

# 085 – Offshore Norge recommended guidelines for sampling and analysis of produced water

Rev 2 - translated version



### FOREWORD

These guidelines are recommended by Offshore Norge's work group for sampling and analysis of produced water, which forms part of the network on discharges to the sea in Offshore Norge's forum for climate and the environment. They were also approved by the director general on 16 December 2022.

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

These Offshore Norge 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 Offshore Norge. Their administration has been allocated to Offshore Norge.

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# 1. INTRODUCTION

All operators on the Norwegian continental shelf (NCS) are required to submit an annual report to the Norwegian Environment Agency (NEA). See section 34c of the management regulations. A major revision of these regulations was implemented in 2020. https://www.ptil.no/globalassets/regelverk/gjeldende-regelverk-2022/styringsforskriften n.pdf

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. These were revised in 2012 and 2013 as revision 1 dated 8 February 2013. The present version is revision 2.

#### 1.1.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 the NEA'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 (OiW) meters, requirements/recommendations for metering water discharges, and calculation rules for reporting multi-component parameter groups.

Offshore Norge 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. Information on produced water discharges must be reported annually to the Footprint (formerly Environmental Web) database. See the latest version of the Offshore Norge guidelines 044 - Recommended guidelines for discharge and emission reporting (2022).

#### 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
NCS	Norwegian continental shelf
NEA	Norwegian Environment Agency
OiW	Oil in water

#### 1.3.References

Department of Energy and Climate Change (2010). Guidance Notes - The Sampling and Analysis of Produced Water and Other Hydrocarbon Discharges, version 2.1, August 2010.

Gillivray, A M, M Yan and R Paton. Measurement of Produced Water Discharges – Regulatory Requirements and Recent Progress. 25th International North Sea Flow Measurement Workshop, 16-19 October 2007.

NEA. M-107 Retningslinjer for rapportering fra petroleumsvirksomhet til havs.

National Measurement System (2010a). An Introduction to Flow Meter Installation Effects, www.tuvnel.com.

National Measurement System (2010b). Good Practice Guide - The Calibration of Flow Meters, www.tuvnel.com.

Norwegian Oil and Gas (2008). Dispergert olje og løste komponenter i produsert vann. Note from the Offshore Norge work group on produced water (PW), May-Nov 2008.

Offshore Norge (2022). Recommended guidelines for discharge and emission reporting (2022)

OSPAR (2005). OSPAR Reference Method of Analysis for the Determination of the Dispersed Oil Content in Produced Water, Agreement 2005-15.

OSPAR (2006). Oil in Produced Water Analysis - Guidelines on Criteria for Alternative Method Acceptance and General Guidelines on Sample Taking and Handling, Agreement 06-06.

Standards Norway (1999). NS-EN ISO 3171 Petroleum liquids - Automatic pipeline sampling. 1999 (ISO 3171:1988).

Standards Norway (2004). NS-EN ISO 3170 Petroleum liquids - Manual sampling. 2004 (ISO 3170:2004).

National Radiation Protection Authority (DSA) (2020). Guideline for radioactive pollution and radioactive waste from oil and gas industry. Guidance no. 13.

Naphthenic acid analysis: A-V-059 method based on OSPAR 2005-15/NS-EN-ISO 9377-2.



### 2. OVERVIEW OF AMENDMENTS

Low-level radioactive elements in produced water, see chapter 3.5.5.

Section 4.2: New text added: "To ensure that environmental analyses are representative, checks of the OiW content in the sample set are recommended along with an assessment of whether the OiW value is to be regarded as representative. To assess whether the OiW content is representative, it is recommended that this value lies within the 90 percentile for measured daily values over the previous year. Where OiW analyses are conducted using an alternative method correlated against the OSPAR reference method, the applicable practice is to prepare a correlation factor using the analysis results from the alternative method measured offshore, with GC-FID onshore."

Reference to established method for analysing naphthenic acids: A-V-059 method based on OSPAR 2005-15/NS-EN-ISO 9377-2.

Section 4.3, Table 4: updated reporting limits.

Chapter 5: General updating of the chapter concerning the use of online OiW analysers.

Section 7.2: Updated first paragraph concerning follow-up of reasons for discrepancies.

Section 8.3: "Where OiW is concerned, a monthly crosscheck is recommended between nonaccredited operational laboratories and accredited laboratories on land. Acceptance criteria should be established for discrepancies in the analyses. The accepted discrepancy between results (uncorrelated) from analyses offshore and on land with the same type of instrument is calculated from the average value for the two measurements (CG-FID onshore and field instrument offshore) compared with the measurements conducted with the field instrument offshore. Establishing a plan for following up variations is recommended. This will describe measures to be initiated in the event of repeated variations over a specified period (such as two-three months)."

Appendices 1 and 2 have been deleted since these can be found in Offshore Norge guidelines 044 - Recommended guidelines for discharge and emission reporting (2022).



# 3. SAMPLING

#### 3.1.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 is high for a number of the components. Samples for environmental analyses of organic components, metals and radioactive elements 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 OiW 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.

#### 3.2.Sampling point

#### **3.2.1.** Positioning 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.

#### 3.2.2. Configuring 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 acquired 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 (Standards Norway, 2004) and NS-EN ISO 3171 (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 in order 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.

#### **3.2.3. Requirements for the sampling point when using online OiW analyser** Many different types of online OiW 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.

# 3.3.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 OiW will be prepared by the laboratory on the installation.

# 3.4.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:

- Name of the installation
- Name of the person taking the sample
- Sample number ie, 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

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

Parameter group	Sample packaging	Preparation and other requirements for packaging
OiW	Glass bottles with teflon seal and	Bottles must be cleaned and rinsed in n-pentane.
	stopper	Hydrochloric acid (abt one ml of 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 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 one ml of 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.



# 3.5.Taking samples

#### 3.5.1. 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.

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.

#### 3.5.2. Sampling to determine OiW

Bottles must be washed 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.

#### 3.5.3. Sampling to determine minerals

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.

#### 3.5.4. Sampling to analyse organic components

Sample bottles sent out to the fields are usually prepared before dispatch. If preparation is done offshore, the bottles must be washed and have concentrated hydrochloric acid (about one ml of 6 N HC1 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.



#### 3.5.5. Sampling to analyse radioactive elements

The following requirements apply when taking samples for analysis of produced water, unless otherwise agreed in writing with the Norwegian Radiation Protection Authority (DSA 2020).

- Four collective samples per year must be analysed when annual discharges exceed three million m<sup>3</sup>. Each sample must comprise part-samples for every day in the quarter. One sample comprising at least 50 ml of produced water must be taken daily
- Four collective samples per year must be analysed when annual discharges are less than three million m<sup>3</sup>. Each sample must comprise part-samples for every day in the quarter. One sample comprising at least 50 ml of produced water must be taken daily
- The samples must be analysed for Ra<sup>-226</sup>, Ra<sup>-228</sup> and Pb<sup>-210</sup>
- When using deposition dissolvers or other 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. A total sample volume of 2 000 ml is recommended, with a minimum of 1 500 ml. For 30 sampling days, 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 1 500 ml.

#### 3.5.6. 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, mercury and radioactive elements. 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.

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.



Parameter	Purpose	Sample	Sample	Comment
group OiW	Determining	<b>type</b> Daily mix	volume Abt 800-	The sample is normally taken as three
	dispersed OiW	sample	900 ml	or four part-samples spread over the
	(daily sampling			day, at fixed times
				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 OiW analysers is described in
				chapter 5
OiW	Characterising	Spot sample	Abt 800-	Three parallel samples are taken over
	produced water		900 ml	a short interval. Each sample bottle is
	(environmental			first filled to one-third of its volume,
	analysis)			all are then filled to two-thirds of the
Metals	Characterising	Spot sample	Abt 125	volume, and finally all are filled to their full sample volume. Taken at
	produced water (environmental		ml	least twice a year.
	analysis)			least twice a year.
NPD and PAH	Characterising	Spot sample	Abt 800-	
	produced water	opor sumple	900 ml	
	(environmental			
	analysis)			
Phenols	Characterising	Spot sample	Abt 800-	
	produced water		900 m	
	(environmental			
	analysis)			
BTEX	Characterising	Spot sample	250 ml	
	produced water			
	(environmental			
<u> </u>	analysis)			
Organic acids	Characterising	Spot sample	250 ml	
	produced water			
	(environmental			
Radioactive	analysis)	Monthly or		See section 3.5.5
elements in	Sampling for analysis of	quarterly mix		See Seculi 3.3.3
produced	radioactive	samples		
water	elements	samples		
walth	elements	1		

# Table 2. Overview of sample types and normal sample volumes for thevarious parameter groups



# 4. ANALYSES

# 4.1.Detection and quantification limits

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

The <u>limit of detection</u> (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 discrepancy for the blank.

The <u>limit of quantification</u> (LOQ) is applied in a more complex matrix where interferences and disruptions can arise, normally specified as 10 times the standard discrepancy 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 the latest revision of the NEA's M-107, half the value of the LOQ is used where the analysis value is lower than the LOQ. However, the LOQ and LOD concepts are not applied with complete consistency in guidelines and regulations.

#### 4.2. 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. Substances to be analysed and reported are specified in the latest revision of the recommended guidelines 044 on annual reporting . To ensure that environmental analyses are representative, checks of the OiW content in the sample set are recommended along with an assessment of whether the OiW value is to be regarded as representative. To assess whether the OiW content is representative, it is recommended that this value lies within the 90 percentile for measured daily values over the previous year.

Where OiW analyses are conducted using an alternative method correlated against the OSPAR reference method, the applicable practice is to prepare a correlation factor using the analysis results from the alternative method measured offshore, with GC-FID onshore.

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

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Parameter group	Standard	LOQ	Comments
OiW	OSPAR 2005-15		The hydrocarbon content must be analysed in line with OSPAR's reference method for OiW (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	ISO 11423-1	0.01 mg/l	Headspace or purge-and-trap techniques must be used to avoid vaporisation of BTEX while preparing the sample.
Toluene Ethylbenzene Xylene		0.02-0.1 mg/lFor each component	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 Guideline 044	0.1 μg/l	Phenols and C1-C9 alkylphenols must be determined using GC-MS. Methods which avoid interference from benzoacids must be utilised. 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. Guideline 044 specifies which components are to be reported pursuant to M-107, latest revision.
Organic acids Formic acid Acetic acid Propionic acid Butanoic acid Pentatonic acid		2 mg/l for each com- ponent	Organic acids must be analysed individually (see Guideline 044). Relevant methods include ion chromatography, isotachophoresis (ITP) or GC-MS. Calibration standards must be documented.
Naphthenic acids			A-V-059 method based on OSPAR 2005- 15/NS-EN-ISO 9377-2. Norwegian standard.



# 4.3.Analysis of metals

When determining metals, methods should be used which give the acid-free content of each metal. Concentrated acids are added to the samples – one ml of hydrochloric acid per 100 ml for metals, and 0.5 ml of hydrochloric acid and 0.5 ml of nitric acid per 100 ml 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 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.

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.

Parameter group	Reporting LOQ (µg/l)	Comments	
Chromium	0.01		
Nickel	0.05 Relevant methods:		
Copper	0.1	AAS / ICP-MS / DRC-ICP-MS /	
Zinc	0.2	HR-ICP-MS	
Cadmium	0.002		
Lead	0.3		
Mercury	0.002	CV-AAS / Au amalgamation	
Arsenic	0.05	HG-AAS / ICP-MS /DRC-ICP-MS	
Barium	0.01	AAS / ICP-MS / DRC-ICP-MS /	
Iron	0.001	ICP-AES	

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



# 4.4.Analysis of radioactive elements

Following preparation of the sample, radioactive elements are determined with the aid of high-resolution germanium detector gammaspectroscopy. 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 Th<sup>228</sup> is performed with a partial extract from the sample. After chemical separation of thorium, Th<sup>228</sup> is quantified with the aid of alpha spectrometry.

Parameter group	LOQ	Comments
Radioactive elements		The level of radioactivity is calculated from the activity of Ra <sup>226</sup> , Ra <sup>228</sup> and Pb <sup>210</sup>
Ra <sup>226</sup>	0.2 Bq/l	In some cases, Th <sup>228</sup> will be included in the analysis (see section 3.5.5)
Ra <sup>228</sup>		
Pb <sup>210</sup>		The specified LOQ applies on the assumption of a sample volume of two litres
Th <sup>228</sup>		

#### Table 5 Analysis of radioactive elements in produced water



# 5. USING ONLINE OIW ANALYSERS

#### 5.1.General

Using online OiW analysers to analyse the oil content in produced water can provide 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

#### 5.2.General requirements when using online OiW 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. Correlating the manual method with OSPAR's standard method for OiW analyses (OSPAR 2006) must be possible. The procedure when 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 3.2.1)
- 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 online analyser
- Manual sampling in parallel with automatic measurements must not affect the online analyser



# 5.3.Calibrating and validating online OiW analysers

One approach to calibration is described in (OSPAR 2006). When calibrating the online analyser, field samples of produced water must be used. Calibration must cover the relevant area for OiW concentrations.

Online analysers used for reporting OiW to the authorities are validated weekly. This can be done by taking samples which are analysed for OiW by the manual method. The frequency of validation can deviate from weekly on the basis of a case-by-case assessment of reliability, and it should be possible to document the reasons for utilising a frequency other than weekly. This is acceptable if the results lie within the 95 per cent confidence interval for the calibration curve. Alternatively, the discrepancy between the manual method and the online analyser must be within, for example,  $\pm 4 \text{ mg/l or } \pm 30 \text{ per cent}$ .

A new sample must be taken should the result fall outside the acceptance criteria. If the new sample lies within the criteria, the calibration curve is accepted. The need for a recalibration must be considered if the result is outside the criteria.

Recalibration may be required when the analyser has been serviced/maintained, if an error has affected the result, or if the weekly validation indicates that the results are not reliable.

Calibration documentation must contain the following information:

- Instrument information
  - tag number
    - serial number
- Date of the most recent calibration
- Signature of the person responsible for the calibration

#### 5.4.Reporting data from online OiW analysers

Data from online OiW analysers must be reported on the basis of OSPAR's official reference method. If the automated online analyser is taken off line, or the results are regarded as unreliable, a switch must be made to the manual method.



# 6. OIL DISCHARGES FROM JETTING OPERATIONS

#### 6.1.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 M-107 (NEA, 2020), 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
- Quantity of jetting water discharged to the sea (m<sup>3</sup>)
- Average oil adhesion to sand (averaged over the year), specified as grams oil per kilogram dry matter (grams of 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.

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

<u>Calculating fixed discharge quantities per jetting</u>: 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.

#### 6.2.Sampling

#### 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 (m<sup>3</sup>/s) is relatively constant throughout the discharge period. The discharge volume (m<sup>3</sup>) 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

#### 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 deepfrozen 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

<u>Method 2: Sample taken from sedimented sand when the jetting water flow has passed</u> <u>through a sand collection tank</u>

• 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

#### 6.3.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 grams of oil/kg DM.

#### 6.4.Calculating quantities discharged from each jetting

The volume discharged (m<sup>3</sup> 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.



# 7. METERING QUANTITIES (VOLUMES) DISCHARGED

## 7.1.Metering principles and maximum uncertainty required 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. The uncertainty provided by the various metering principles depends in part on:

- Installing the meter in line with the manufacturer's instructions
- Regular maintenance of the meter
- Actual water flow at the metering point and possible deposition in the pipe

#### 7.2.Documenting 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 ±10 per cent between the meters, the reason for the discrepancy should be assessed and consideration given to preventive maintenance, meter recalibration or replacement with a calibrated meter. 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 a 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)



# 8. UNCERTAINTIES

#### 8.1.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 main elements in 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. Accredited laboratories can specify uncertainty for the various analysis parameters, and it is possible to estimate uncertainty in water flow metering from an onsite verification/calibration.

## 8.2.Contributors to uncertainty when sampling

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

- Variations in the produced water's composition
- Condition of the sampling point
- Deficient sampling procedures

Errors which arise during sampling, and which contribute to 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. Chance errors arising from variations in the produced water's content of organic components and metals are regarded as relatively minor (Norwegian Oil and Gas, 2008), and two annual samples are regarded as sufficient. 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, sampling procedures/equipment which are not adapted to the sampling conditions, 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)
- 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 make sure 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.

### 8.3.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 ± 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.

Where OiW is concerned, a monthly crosscheck is recommended between non-accredited operational laboratories and accredited laboratories on land. Acceptance criteria should be established for discrepancies in the analyses. Accepted discrepancies between results (uncorrelated) from analyses offshore and on land with the same type of instrument are calculated from the average value for the two measurements (CG-FID onshore and field instrument offshore) compared with the measurements conducted with the field instrument offshore. Establishing a plan for following up variations is recommended. This will describe measures to be initiated in the event of repeated deviations over a specified period (such as two-three months).

#### 8.4.Uncertainty in metering water discharges

See section 5.2.

#### 8.5.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.

<u>Sampling</u>: A description of how the sample is taken. Not in detail, but with reference, for instance, to conformity with standards or the Offshore Norge guidelines. In addition, the operator must – in the event of an NEA audit – be able to document through procedures, logging and physical inspection that the sampling is conducted in accordance with the abovementioned standard and the Offshore Norge guidelines.

<u>Water flow metering</u>: Specification of the calculated uncertainty at the most recent verification. Brief description of the verification.

<u>Analysis uncertainty</u>: Specification of the identified uncertainty for the various parameters/parameter groups must be provided by an accredited laboratory. If an online OiW analyser is used, provide a brief description of how this is checked.



# 9. REPORTING

Reporting to the NEA and Footprint must accord with recommended guidelines 044 on annual discharge and emission reporting (Offshore Norge, most recent version). Pursuant to M-107, 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 the NEA's expectations.

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 performing 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