenol 4.18 5.14 81
4-n-pentylphenol 0.03 J

Surrogate Recoveries (%)
Phenol-d5 20 N
4-Methylphenol-d8 45
2,4-Dimethylphenol-d10 54
4-ethylphenol-d10 53
4-n-Propylphenol-d12 55
4-n-pentylphenol-d16 54