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# 085 – Norwegian Oil and Gas recommended guidelines for sampling and analysis of produced water

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Translated version

## FOREWORD

These guidelines are recommended by the Norwegian Oil and Gas specialist network for sampling and analysis of produced water and by its committee for the environment. They have also been approved by the director general.

The work group has had the following membership:

- Trude Haaskjold Eide Statoil
- Turid Gylta Bertelsen Statoil
- Iselin Haaland BP
- Monica Aasberg ConocoPhillips
- Els Holsbrink-Denkens Shell
- Eyvind Sørhaug Talisman-energy
- Ragnar Storhaug Aquateam
- Eilen A Vik Aquateam
- Torgeir Rødsand ALS Laboratory Group Norway AS
- Torbjørn Tyvold Intertek West Lab

The responsible manager in Norwegian Oil and Gas is the manager for discharges to the sea, who can be contacted via the Norwegian Oil and Gas switchboard on +47 51 84 65 00.

The guidelines give expression to a collective solution which has been negotiated between the operators in consultation with expertise from the laboratory sector.

These Norwegian Oil and Gas guidelines have been developed with broad industry participation from interested parties in the Norwegian petroleum sector, and are owned by the Norwegian petroleum industry represented by Norwegian Oil and Gas. Their administration has been allocated to Norwegian Oil and Gas.

Norwegian Oil and Gas  
Vassbotnen 1, NO-4313 Sandnes  
P O Box 8065  
NO-4068 Stavanger  
Telephone: +47 51 84 65 00  
Telefax: +47 51 84 65 01  
Website: [www.norskoljeoggass.no](http://www.norskoljeoggass.no)  
E-mail: [firmapost@norog.no](mailto:firmapost@norog.no)

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## 1 INTRODUCTION

Guidelines for sampling and chemical analysis of produced water to identify organic and inorganic components as well as radioactive elements were originally developed by the Norwegian Oil and Gas work group on discharges to the sea in 2003. Because the Norwegian Climate and Pollution Agency (Klif) has introduced certain new requirements for monitoring discharges, the guidelines have been revised by the Norwegian Oil and Gas work group in relation to new requirements for discharge reporting – revision of Norwegian Oil and Gas guidelines 085.

### 1.2 Purpose

The purpose of the guidelines is to achieve the most uniform possible practice in order to obtain comparable analysis results for produced water from different producing fields, regardless of where the samples are taken and which laboratories conduct the analyses. In order to fulfil Klif's regulations for discharge monitoring, the guidelines include a number of requirements on the sampling point, how samples should be taken, analysis techniques related to separation, quantification limits and uncertainty assessments. The guidelines apply to sampling and analysis of produced water and jetting sand, regardless of whether the water is discharged or injected below ground for periods.

In addition, the guidelines specify procedures for implementing online oil in water meters, requirements/recommendations for metering water discharges, and calculation rules for reporting multi-component parameter groups.

Norwegian Oil and Gas recommends that characterisation of produced water is carried out at least twice a year. This frequency must be increased on installations where the composition of produced water changes – from receiving new wellstreams, for example, new satellite developments, other installations or new treatment facilities – so that possible alterations are documented. Data for produced water discharges must be reported annually to the Environmental Web (EW) database. See the Norwegian Oil and Gas guidelines 044 on reporting of discharges.

### 1.2 Terminology, definitions and abbreviations

AAS: Atomic absorption spectroscopy

BTEX – Benzene, toluene, ethylbenzene and xylene. Typical volatile organic compounds(VOC)

CV-AAS: Cold vapour atomic absorption spectroscopy

DRC-ICP-MS: Dynamic reaction cell inductively coupled plasma mass spectrometry

GC-FID: Gas chromatograph with a flame ionisation detector

GC-MS: Gas chromatograph with a mass spectrometer detector

HG-AAS: Hydride generation atomic absorption spectroscopy

HR-ICP-MS: High resolution inductively coupled plasma mass spectrometry

ICP-AES: Inductively coupled plasma atomic emission spectroscopy

ICP-MS: Inductively coupled plasma mass spectrometry

ITP: Isotachophoresis

LOD: Limit of detection

LOQ: Limit of quantification

NPD: Naphthalenes, phenanthrenes and dibenzothiophenes. Indicators of oil pollution  
PAH: Polyaromatic hydrocarbons

### 1.3 References

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Ospar. Oil in Produced Water Analysis - Guidelines on Criteria for Alternative Method Acceptance and General Guidelines on Sample Taking and Handling, Agreement 06-06.

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Standards Norway. NS-EN ISO 3170 Petroleumsvæsker Manuell prøvetaking. 2004 (ISO 3170:2004).

## 2 OVERVIEW OF AMENDMENTS

### 2.1 Summary

Klif presented new requirements for certain of the operators on the Norwegian continental shelf (NCS) in December 2011. This has required some amendments to the guidelines.

Norwegian Oil and Gas still recommends that characterisation of the produced water is carried out at least twice a year.

Water samples for analysis of radioactive elements can now be kept in plastic bottles. Glass bottles can also be used, but plastic is recommended to reduce the risk of breakages.

Oil in water was earlier analysed in accordance with ISO NS EN 9377-2, but is analysed today in accordance with Ospar 2005-15, a modification of NS-EN ISO 9377-2.

Low-level radioactive elements in produced water. The Norwegian Radiation Protection Authority specified new requirements in 2011 and 2012, which clarify sampling frequencies.

Plastic bottles must be used when sampling for analysing produced water with regard to metals, including arsenic. An exception continues to be made for mercury, which must be kept in glass bottles with a teflon seal and stopper.

The quantification limit for radioactivity in water was earlier specified as 0.2 becquerels per litre (Bq/l). According to the Norwegian Institute for Energy Technology (IFE), this was an error. The limit is now specified as 0.5-1.0 Bq/l.

## 1 SAMPLING

### 1.1 General

Sampling must be conducting in such a way that the most representative possible samples are obtained from the discharge point. The possibility of contamination from the surroundings or for vaporisation are high for a number of the components. Samples for analysing organic components, metals and radioactive components must be taken under normal operational conditions. In the event of a possible temporary halt to produced water discharges, the samples must be taken after a period of normal flow. Samples for analysing oil in water must be taken at fixed times during the day, without regard to whether operational conditions are normal. General requirements for and recommendations on sampling are provided below.

### 1.2 Sampling point

#### 1.2.1 Positioning of the sampling point

The sampling point must be positioned adjacent to or immediately downstream from relevant treatment units, and in a location where it is possible to obtain a representative sample of the whole water flow being discharged to the sea. Water turbulence must be good and the produced water flow must not be diluted in the area where the sampling point is positioned. The sampling point should be positioned after the flow meter for produced water. If water flow at the sampling point is continuous, the point must be positioned after the flow meter.

#### 1.2.2 Configuration of the sampling point

It is recommended that the sampling point be positioned in a vertical section of the flowline, because the probability that layering will occur in the water flow there is substantially lower than with a position on a horizontal piping section. Under given conditions, the sampling point can also be positioned on a horizontal section. This is then conditional on measures being taken to ensure adequate turbulence. A pitot tube extended into the water flow should be used to take samples. It should have a minimum diameter of 0.5 inches.

The distance from the pipe wall to the intake end of the pitot tube should be a minimum of  $0.25 \cdot D$  (where  $D$  = the pipe diameter). The intake opening of the pitot tube should face the water flow. Should it prove difficult in practice to use a pitot tube to take samples, they can be taken directly through the flowline wall. This is conditional on turbulent flow being present in the pipe, so that under- or over-reporting of quantities is avoided.

Taking samples directly through the flowline wall at the top or bottom of horizontal flowlines is not recommended and should be avoided.

More detailed information on the configuration of the sampling point can be found in NS-EN ISO 3170 and NS-EN ISO 3171 (Standards Norway, 2004), (Standards Norway, 1999). These standards have been established for sampling petroleum liquids, but the sections concerning configuration of the sampling point are also relevant for taking samples of produced water.

The distance between the intake opening on the pitot tube and the shutoff valve where the sample is transferred to the sample bottle should be as short as possible. This is important to avoid dead volume which can cause unrepresentative samples to be taken in cases where the sampling system is inadequately flushed through before the sample is taken. Where possible, the water should be allowed to flow continuously at the sampling point.

Materials used in the sampling system must not contaminate the sample. Stainless steel will normally be a natural choice offshore. Special properties of the produced water or safety conditions could make it necessary to use special alloys. Plastic or rubber must not be used.

### 1.2.3 Requirements for the sampling point when using online oil in water analysers

Many different types of online oil in water analysers are available on the market. Some carry out analyses in a bypass loop from the main produced-water flow, others have sensors placed directly in the main flow.

When using analysers which require a bypass loop, the bypass flow must be sampled from a correctly configured sampling point in order to ensure representative samples. This is described in more detail in section 3.2.2. Where special requirements for pressure in the bypass loop exist, it may be necessary to pump the water to the online analyser. The distance between the sampling point and the online analyser should be as short as possible.

A sensor installed in the main flow must be positioned in such a way that it is exposed to a representative section of the whole water flow, corresponding to the positioning of a pitot tube as described in section 3.2.2.

### 1.3 Requirements for the sampling bottle

Sampling bottles must be washed and prepared at the analysis laboratory and labelled for their purpose. See table 1. Bottles for samples taken quarterly or monthly (radioactive elements) and for those taken every six months (organic components and metals) will normally be prepared at the laboratory on land. The daily samples for analysis of oil in water will be prepared by the laboratory on the installation.

**Table 1. Packing requirements for produced-water sampling**

Parameter group	Sample packaging	Preparation and other requirements for packaging
Oil in water	Glass bottles with teflon seal and stopper	Bottles must be cleaned and rinsed in n-pentane.  Hydrochloric acid (abt 1 ml 6 N HCl per 100 ml sample) must be added to the sample bottles.
Metals incl arsenic	Plastic bottles (polyethylene)	Bottles must be washed in nitric acid and rinsed with de-ionised water.
Mercury	Glass bottles <sup>1</sup> with teflon seal and stopper	
Organic components	Glass bottles with teflon seal and stopper	Before dispatch of the sample packaging from the laboratory, the bottles must be machine-washed and rinsed with de-ionised water.  Hydrochloric acid (abt 1 ml 6 N HCl per 100 ml sample) must be added to the sample bottles.
Radioactive elements	Plastic bottles (polyethylene)	The sample bottles must be washed, but no special preparation is required.  Glass bottles can also be used, but plastic is recommended to reduce the risk of breakages.

<sup>1</sup> A study is under way to establish whether mercury can also be analysed from the same sample bottles (plastic) as the other metals.

### 1.4 Labelling and logging

The various operators and laboratories may have different routines for logging and labelling samples. A necessary condition is that operator (client) and laboratory share an understanding of the way samples are to be labelled and logged. In general terms, it is recommended that samples sent to the laboratory should be accompanied by a sample log which contains the following information as a minimum:

- The name of the installation
- The name of the person taking the sample
- The sample number – in other words, an unambiguous reference for the samples in the consignment
- Date and time when the sample was taken

- An unambiguous reference for the sampling point
- The preservation method
- Observations and measurements when taking the sample (colour, odour, viscosity, salinity, much/little oil, etc)
- Possible discrepancies in the sampling

Labels on the sample bottles must not be susceptible to damage by possible freezing/defrosting and by humidity in general. As a minimum, the labels on the bottles must provide the following information:

- Sample number
- Name of the installation
- Sampling point, possibly tag number
- Date and time when the sample was taken
- Method of preservation

## 1.5 Taking samples

### 1.5.1 General

The sampling point must be clearly marked, and the area around it kept clean and tidy. Valves and other equipment must be maintained and function as intended. Before each sample is taken, the sampling system must be flushed well. This is particularly important with sampling points which are used infrequently. Flushing is carried out to prevent particles deposited in the sampling system being transferred to the sample. As a minimum, the water must be allowed to flow through the sampling point long enough for it to have been completely replaced in the system three times. The temperature of a bypass flow must be virtually the same as in the main flow to be sampled. To prevent the sample being polluted by possible oil from the valve on the sampling pipe, this must not be moved immediately before or during the sampling.

Table 2 provides an overview of sample types and volumes normally used for the various components. Sample volumes must be proportionate to the type of analyses to be carried out, and must be clarified with the relevant analysis laboratory. Variations from the sample volumes cited in table 2 could accordingly occur.

**Table 2. Overview of sample types and normal sample volumes for the various parameter groups**

Parameter group	Sample type	Sample volume	Comment
Oil in water	Daily mix sample (daily sampling)	Abt 800-900 ml	The sample is normally taken as three or four part-samples spread over the day.  Eg: 1 000 ml sample (collection) bottle: <u>3 part-samples</u> : one part-sample of 300 ml taken three times per day <u>4 part-samples</u> : one part-sample of 200 ml taken four times a day  Use of oil in water analysers is described in chapter 5
Oil in water	Spot sample	Abt 800-900 ml	Three parallel samples are taken over a short interval. Each sample bottle is first filled to one-third of its volume, all are then filled to two-thirds of the volume, and finally all are filled to their full sample volume.
Metals	Spot sample	Abt 125 ml	
NPD and PAH	Spot sample	Abt 800-900 ml	
Phenols	Spot sample	Abt 800-900 ml	
BTEX	Spot sample	250 ml	
Organic acids	Spot sample	250 ml	
Radioactive elements	Monthly samples	2 000 ml	67 ml of water are taken daily and transferred to the sample bottle, assuming 30 sampling says.

The sample bottles must not be filled to more than the specified sample volume. If that happens, the sample must be discarded and a new sample taken with a fresh bottle. Do not pour away part of a sample from the sample bottle in order to adjust the volume sampled.

The necessary HSE precautions must be taken, given that produced water can have a high temperature and hydrogen sulphide may be driven off when acid has been added to the sample bottles. Normal precautions must also be taken when using acid. BTEX components are volatile, and unnecessary exposure to benzenes must be avoided. It is assumed that these considerations are covered in the operator's HSE system.

### 1.5.2 Sampling to determine oil in water

The bottles must be washed, rinsed with pentane, and have acid added to acidify the sample. When sampling, the water must flow freely down to the sample (collection) bottle. Three or possibly four part-samples are normally taken during the day. The sample bottle must be filled to 80-90 per cent of its full volume.

### 1.5.3 Sampling to determine metals

The bottles must be washed in nitric acid and rinsed with deionised water. During sampling, the water must flow freely down into the sample bottle with the smallest possible gap between bottle and sample offtake without them actually touching. If possible, the offtake pipe should be fitted with a length of silicon rubber hose to prevent contact between metallic components and the sample bottle. The storage method must be based on the requirements of the specific analysis methods to be used, and be specified in advance by the analysis laboratory.

### 1.5.4 Sampling to analyse organic components

Before sampling, the sample bottles must be washed and have concentrated hydrochloric acid (about 1 ml 6 N HCl per 100 ml sample) added at the analysis laboratory. During sampling, the jet of produced water should flow in a way which ensures that as little air as possible is mixed into the sample. This is particularly important for BTEX samples, since these components are volatile. When taking samples for analysis where volatile components are involved, gas-tight sampling containers/piping must be used.

### 1.5.5 Sampling to analyse radioactive elements

The following requirements apply when taking samples for analysis of produced water (Norwegian Radiation Protection Authority, 2011, Norwegian Radiation Protection Authority, 2012).

- Quantity of produced water <3 mill cu.m/y: four monthly mixed samples (one per quarter)
- Quantity of produced water >3 mill cu.m/y: 12 monthly mixed samples
- The samples must be analysed for Ra<sup>226</sup>, Ra<sup>228</sup> and Pb<sup>210</sup>
- When using deposition dissolvers, other chemicals or alternative methods for removing deposits which could be significant for the specific activity of radioactive substances in produced water during the sampling period, the sample must also be analysed for Th<sup>228</sup>. This must be described in the sampling log for the relevant period, the sample is taken as a monthly mixed sample.

This means that a part-sample is taken daily with a measuring cylinder and transferred to the sample (collecting) bottle for sending to the laboratory. The water must flow freely down into the measuring cylinder during sampling. A washed cylinder must be used to take each part-sample. The sample bottle must be washed to protect against contamination, but no special preparation of the bottle is required. Example: With 30 sampling days and a minimum sample volume of 2 000 ml, a part-sample of 67 ml must be taken daily.

During sampling periods with planned turnarounds which cause discharge shutdowns, so that the desired sample volume of 2 000 ml cannot be achieved, the daily part-sample should be increased. To achieve the desired quantification limit, the sample volume must be at least 2 000 ml.

It could be advantageous to take a larger daily part-sample, even though no turnaround shutdown is planned – by filling an extra sample bottle, for example. This can provide

additional assurance should an unexpected production stoppage occur, the sample bottle get broken during transport or a need arises to re-analyse as a result of a deviant result or an unsuccessful analysis.

### 1.5.6 Storage and transport of samples

It is normally impossible to analyse samples immediately, and they must therefore be preserved at a pH <2. However, that does not apply to samples to be analysed for metals and mercury. These are transferred without preservation. Sample bottles to which concentrated acids have been added before dispatch to the installation must be transported by boat. They must be accompanied by datasheets on the acids. After sampling, the bottles must be stored in a dark and cool place (4-8°C) unless otherwise agreed. The samples should be shipped ashore by the first available vessel. Helicopter transport can also be used, but not all helicopter types permit the carriage of produced water. Generally speaking, the rule is that clear agreements must be entered into on the transport of samples from the installation all the way to the analysis laboratory. Sample consignments must not be left standing at some point along the transport route because somebody has "forgotten" to order onward transport. During transport, the samples should be packed in a rigid box (such as an aluminium case) to prevent breakages and contamination by light.

If samples are dispatched by helicopter on the day they have been taken, and acid for preservation has not been added to the sample bottles in advance or is not available on the installation, the samples should be preserved with acid immediately on their arrival at the laboratory. Samples received by the laboratory must be stored in a dark and cool place (4-8°C) until they are analysed.

## 2 ANALYSES

### 2.1 DETECTION AND QUANTIFICATION LIMITS

When assessing analysis methods and results, it is important to correctly understand the following two concepts.

The limit of detection (LOD) for an analysis method is defined as the limit at which the smallest quantity of a substance can be detected in relation to a blank sample which does not contain this substance within a confidence interval. This is usually specified as three times the standard deviation for the blank.

The limit of quantification (LOQ) is applied in a more complex matrix where interferences and disruptions can arise, normally specified as 10 times the standard deviation for the blank.

Accredited laboratories normally report down to the LOQ. With analysis values below the LOQ, <LOQ for the relevant analysis is used. When reporting data pursuant to TA 3010-2013 (Klif, 2013), the LOQ is always used where relevant. However, the LOQ and LOD concepts are not to be used with complete consistency in guidelines and regulations.

### 2.2 Analysis of organic components

Table 3 shows analysis standards and normal LOQs for the principal groups of organic components to be analysed. All parallel samples must be analysed. See appendix 1 for further information on the individual compounds in the main groups. The list in appendix 1 is identical with Klif's reporting requirements pursuant to TA 3010-2013 (Klif, 2013). For reporting to Klif and the EW, see 044-Norwegian Oil and Gas – *Anbefalte retningslinjer for utslippsrapportering* (Norwegian Oil and Gas, 2012).

**Table 3 Overview of analyses of organic components to be conducted with produced water**

Parameter group	Standard	LOQ	Comments
Oil in water	Ospar 2005-15		The hydrocarbon content must be analysed in line with Ospar's reference method for oil in water (Ospar, 2005). This is a modification of NS-EN ISO 9377-2. Other methods can also be used (such as online analysis equipment or simpler methods used for daily follow-up on the installation) if these are calibrated with the Ospar reference method and if this can be documented. This is described in (Ospar, 2006).
BTEX Benzene Toluene Ethylbenzene Xylene	ISO 11423-1	0.01 mg/l  0.02-0.1 mg/l For each component	Headspace or purge-and-trap techniques must be used to avoid vaporisation of BTEX while preparing the sample.  The specified standard uses GC-MS (gas chromatograph with mass spectrometer detector), but GC-FID (gas chromatograph with flame ionisation detector) can also be utilised.
Phenols Alkylphenols C1-C9	See appendix 2	0.1 µg/l	Phenols and C1-C9 alkylphenols must be determined using GC-MS. Methods which avoid interference from benzoacids must be used. Specification of time window for integration.
NPD and PAH		0.1 µg/l	NPD and PAH must be determined with the aid of GC-MS. Appendix 1 specifies which components are to be reported pursuant to TA 3010-2013 (Klif, 2013).
Organic acids Formic acid Acetic acid Propanoic acid Butanoic acid Pentanoic acid  Naphthenic acids		2 mg/l for each component	Organic acids must be analysed individually (see appendix 1). Relevant methods include ion chromatography, isotachopheresis (ITP) or GC-MS. Calibration standards must be documented.  Must be reported if relevant.

## 2.3 Analysis of metals

When determining metals, methods should be used which provide the acid-free content of each individual metal. Concentrated acids are added to the samples – 1 ml hydrochloric acid per 100 ml of sample for metals, 0.5 ml hydrochloric acid and 0.5 ml nitric acid per 100 ml of sample for mercury. Where available, supplementary information on chemical speciation is also desirable. This relates to knowledge about bioavailability and the potential for harmful effects on marine life. Methods which can detect the individual level down towards the background level in seawater must be used when determining metals. The LOQ requirement for the method (total content of each metal) is specified on the basis of knowledge about the background level of metals in the North Sea. Table 4 presents analytical methods and normal LOQs for metals to be detected by analysis.

**Table 4. Overview of analyses for metals to be conducted with produced water**

Parameter group	Standard	LOQ (µg/l)	Comments
Chromium		1.5	Relevant methods: AAS/ICP-MS/DRC-ICP-MS/HR-ICP-MS
Nickel		9	
Copper		6	
Zinc		15	
Cadmium		6	
Lead		1.5	
Mercury		0.1	CV-AAS/Au amalgamation
Arsenic		1	HG-AAS/ICP-MS/DRC-ICP-MS
Barium		10	AAS/ICP-MS/DRC-ICP-MS/ICP-AES
Iron		1	

AAS: Atomic absorption spectroscopy

DRC-ICP-MS: Dynamic reaction cell inductively coupled plasma mass spectrometry

HR-ICP-MS: High resolution inductively coupled plasma mass

CV-AAS: Cold vapour atomic absorption spectroscopy

HG-AAS: Hydride generation atomic absorption spectroscopy spectrometry

ICP-MS: Inductively coupled plasma mass spectrometry

ICP-AES: Inductively coupled plasma atomic emission spectroscopy

The time interval between adding the acid to the sample and taking a sub-sample for analysis must be a minimum of 24 hours, and the sample should not stand longer than 48 hours.

During this holding time, the acid-/easily-soluble metals will be freed from possible particles in the water and transferred to the water phase before the analysis is conducted.

## 2.4 Analysis of radioactive components

Following preparation of the sample, radioactive elements are determined with the aid of high-resolution germanium detector gamma spectroscopy. This method identifies all radioactive substances which emit gamma rays.

A sample volume larger than 2 000 ml will provide an LOQ below the one specified in table 5. A count time of 12-24 hours is normally used for produced water. Extending this time will also provide an LOQ below the one specified in table 5.

Possible analysis for  $\text{Th}^{228}$  is performed with a partial extract from the sample. After chemical separation of thorium,  $\text{Th}^{228}$  is quantified with the aid of alpha spectrometry.

Parameter group	Standard	LOQ	Comments
Radioactive elements		0.5-1.0 Bq/l	The level of radioactivity is calculated from the activity of $\text{Ra}^{226}$ , $\text{Ra}^{228}$ and $\text{Pb}^{210}$ . In some cases, $\text{Th}^{228}$ will be included in the analysis (see section 3.5.5). The specified LOQ applies on the assumption of a sample volume of two litres.

## 3 USING ONLINE OIL IN WATER ANALYSERS

### 3.1 General

Using online oil in water (OiW) analysers to analyse the oil content in produced water offers many advantages (Department of Energy and Climate Change, 2010).

- Direct information on the “actual” discharge of oil
- Continuous process information about oil in produced water, unlike data from single samples taken daily
- If the signal from the OiW analyser is linked to a water flow meter (cu.m/s), the quantity of oil being discharged at any time can be calculated
- Reduced exposure to solvents for lab staff
- Operating disruptions can quickly be registered so that the operator can intervene, which could reduce oil discharges
- Lab personnel on the installations spend less time on sampling and analysis.

Installing an online OiW analyser as the basis for reporting to the regulator must be approved by Klif. Implementing it must comply with the Ospar guidelines for using such equipment (Ospar, 2006).

### 3.2 General requirements when using online oil in water analysers

Before installing an online OiW analyser which will form the basis for reporting to the regulator, a manual method for OiW analyses must be implemented on the installation. Correlation of the manual method with Ospar’s standard method for OiW analyses (Ospar, 2005) must be possible. The procedure for implementing the manual method is described in (Ospar, 2006). This method will be used to calibrate and validate the online analyser, and function as a back-up if the online analyser fails to give satisfactory results.

Emphasis must be given to the following considerations when choosing a sampling point and position for the online analyser.

- The sampling point must have good turbulence (see section 3.2.3)
- The online monitor must be easily accessible for day-to-day operation and maintenance
- A sampling point for manual sample-taking must be available in the immediate vicinity of the water offtake point for the online analyser
- Manual sampling in parallel with automatic measurements must not affect the supply of water to the online analyser
- The supply line for water to the online analyser must be as short as practicable
- A decision must be taken on whether water which has passed through the online analyser can be discharged or must be returned to the flow

### 3.3 Calibrating and validating online oil in water analysers

Oil from the relevant installation must be used when calibrating the online analyser in the laboratory. This calibration must cover the whole range of OiW concentrations, and embrace at least 10 data points. The calibration procedure is described in (Ospar, 2006). On the basis of parallel measurements with the online analyser (X values) and results from analyses with the manual method (Y values, average value of three parallel samples for each data point), a calibration curve will be calculated with linear regression in a 95 per cent confidence interval. The calibration curve must be validated weekly by taking three samples with the manual method to be analysed for OiW. The results are accepted if they fall within the 95 per cent confidence interval for the calibration curve. A new sample must be taken if the result falls outside the 95 per cent confidence interval for the calibration curve. Should this in turn fall outside the 95 per cent confidence interval, a further sample must be taken. If that falls within the 95 per cent confidence interval, the calibration curve is accepted. Should it fail to do so, a new calibration must be undertaken.

At the end of each calendar month, the calibration curve must be updated by including the results of the weekly validation in the calculation base for the calibration curve. This is conditional on the validation result falling within the 95 per cent confidence interval.

The calibration curve must also contain the following information:

- Serial number of the online analyser
- Date of the most recent calibration
- The regression coefficient
- The signature of the person responsible for the calibration.

A new calibration is required if the analyser has been serviced/maintained, if an error has affected the result, if the weekly calibration indicates that the results are not reliable, or if a significant change has occurred in the composition of the produced water.

### 3.4 Reporting data from online oil in water analysers

Data from online OiW analysers must be reported on the basis of Ospar's official reference method (see table 3). This means that the results from the calibration curve must be converted to the applicable calibration curve for the manual method in relation to Ospar's reference method.

### 3.5 Responsibility for maintenance and operation

The operator is responsible for ensuring that a satisfactory calibration takes place and that all procedures related to operation and maintenance of the online analyser are implemented. If the automated online analyser is taken off line, or the results are regarded as unreliable, an immediate switch must be made to a manual method approved by Klif.

## 4 OIL DISCHARGES FROM JETTING OPERATIONS

### 4.1 General

Sand and other particles which accumulate in process equipment are removed by jetting. These operations involve the discharge of dispersed oil as well as oil adhering to the solid particles. Discharges of oil adhering to sand must not exceed one per cent on a dry-matter basis. Pursuant to TA 3010-2013 (Klif, 2013), the following are to be reported in connection with jetting operations:

- Total oil discharges per year – in other words, dispersed oil in the water phase and oil adhesion to sand
- Average oil adhesion to sand (averaged over the year), specified as grams oil per kilogram dry matter (g oil/kg DM).

Representative samples must accordingly be taken before discharging particles which have passed through the treatment system, in order to determine the total volume of oil discharged from jetting as well as the oil volume adhering to particles.

Various approaches can be used to calculate total oil discharges related to jetting operations:

Sampling during each jetting operation: Samples are taken to calculate the oil discharged. The sum of discharges from all jettings on an annual basis are reported as the total volume.

Calculating fixed discharge quantities per jetting: This approach assumes that jetting takes place at fixed intervals. A factor (the jetting factor) is calculated for each process unit being jetted. This factor specifies how much oil is discharged by each jetting. Samples are taken at fixed intervals (every third month, for instance) during jetting of the relevant unit(s). The jetting factor is calculated as the average of the analysis values for a specified number of the most recent samplings (the eight most recent, for example) for the relevant process units. Each new data set forms the basis for calculating the jetting factor, while the oldest data set is removed (floating average). The sum of discharges from all jettings on an annual basis is reported as the total volume.

The design of the treatment system on the individual installation determines the construction of the sampling programme and the taking of samples. Generally speaking, however, provision must be made for sampling at the discharge point from the treatment system.

### 4.2 Sampling

#### 4.2.1 Sampling to determine total oil discharges from jetting operations

- The sampling point must provide good mixing so that as representative a sample as possible can be taken of water and sand/sludge accompanying the discharge
- It is advantageous if the water flow (cu.m/s) is relatively constant throughout the discharge period. The discharge volume (cu.m) must be recorded or calculated
- Part-samples must be taken at regular intervals during the discharge and then merged to create a mixed sample. The number of part-samples will depend on the duration of the jetting operation, but at least three should be taken (at the start of the discharge, at its midpoint and at its conclusion). Where the oil content is likely to vary

significantly over the duration of the discharge, the number of part-samples should be increased. The interval from starting the jetting until the first part-sample is taken will depend on the position of the sampling point. It is important that the interval between each sample remains more or less constant

- The mixed sample is collected in a glass bottle with a wide neck, which has been cleaned in the same way as bottles for OiW analyses
- Once sampling is completed, the sample is sent to the lab for analysis of the total oil content

#### 4.2.2 Sampling to determine oil adhesion to sand

Samples are taken simultaneously with sampling to determine the total discharge of oil. Two procedures for taking samples are described below. The sample to be analysed for determining oil adhesion to sand must be at least 10 g DM. This means it could be difficult to collect a sample of sufficient size during a single jetting operation, and sampling must accordingly be extended over several jettings.

##### Method 1: Sample taken from the water flow

- During the discharge, part-samples of water containing jetting sand are taken and collected in one-litre glass bottles with a wide neck
- To ensure a sufficient volume of sand, it could be necessary to decant the water and refill the bottle. This operation is repeated until a sufficient amount of sand for doing the analysis has been accumulated – a minimum of 10 g DM, although a larger sample is advantageous
- Decanters of water and sand can be transferred to smaller containers for dispatch to the external analysis laboratory
- The sample can be stored in a refrigerator for a week, but should preferably be deep-frozen to prevent the degradation of oil components
- The sample must not be preserved with acid, because this could wash oil components out of the sample
- In cases where 10 g DM cannot be attained, the sand can be accumulated over several jetting operations. In that case, the samples must be frozen after each sampling. When a sufficient quantity of sand for analysis has been obtained, these samples are mixed together and sent to the analysis laboratory. The analysis result will then apply to the whole collection period.

##### Method 2: Sample taken from sedimented sand when the jetting water flow has passed through a sand collection tank

- The water must be drained from the collection tank before the sample is taken, and possible oil which may accumulate on top of the sand must be removed before the sand is mixed, so that the most homogenous possible sample can be taken
- A sample of at least 10 g DM must be taken (a larger sample is advantageous), and transferred to a glass bottle with a wide neck
- The sample must not be preserved with acid, because this could wash oil components out of the sample

### 4.3 Analysis

Dispersed oil and oil adhering to sand is analysed pursuant to Ospar's reference method (OSPAR, 2005). Oil adhesion to sand is specified in g oil/kg DM.

### 4.4 Calculating quantities discharged from each jetting

The volume discharged (cu.m per jetting) and the concentration of dispersed oil in the sample provide the basis for calculating the total discharge of oil from the jetting operation.

## 5 METERING QUANTITIES (VOLUMES) DISCHARGED

### 5.1 Metering principles and requirements for maximum uncertainty when metering

Metered water flow is an important parameter when reporting discharge quantities. Such metering is normally done on the discharge line for produced water. The normal practice is to use meters which assume measurement in enclosed pipes. Various metering principles are used, but electromagnetic flow meters, ultrasonic meters, orifice plates and coriolis meters are the most common. (Gillivray, Yan and Paton, 2007). No standard method for metering discharge quantities currently exists.

Discharge quantities should be measured and recorded with a maximum uncertainty of  $\pm 10$  per cent. Among other factors, the uncertainty provided by the various metering principles depends on:

- Installing the meter in line with the manufacturer's instructions
- Regular maintenance of the meter.

### 5.2 Documentation of measurement uncertainty when metering water discharges

The manufacturer of the water meter normally has a calibration certificate which applies to the specific device. This calibration is performed in a test rig at the manufacturer and does not necessarily remain valid after installation in the field. After installing the meter out on the facility, the temperature, pressure, density and viscosity of the produced water could influence the metered results. The latter could also alter over time from operating the instrument section and deposition in the actual meter. To specify uncertainty in the water metering, an onsite verification must accordingly be carried out with the water to be metered. Verification in this context means a check against a method or meter with a known uncertainty. If the verification of the metering results shows a variance exceeding  $\pm 10$  per cent, calibration must be carried out. Good background information on the installation and verification of water flow meters can be found in such sources as the (National Measurement System, 2010a) and the (National Measurement System, 2010b).

To verify compliance with the maximum requirement for uncertainty, the operator must be able to document the following:

- Results from onsite verification of the water flow meter, specified as uncertainty in per cent of the relevant metering range
- That a meter with a relevant metering range is used
- The manufacturer's data sheet with specification of measurement accuracy
- That the installation instructions have been followed:
  - requirement for the straight section before/after the meter
  - ensuring that the pipe is filled with flowing liquid
  - programming data for ensuring that the metering is conducted correctly (pipe diameter, for instance)
- measuring diameters in orifice and venturi meters (checking wear/corrosion/deposition)

- meter zero checked
- linearity of the meter checked by an instrumentation technician
- the meter's integrator function (counter which sums water volume on the basis of flow).

## 6 UNCERTAINTIES

### 6.1 General

All measurements and analyses involve a certain degree of uncertainty. Figures reported for produced-water discharges accordingly also contain some degree of uncertainty. Factors which contribute to overall uncertainty in the reported figures relate primarily to the following three sections of the measurement process:

- Sampling
- Analysis of the sample
- Metering of water flow

Of these, the most difficult uncertainty to quantify is that which arises in sampling. In many cases, this also makes the biggest contribution to overall uncertainty. Accredited laboratories can specify uncertainty for the various analysis parameters, and it is possible to determine uncertainty in water flow metering from an onsite verification/calibration.

### 6.2 Contributors to uncertainty when sampling

The main elements which could contribute to uncertainty in sampling are:

- Variations in the produced water's composition
- Weaknesses in the sampling point
- Deficient sampling procedures
- Lack of expertise in personnel taking the sample
- Deficient procedures for packing and storing samples until they reach the laboratory

Errors which arise during sampling, and which are the contributory source of uncertainty, can be divided between chance and systematic mistakes. Variations in the composition of the water flow being sampled will normally be the biggest source of chance errors. To reduce these, for example, the number of samples taken can be increased. Norwegian Oil and Gas appointed a work group in 2008 which assessed as one of its jobs how many samples of organic components and metals were needed to form the basis for calculating annual discharges (Norwegian Oil and Gas, 2008). Based on an evaluation of data from two annual samplings (three parallel samples on each occasion) from 16 installations on different North Sea fields, the group concluded that the composition of the produced water was relatively constant on the individual facility. Against that background, it was concluded that an increase in sampling frequency from two to four-six times a year would not provide a significantly better knowledge base for estimating the contribution from the individual installation and from overall offshore operations. Chance errors arising from variations in the produced water's content of organic components and metals are accordingly regarded as relatively minor. This conclusion naturally assumes that the facility receives the same type of liquid flows. Sampling frequency must be increased on installations where the composition of the produced water changes – because of new wellstreams, new satellite developments, other installations or a new treatment plant – so that the changes are documented.

Systematic errors could arise at every stage in the sampling process, such as an incorrectly configured sampling point, personnel with inadequate expertise or deficient procedures for

storing and transporting samples. To reduce the effect of systematic errors on sampling, it is accordingly important that the operator gives emphasis to the following considerations:

- Select sampling points which satisfy basic requirements for positioning and configuring such points (see section 3.2)
- Develop procedures which describe, in a clear and easily understandable manner, how sampling is to be conducted, including a system for documenting that the specified procedures have been followed with each sampling
- Establish a system to register non-conformities (improvement system) when sampling is not conducted in accordance with established procedures
- Verify that personnel involved in sampling have the necessary competence to do the work in compliance with applicable procedures
- Enter into clear agreements with the laboratory (both internal and possibly external) so that procedures for storing and transporting samples to the laboratory ensure that sample composition remains unchanged

Taken together, these steps will reduce the contribution of systematic errors to sampling. However, putting a figure on this contribution to uncertainty is a complicated business.

### 6.3 Contributors to uncertainty in the chemical analysis

The laboratory must be able to specify the uncertainty attached to each analysis result. This uncertainty is an estimate which characterises an interval (the confidence interval) covering the true value for the sample. The uncertainty must always be cited using the  $\pm$  sign. A 95 per cent level of confidence is normally used. This means that there is a 95 per cent probability that the true value for the sample lies within the specified interval. Accredited laboratories participate regularly in comparative laboratory trials (ring tests) so that an acceptable level of quality control can be achieved. However, ring tests are not arranged for some parameters. Where unaccredited operational laboratories are concerned, a system must be established for parallel analysis of samples (cross-checking) with accredited laboratories to achieve an acceptable level of quality control.

The use of matrix spikes is recommended with all analysis methods.

### 6.4 Uncertainty in metering water discharges

The result from the most recent verification of water flow metering, specified as  $\pm$  per cent, is used in annual reporting of discharge quantities pursuant to TA 3010-2013. See chapter 6.

## 6.5 Assessing overall uncertainty for produced water discharges

Overall uncertainty must be assessed as a combination of system description and actual figures for the calculated uncertainty.

Sampling: A description of how the sample is taken. Not in detail, but with reference, for instance, to conformity with standards or the Norwegian Oil and Gas guidelines. In addition, the operator must – in the event of a Klif audit – be able to document through procedures, logging and physical inspection that the sampling is conducted in accordance with the above-mentioned standard and the Norwegian Oil and Gas guidelines.

Water flow metering: Specification of the calculated uncertainty at the most recent verification. Brief description of the verification – “checked with radioactive tracer”, for example, or “checked with clamp-on ultrasonic meter with a known metering uncertainty”.

Analysis uncertainty: Specification of the identified uncertainty for the various parameters/parameter groups. State whether an accredited laboratory is used. If an online OiW analyser is used, provide a brief description of how this is checked – pursuant to Ospar agreement 06-06 (OSPAR, 2006), for instance.

## 7 REPORTING

Reporting to Klif and Environment Web (EW) must accord with 044-Norwegian Oil and Gas *Veiledning til den årlige utslippsrapporteringen* (Norwegian Oil and Gas, 2012). Tables 3.2 and 3.3 in appendix 1 provide an overview of the parameters to be included in the reporting to Klif.

Pursuant to TA-3010, 50 per cent of the LOQ is used for calculating discharges in cases where the concentration of the relevant component or compound is below the quantification limit. This calculation rule could mean a substantial over-estimation of the discharges in many cases, but it accords with normal practice in the environmental sector.

The calculation rule provides room for various interpretations when calculating and reporting totals for parameter groups comprising several components – BTEX, NPD, total PAH 16 EPA without naphthalene and phenanthrene, and organic acids. When reporting to a common database, however, it is important that all operators observe the same calculation rules. The following rules apply when doing the calculations:

- If one or more of the components in the relevant parameter group is/are reported with analysis values above the LOQ, they are summed with 50 per cent of the LOQ for each of the other components in the group
- If all the components in the parameter group are reported with analysis values below the LOQ, they are summed at 50 per cent of the LOQ for each component in the group

## Appendix 1. Heavy metals and organic components to be reported pursuant to TA 3010-2013

*Table 3-2. Discharges of heavy metals in produced water*

<b>Heavy metals</b>	<b>Concentration</b>	<b>Discharge (kg)</b>
Arsenic		
Lead		
Cadmium		
Copper		
Chromium		
Mercury		
Nickel		
Zinc		
Total heavy metals		

**Table 3-3. Discharges of organic compounds in produced water**

	<b>Compounds</b>	<b>Concentration</b>	<b>Discharges (kg)</b>
<b>BTEX</b>	Benzene		
	Toluene		
	Ethylbenzene		
	Xylene		
Total BTEX			
<b>PAH</b>	Naphthalene		
	C1-naphthalene		
	C2-naphthalene		
	C3-naphthalene		
	Phenanthrene		
	Anthracene*		
	C1-Phenanthrene		
	C2-Phenanthrene		
	C3-Phenanthrene		
	Dibenzothiophene		
	C1-dibenzothiophene		
	C2-dibenzothiophene		
	C3-dibenzothiophene		
Total NPD			
	Acenaphthylene*		
	Acenaphthene*		
	Fluorene*		
	Fluoranthene*		
	Pyrene*		
	Chrysene*		
	Benzo(a)anthracene*		
	Benzo(a)pyrene*		
	Benzo(g,h,i)perylene*		
	Benzo(b)fluoranthene*		
	Benzo(k)fluoranthene*		
	Indeno(1,2,3-cd)pyrene*		
	Dibenz(a,h)anthracene*		
Sum US EPA list of 16 PAH without naphthalene and phenanthrene (starred)			
<b>Phenols</b>	Phenol		
	C1-Alkylphenol		
	C2-Alkylphenol		
	C3-Alkylphenol		
	C4-Alkylphenol		
	C5-Alkylphenol		
	C6-Alkylphenol		
	C7-Alkylphenol		
	C8-Alkylphenol		
	C9-Alkylphenol		
<b>Organic acids</b>	Formic acid		
	Acetic acid		
	Propanoic acid		
	Butanoic acid		
	Pentanoic acid		
	Naphthenic acid (when relevant)		
Total organic acids			

## Appendix 2. Preparation and analysis of phenols and alkylphenols

### 1. Background

The method described below builds on the results of a methodological comparison conducted between four laboratories in 2002. Emphasis has been given to the highest possible degree of standardisation for the analyses.

Phenol and C1-C9 alkylphenols must be analysed with the aid of solvent extraction followed by GC-MS. This approach makes it possible to combine the analysis of alkylphenols and PAH.

### 2. Preparation

Before extraction, check the pH of the samples. This must be around 2. The water samples are transferred quantitatively from the bottles to a suitable extraction container (separatory funnel), and is then extracted three times with 100 ml, 50 ml and 30 ml of dichloromethane. For working environment reasons, it is recommended that extraction is accomplished by stirring. This involves adding about 150 ml of dichloromethane to the sample and stirring it twice with a magnetic stirrer. The stirring must be sufficiently vigorous that a vortex forms at the bottom of the bottle.

The solvent for the first extraction can be used to wash the inside of the sample bottle as well as the teflon stopper before being added to the separatory funnel. Surrogate internal standard (SIS) – deuterated C1, C2 and C3 phenol – are added to the sample before the solvent is added. Approximate levels for these are 100 µg of C1 phenol and 50 µg of C2 and C3 phenol per litre of water. The extracts are combined and cleaned with gel permeation chromatography (exclusion volume 1 000 Å). This will remove background noise and benzoacids from the sample. The extracts are concentrated to about 1 ml (with the aid of turbovap, for example), and recovery internal standard (RIS) added (about 2.5 µg per 1 ml of sample). If necessary, the samples can be diluted and more RIS added if the analysis shows that components are becoming saturated.

An alternative treatment technology for removing background noise and benzoacids can be used. If an alternative method is used, it must be documented with regard to known additions of alkylphenols measured against today's method based on gel permeation chromatography.

### 3. Instrumental analysis

The samples are analysed with the aid of GC-MS SIM in a non-polarised or weakly polarised capillary column. Recommended analysis conditions are:

- Initial temperature 40°C
- Time at initial temperature 1 minute
- Temperature programme 6°C per minute
- Final temperature 300°C
- Time at final temperature 20 minutes
- Injector temperature 300°C (alt on-column)
- Ion source temperature 280°C
- Gas speed 1 ml/minute (He)

Components to be included in the analysis with respective ions for GC-MS SIM are specified in table 2.1.

#### 4. Quantification

Phenol is quantified by integrating the specific peak and using the relative response factor (RRF) for phenol compared with the internal standard.

C1 alkylphenols are quantified in the same way as the sum of the individual components o-cresol and m/p-cresol. RRF is used for o-cresol.

C2-C5 alkylphenols are quantified by baseline integration of all the components for the respective groups. The parent component phenol is used for calculating response factors. Because of the risk of interference with other components, C6-C9 alkylphenols are quantified as the sum of the individual components from each group (see table 2.1).

Phenanthrene is an internal standard for all alkylphenols from C4 to C9. Experience shows that phenanthrene does not behave similarly to all these alkylphenols. The heavier alkylphenols with long straight-chain alkyl groups, in particular, behave very differently. This means that the internal standard correction does not function as it should. It is therefore desirable to choose better-adapted internal standards for some of the components, such as deuterated n-heptylphenol, for example, to represent the straight-chain alkylphenols and deuterated 2,6-di-tert-butylphenol to represent the branched-chain ones.

#### 5. Quality control

The laboratory which conducts the analyses must submit documentation to show that the analyses maintain a level of quality which corresponds to the requirements for accreditation or good laboratory practice (GLP). An example of the way such a quality control could be conducted is presented below.

Samples to document background levels from the laboratory, and the accuracy and precision of the analyses, must be taken and analysed for each analysis of a set of genuine samples. This must be done for at least every 20th sample prepared.

##### Samples for quality control:

- A blind sample is created by going through all the preparatory and analytical stages for pure solvent from the same consignment as the extraction agent
- The laboratory's control sample is produced by adding all the analytes to pure solvent, which is prepared and analysed in the same way as the samples
- Matrix spike sample – a genuine sample to which all the analytes to be determined have been added
- Reproducibility is tested by preparing and analysing a parallel of a genuine sample or of the matrix spike sample
- Accuracy is tested by adding a selection of the analytes to a glass GC column with solvent which is then analysed, SIS and RIS.

##### Quality requirements:

- The level of the blind sample must be lower than the smallest reported result
- 70-130 per cent recovery from the laboratory's control sample and matrix spike sample
- Less than 30 per cent deviation in parallel of the sample or the matrix spike 30-130 per cent recovery of SIS

**Table 2.1 Overview of analytes and quantification parameters**

Compound	~RT (min)	Ions	Homologue	SIS	RIS
Phenol	13.25	94, 66		Phenol-d5	Acenaphthene-d10
<b>C1 phenols</b>			phenol	4-Methylphenol-d8	
2-methylphenol	15.31	108, 107		4-Methylphenol-d8	
4-methylphenol	15.86	107, 108		4-Methylphenol-d8	
<b>C2 phenols</b>		107, 122	phenol	2,4-Dimethylphenol-d3	
4-ethylphenol	18.24	107, 122		2,4-Dimethylphenol-d3	
2,4-dimethylphenol	17.83	122, 107		2,4-Dimethylphenol-d3	
3,5-dimethylphenol	18.33	122, 107		2,4-Dimethylphenol-d3	
<b>C3 phenols</b>		121, 107	phenol	4-n-Propylphenol-d12	
4-n-propylphenol	20.56	107, 136		4-n-Propylphenol-d12	
2,4,6-trimethylphenol	19.43	121, 136		4-n-Propylphenol-d12	
2,3,5-trimethylphenol	20.95	121, 136		4-n-Propylphenol-d12	
<b>C4 phenols</b>		135, 150	phenol	Phenanthrene-d10	
4-n-butylphenol	22.92	107, 150		Phenanthrene-d10	
4-tert-butylphenol	21.4	150, 107		Phenanthrene-d10	
4-isopropyl-3-methylphenol	22.3	150, 135		Phenanthrene-d10	
<b>C5 phenols</b>		149, 164		Phenanthrene-d10	
4-n-pentylphenol	25.13	107, 164		Phenanthrene-d10	
2-tert-butyl-4-methylphenol	22.72	149, 164		Phenanthrene-d10	
4-tert-butyl-2-methylphenol 2	22.89	149, 121		Phenanthrene-d10	
<b>C6 phenols</b>				Phenanthrene-d10	
4-n-hexylphenol	27.27	107, 178		Phenanthrene-d10	
2,5-diisopropylphenol	24.54	163, 178		Phenanthrene-d10	
2,6-diisopropylphenol	22.98	163, 107		Phenanthrene-d10	
2-tert-butyl-4-ethylphenol	24.34	163, 135		Phenanthrene-d10	
6-tert-butyl-2,4-dimethylphenol	23.62	163, 135		Phenanthrene-d10	
<b>C7 phenols</b>				Phenanthrene-d10	
4-n-heptylphenol	29.30	107, 192		Phenanthrene-d10	

Compound	~RT (min)	Ions	Homologue	SIS	RIS
2,6-dimethyl-4-(1,1-dimethylpropyl)phenol	26.04	163, 192		Phenanthrene-d10	
4-(1-ethyl-1-methylpropyl)-2-methylphenol	27.04	163, 121		Phenanthrene-d10	
(2,6-diisopropyl-4-methylphenol)	26.37	177, 192		Phenanthrene-d10	
<b>C8 phenols</b>				Phenanthrene-d10	
4-n-octylphenol	31.22	107, 206		Phenanthrene-d10	
4-tert-octylphenol	28.2	135, 107		Phenanthrene-d10	
2,4-di-tert-butylphenol	26.93	177, 206		Phenanthrene-d10	
2,6-di-tert-butylphenol	24.78	191, 206		Phenanthrene-d10	
<b>C9 phenols</b>				Phenanthrene-d10	
4-n-nonylphenol	33.05	107, 220		Phenanthrene-d10	
2-methyl-4-tert-octylphenol	28.97	149, 121		Phenanthrene-d10	
2,6-di-tert-butyl-4-methylphenol	26.17	205, 220		Phenanthrene-d10	
4,6-di-tert-butyl-2-methylphenol	26.67	205, 220		Phenanthrene-d10	
<b>Internal standards</b>					
<b>SIS</b>					
Phenol-d5 13.21 99, 71 Acenaphthene-d10	13.21	99, 71			
4-Methylphenol-d8 15.76 115, 85 Acenaphthene-d10	15.76	115, 85			
2,4-Dimethylphenol-d3 17.81 125, 110 Acenaphthene-d10	17.81	125, 110			
4-n-Propylphenol-d12 20.38 113, 147 Acenaphthene-d10	20.38	113, 147			
Phenanthrene-d10					
RIS					
Acenaphthene-d10 26.85 164, 162	26.85	164, 162			