

Guidance Notes

for

The Sampling and Analysis of Produced Water and Other Hydrocarbon Discharges

The Offshore Petroleum Activities
(Oil Pollution Prevention and Control) Regulations
2005

Energy Development Unit
Offshore Environment and Decommissioning (EDU-OED)

CONTENTS

| | Page | |
|------|---|----|
| 1 | DEFINITIONS AND ABBREVIATIONS | 6 |
| 1.1 | Definitions | 6 |
| 1.2 | Normative References | 7 |
| 1.3 | Abbreviations | 8 |
| 2 | POINT OF CONTACT | 9 |
| 3 | INTRODUCTION | 10 |
| 3.1 | The Offshore Petroleum Activities (Oil Pollution Prevention and Control) Regulations 2005 (OPPC) | 10 |
| 3.2 | OPPC - Dispersed oil in produced water discharges to sea | 10 |
| 3.3 | Objectives of the guidance notes | 11 |
| 4 | PRODUCED WATER SAMPLING AND ANALYSIS REQUIREMENTS FOR OFFSHORE OIL AND GAS FACILITIES LOCATED IN THE UKCS | 12 |
| 4.1 | Offshore sampling general guidance | 12 |
| 4.2 | Offshore installations discharging >2 tonnes of dispersed oil to sea per annum | 12 |
| 4.3 | Offshore installations discharging <2 tonnes of dispersed oil to sea per annum | 12 |
| 4.4 | Offshore installations – produced water injection/re-injection | 13 |
| 4.5 | Offshore installations – produced water batch-wise discharge | 13 |
| 4.6 | Offshore installations – displacement water discharge | 13 |
| 4.7 | Compilation of monthly dispersed oil in produced water figure | 13 |
| 4.8 | Training requirements for personnel | 13 |
| 5 | PRODUCED WATER SAMPLE POINTS AND SAMPLING | 14 |
| 5.1 | Produced water sample point location | 14 |
| 5.2 | Design of produced water sample point | 14 |
| 5.3 | Produced water sampling when using online oil in water monitors | 14 |
| 5.4 | Produced water flow rate and sample point condition | 15 |
| 5.5 | Offshore produced water sample bottle requirements | 15 |
| 5.6 | Labelling and documentation requirements for sending samples for onshore analysis | 16 |
| 5.7 | Sample collection & treatment following sampling | 16 |
| 5.8 | Sample analysis and storage times | 17 |
| 5.9 | Taking duplicate produced water samples | 17 |
| 5.10 | Florsil | 17 |
| 6 | MEASUREMENT OF DISPERSED OIL IN PRODUCED WATER USING INFRARED ANALYSIS METHOD – DECC IR METHOD | 18 |
| 6.1 | Scope | 18 |
| 6.2 | Summary of Method | 18 |
| 6.3 | Apparatus | 18 |
| 6.4 | Reagents | 19 |
| 6.5 | Method of calibration | 19 |

| | | |
|-------|---|----|
| 6.6 | Method of Sampling | 22 |
| 6.7 | Extraction | 22 |
| 6.8 | Infra-red Spectroscopy | 23 |
| 6.9 | Calculation and Results | 23 |
| 6.10 | Annex A – DECC IR Method for determination of Oil on Sand/Scale | 25 |
| 7 | MEASUREMENT OF DISPERSED OIL IN PRODUCED WATER USING INFRARED ANALYSIS METHOD – DECC TRIPLE PEAK METHOD | 31 |
| 7.1 | Scope | 31 |
| 7.2 | Principle | 31 |
| 7.3 | Reagents | 31 |
| 7.4 | Calibration Reagents | 32 |
| 7.5 | Preparation of Stock Solution | 32 |
| 7.6 | Apparatus | 32 |
| 7.7 | Sampling | 33 |
| 7.8 | Preparation of Chromatographic Columns | 33 |
| 7.9 | Infra red spectrometer calibration | 33 |
| 7.10 | Procedure | 33 |
| 7.11 | Calculation of oil content | 34 |
| 7.12 | Expression of results | 34 |
| 7.13 | Annex B – Method of calibration & calculation by solving simultaneous equations using instruments with computer control | 35 |
| 7.14 | Annex C – Procedure for calibration check and analysis | 37 |
| 8 | IMPLEMENTATION OF THE OSPAR REFERENCE METHOD | 40 |
| 8.1 | Introduction | 40 |
| 8.2 | Using the OSPAR Reference Method directly. | 40 |
| 8.3 | Use of alternative oil in water analysis methods to the OSPAR Reference Method | 41 |
| 8.3.1 | Acceptance criteria for alternative analysis methods | 41 |
| 8.3.2 | Methodologies to demonstrate equivalent results | 41 |
| 8.4 | General approach on how to correlate an alternative analysis method | 41 |
| 8.4.1 | Method A1 - Correlation using laboratory prepared standard oil in water solutions when the alternative analysis method uses a solvent other than n-pentane. | 42 |
| 8.4.2 | Generation of Correlation Graph | 42 |
| 8.4.3 | Correlation standards preparation | 42 |
| 8.4.4 | Validation and re-correlation requirements | 43 |
| 8.5 | Method A2 – Correlation using laboratory prepared standard oil in water solutions when the alternative analysis method uses n-pentane as the solvent | 44 |
| 8.6 | Dealing with alternative method analyser instrument breakdown | 45 |
| 8.7 | General correlation issues covering methods A1 & A2. | 45 |
| 8.7.1 | Preparation of correlation graphs and statistical analysis | 45 |
| 8.7.2 | Labelling of axis | 45 |
| 8.7.3 | Straight line graphs | 45 |
| 8.7.4 | Correlation graph going through the origin | 46 |
| 8.7.5 | Reporting of oil in water values to DECC | 46 |
| 8.7.6 | Use of Accredited Laboratories | 46 |
| 8.7.7 | Other calibration procedures | 46 |

| | | |
|---------|--|----|
| 9 | OSPAR REFERENCE METHOD (ISO 9377-2 as modified by OSPAR) | 47 |
| | Annex D – UK Comments on the OSPAR Reference Method | 70 |
| 10 | USE OF ONLINE OIL IN WATER ANALYSERS 31 | 73 |
| 10.1 | Introduction | 73 |
| 10.2 | General approach | 73 |
| 10.2.1 | Requirement for calibrated alternative analyser | 73 |
| 10.2.2 | Procedure for the implementation of an online monitor: | 73 |
| 10.3 | Specific Issues | 74 |
| 10.3.1 | Installation | 74 |
| 10.3.2 | Sampling | 74 |
| 10.3.3 | Correlation | 74 |
| 10.3.4 | Construction of a correlation graph | 74 |
| 10.3.5 | Re-correlation requirements | 74 |
| 10.3.6 | Validation | 75 |
| 10.3.7 | Monthly correlation graph update | 75 |
| 10.3.8 | Approval from DECC | 75 |
| 10.3.9 | Reporting of oil in water data | 75 |
| 10.3.10 | Reporting of oil in water data from an online monitor | 76 |
| 10.3.11 | Dealing with online monitor breakdown | 76 |
| 10.3.12 | Responsibility | 76 |
| 10.3.13 | Other calibration approaches | 76 |
| 11 | BI-ANNUAL PRODUCED WATER SAMPLING AND ANALYSIS | 77 |
| 11.1 | Introduction | 77 |
| 11.2 | Bottles Required for Sampling | 77 |
| 11.2.1 | Bottles for PAH analysis | 77 |
| 11.2.2 | Bottles for BTEX analysis | 77 |
| 11.2.3 | Bottles for metal analysis (other than Mercury) | 77 |
| 11.2.4 | Bottles for mercury analysis | 77 |
| 11.2.5 | Bottles for organic acid (or Volatile Fatty Acid – (VFA)) analysis | 78 |
| 11.2.6 | Bottles for alkyl phenol analysis | 78 |
| 11.2.7 | Oil in water analysis | 78 |
| 11.3 | Packaging | 78 |
| 11.4 | Sampling Methods | 78 |
| 11.4.1 | General | 78 |
| 11.4.2 | PAH analysis | 78 |
| 11.4.3 | BTEX analysis | 78 |
| 11.4.4 | Metal analysis (other than Mercury) | 78 |
| 11.4.5 | Mercury analysis | 79 |
| 11.4.6 | Organic acid | 79 |
| 11.4.7 | Alkyl Phenol analysis | 79 |
| 11.4.8 | Oil in water | 79 |
| 11.5 | Analysis Methods | 79 |
| 11.5.1 | PAH analysis | 79 |
| 11.5.2 | BTEX analysis (Benzene, Toluene, Ethyl Benzene, (o,m,p Xylene) | 80 |
| 11.5.3 | Metals (Cd,Pb,Zn,Ni,As,Cr, Cu) | 80 |
| 11.5.4 | Alkyl phenol content | 81 |
| 11.5.5 | Organic acid content | 81 |
| 11.5.6 | Mercury content | 81 |

| | | |
|--------|---|----|
| 11.5.7 | Oil in water content | 81 |
| 11.6 | Reporting of test results | 82 |
| 12 | HYDROCARBON ANALYSIS OF NON-PRODUCED WATER DISCHARGE STREAMS | 83 |
| 12.1 | Measurement of crude oil on water based mud drill cuttings | 83 |
| 12.2 | Measurement of hydrocarbons on thermally treated Organo-Phase Fluid (OPF) drill cuttings | 83 |
| 12.3 | Measurement of crude oil on sand or scale | 84 |
| 12.4 | Measurement of oil in hazardous and non-hazardous drainage systems | 84 |
| 12.5 | Measurement of hydrocarbons in well-bore clean-up samples | 84 |
| | REFERENCES | 85 |
| | Appendices - Worked examples illustrating correlation methods developed in Chapter 8. | 86 |
| | Appendix A - Calibrating an Alternative Method against the OSPAR Reference Method using Laboratory Prepared Calibration Standards | 87 |
| | Appendix B - Correlating An Online Monitor against an Approved Alternative Method | 89 |

1 DEFINITIONS AND ABBREVIATIONS

1.1 Definitions

Accuracy: closeness of the agreement between result and true value.

Arithmetic mean: sum of measured values divided by the number of values.

Alternative method: any oil in water analysis method other than the OSPAR Reference Method.

Bias: consistent deviation of the measured value from the accepted reference value. It is a systemic error source, relating to the indication of a measuring instrument.

Calibration: a set of operations that establishes, under specific conditions, the relationship between the output of a measurement system and the accepted values of the calibration standards (e.g. amount or quantity of analyte).

Confidence interval: a number expressing the degree of confidence in a quoted result, e.g. 95%. The probability that the value of the measurement lies within the quoted range of uncertainty.

Correlation: interdependence or relationship between data from an alternative method and that from a reference method.

DECC IR method: a method that is based on TTCE extraction followed by infrared quantification at a wavelength of 2930 cm^{-1} . See details in Section 6 of the guidance notes. Accepted alternative method to OSPAR Reference Method.

DECC Triple Peak method: a method that is based on TTCE extraction followed by infrared quantification at three wavelengths. See details in Section 7 of the guidance notes. Accepted alternative method to OSPAR Reference Method.

Discharge limit: means a limit value for a concentration in mg/l , calculated on the basis of the total weight of the relevant substances discharged per month, divided by the total volume of water discharged during the same period.

Dispersed oil: means hydrocarbons as determined according to the reference method of analysis given in section 3.1 of the OSPAR Agreement 2005-15, which defines dispersed oil as: The sum of the concentrations of compounds extractable with n-pentane, not adsorbed on Florisil and which may be chromatographed with retention times between those of n-heptane (C_7H_{16}) and n-tetracontane ($\text{C}_{40}\text{H}_{82}$) excluding the concentrations of the aromatic hydrocarbons toluene, ethyl benzene and the three isomers of xylene.

Florisil: a trade name for a prepared diatomaceous substance, mainly consisting of anhydrous magnesium silicate.

Linear regression: in this document it is the same as least-squares linear regression, which works by finding the “best line” through the data that minimises the sums of squares of the residuals. It can be further defined as the process of finding the equation of a straight line that best fits the data and is the relation between variables when the regression equation is linear:

e.g., $y = ax + b$

Minitab: a trade name for commercially available statistical software package. See www.minitab.com for details.

Oil: OPPC definition: means any liquid hydrocarbon, or substitute liquid hydrocarbon, whether obtained from plants or animals, or mineral deposit or by synthesis.

OSPAR definition: the total of hydrocarbons as may be determined according to the methods of analysis given in section 7 of OSPAR Recommendation 2001/1.

OSPAR Reference Method: means ISO 9377-2 GC-FID method with modifications as detailed in OSPAR documents. See sections 8 & 9 of these guidance notes.

Precision: a statement of closeness of agreement between independent measured values under stipulated conditions and is usually stated in terms of standard deviation.

Regression coefficient: when the regression line is linear ($y = ax + b$) the regression coefficient is the constant (a) that represents the rate of change of one variable (y) as a function of changes in the other (x); it is the slope of the regression line.

Repeatability (of an instrument or of measurement results): closeness of the agreement between repeated measurements of the same property under the same conditions.

Reproducibility: closeness of the agreement between measurements of the same property carried out under changed conditions of measurements (e.g. by a different person or a different instrument, or at a different time).

Standard deviation: the positive square root of the variance, giving a measure of the distribution of values in a Normal probability distribution.

Uncertainty (of measurement): quantified doubt about the result of a measurement.

Validation: confirmation that initial calibration has not changed and is still valid.

Variance: a measure of the dispersion of a set of measurements, giving a measure of the distribution of values in a normal distribution.

1.2 Normative references

The following standards are referenced within these guidance notes and contain provisions which should be referred to when carrying out the methods detailed within this document. At the time of publication, the editions indicated were valid. All standards are subject to revision, and users of these Guidance Notes are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of ISO and IEC maintain registers of currently valid International Standards

IP 426:98 (04), Determination of the oil content of effluent water - Extraction and infra-red spectrometric method.

ISO 385:2005, Laboratory glassware – Burettes : General requirements.

ISO 835:2007, Laboratory glassware – Graduated pipettes : General requirements.

ISO 1042:1998, Laboratory glassware – One mark volumetric flasks.

ISO 3171:1988, Petroleum liquids – Automatic pipeline sampling

ISO 3696:1987, Water for analytical laboratory use – Specification and test methods.

ISO 5667-3:2003, Water quality - Sampling - Part 3: Guidance on the preservation and handling of samples.

ISO 8466-1:1990, Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics - Part 1: Statistical evaluation of the linear calibration function.

ISO 9377-2:2000, Water quality – Determination of Hydrocarbon Index – Part 2: Method using solvent extraction and gas chromatography.

OSPAR Agreement 2005-15: OPSAR reference method of analysis for the determination of the dispersed oil content in produced water.

OSPAR Agreement 2006-6: Oil in produced water analysis – Guideline on criteria for alternative method acceptance and general guidelines on sample taking and handling.

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1.3 Abbreviations

| | |
|------------|---|
| AAS | Atomic Absorption Spectroscopy |
| BTEX | Benzene, Toluene, Ethyl-benzene, Xylene |
| DRC-ICP-MS | Dynamic Reaction Cell Inductively Coupled Plasma Spectroscopy |
| DECC | Department of Energy and Climate Change https://www.og.decc.gov.uk/ |
| EEMS | Environmental Emissions Monitoring System |
| EDU | Energy Development Unit |
| FPSO | Floating, Production, Storage and Offloading |
| FT-IR | Fourier Transform Infrared Spectroscopy |
| GC | Gas Chromatography |
| GC-FID | Gas Chromatography – Flame Ionisation Detection |
| GC-MS | Gas Chromatography and Mass Spectrometry |
| GC-MS-MS | Gas Chromatography-Mass Spectrometry-Mass Spectrometry |
| HR-ICP-MS | High Resolution Inductively Coupled Plasma Mass Spectroscopy |
| ICP-AES | Inductively Coupled Plasma-Atomic Emission Spectrometry |
| IP | Institute of Petroleum (now Energy Institute) (http://www.energyinst.org.uk/) |
| IR | Infrared |
| ISO | International Organization for Standardization http://www.iso.org/iso/en/ISOOnline.frontpage |
| ISO WD | International Organization for Standardization Working Document |
| JIP | Joint Industry Project |
| MSDS | Material Safety Data Sheets |
| NPD | Naphthalene, Phenanthrene and Dibenzothiaphene |
| OCR | Offshore Chemical Regulations |
| OED | Offshore Environment and Decommissioning |
| OGUK | Oil and Gas UK (formerly UKOOA) http://www.oilandgas.org.uk |
| OIC | Offshore Industry Committee |
| OIW | Oil in Water |
| OIWAM | Oil in Water Analysis Method |
| OPF | Organic Phase Fluid (referring to drilling operator) |
| OPPC | Offshore Pollution Prevention and Control |
| OSPAR | Oslo Paris Commission http://www.ospar.org/ |
| PAH | Polycyclic or Polynuclear Aromatic (or Polyaromatic) Hydrocarbon |
| PARCOM | Paris Commission |
| POPA | Prevention of Oil Pollution Act |
| PON | Petroleum Operations Notice |
| TEX | Toluene, Ethyl-benzene, Xylene |
| TTCE | Tetrachloroethylene |
| UKCS | United Kingdom Continental Shelf |
| US EPA | United States Environment Protection Agency |
| UV | Ultraviolet |
| VFA | Volatile Fatty Acid |
| WBM | Water Based Mud |

2 POINT OF CONTACT

For specific technical queries regarding these guidance notes please contact:

Andrew Taylor, Environmental Inspector, on:

☎ Tel : 01224 254080

☎ Fax : 01224 254019

E-mail: andrew.taylor@decc.gsi.gov.uk

Código de campo alterado

or contact the Offshore Inspectorate Team at:

E-mail: offshore.inspectorate@decc.gsi.gov.uk

Código de campo alterado

☐ Written enquiries should be sent to:

Department of Energy and Climate Change
Energy Development Unit
Offshore Environment and Decommissioning (EDU-OED)
Atholl House
86-88 Guild Street
Aberdeen
AB11 6AR
United Kingdom

Future Revisions from Version 2.1

Future revisions to the Produced Water Sampling & Analysis Guidance Notes can be noted from the revision number. Major revisions to the document will be noted by a change to the first number, e.g. 3.1, 4.1, etc. Minor changes to correct errors or provide small clarifications will be noted by a change to the second number, e.g. 2.2, 2.3, 2.4, etc. Major revisions will be put out to industry for comment. Minor revisions will not be so notified and users of the document should ensure that they are using / referring to the latest version. Changes will be identified within the document.

3 INTRODUCTION

3.1 The Offshore Petroleum Activities (Oil Pollution Prevention and Control) Regulations 2005 (OPPC)

The OPPC Regulations prohibit the discharge of oil into the sea unless it is in accordance with the schedule conditions of a permit issued to cover the discharge. In support of OPPC, the Energy Development Unit - Offshore Environment and Decommissioning (EDU-OED) branch has provided clear technical guidance on suitable methods for the sampling and analysis of produced water (and other samples containing hydrocarbons) in order to enable industry to comply fully with the regulations.

Many of the schedule conditions contained in an OPPC permit depend on the accurate measurement of oil. The accurate measurement of oil in produced water is particularly important when considering the monthly dispersed oil in water discharge limit (30mg/l), produced water upsets and the calculation of hydrocarbon discharge quantities.

Summary - Oil in water analysis methods from 1 January 2007

The OSPAR / DECC approved oil in produced water analysis reference method is the OSPAR Reference Method which is a modified version of the ISO 9377-2 method. It is anticipated that most offshore facilities may continue to use the DECC IR method as an 'alternative' offshore method. Such an 'alternative' method must be correlated to the OSPAR Reference Method using procedures outlined in these guidance notes and in line with OSPAR Agreement 2006-06. Other facilities may opt to use the OSPAR Reference Method directly offshore. Operators may opt to use 'alternative' methods other than the DECC IR method, such as UV, but this should be discussed with DECC before being implemented offshore.

The OSPAR Reference Method is the standard method for dispersed oil in produced water analysis in the UK for both oil and gas facilities. Dispersed oil in produced water figures reported to DECC & EEMS must be reported in terms of this method.

Note: The OSPAR reference method is to be used ONLY for the determination of dispersed oil in produced water. This method is not to be used for the determination of oil in other discharges under OPPC, e.g. oil on sand, drains discharges, etc. From an OPPC perspective, the OSPAR Reference Method is only to be used for determination of discharges permitted under Schedule 1, 2 & 3 permits.

3.2 OPPC - Dispersed oil in produced water discharges to sea

For the discharge of dispersed oil in produced water to sea, the following sampling and analysis requirements are specifically mentioned in the OPPC permit schedule conditions:

- (a) Requirement to analyse produced water / displacement water discharges for dispersed oil.
- (b) Analysis of hazardous / non-hazardous drainage discharges for oil in water content, where sampling facilities exist.
- (c) Provision for the use of alternative analysis methods provided that DECC approves them.

- (d) Requirement for sampling and analysis, on a bi-annual basis, of produced water samples for:
 - (i) Total Aliphatics.
 - (ii) Total Aromatics.
 - (iii) Total Hydrocarbons.
 - (iv) BTEX (Benzene, Toluene, Ethyl Benzene and Xylene).
 - (v) NPD (Naphthalene, Phenanthrene and Dibenzothiophene, including C1-C3 Alkyl Homologues).
 - (vi) 16 EPA PAH's (excluding Naphthalene and Dibenzothiophene).
 - (vii) Organic Acids (Total Organic Acids, Formic, Acetic, Propionic, Butanoic, Pentanoic and Hexanoic Acids).
 - (viii) Phenols (Total Phenols, C0-C3 Phenols, C1, C2, C3, C4, C5, C6, C7, C8, C9 Alkyl Phenols plus Homologues).
 - (ix) Metals (Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Zinc)

3.3 Objectives of these guidance notes

- (a) To have one document covering all relevant aspects of oil in produced water sampling and analysis for UK offshore oil and gas facilities.
- (b) To provide guidance on how to correlate alternative oil in produced water analysers for use offshore, (including online monitoring methods), so that the resultant data can be accepted for reporting purposes.
- (c) To provide an updated version of the DECC IR method for the analysis of oil in produced water from offshore oil facilities.
- (d) To provide guidance on how to analyse produced water samples obtained from offshore gas / gas condensate facilities for aliphatic, aromatic and total hydrocarbon content using a modified version of the IP426/98 analysis method (Triple Peak Method).
- (e) To update requirements for the bi-annual analysis of produced water for dispersed, aromatic and non-oil components.
- (f) To provide updated guidance on how to implement the OSPAR Reference Method.
- (g) To provide updated guidance on the hydrocarbon analyses of non-produced water discharge streams, e.g. oil on sand / scale, oil (base oil and reservoir oil) on cuttings, oil (base oil and reservoir oil) in near wellbore clean-ups, crude oil on Water Based Mud (WBM) cuttings and oil in hazardous and non-hazardous drainage samples.

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https://www.og.decc.gov.uk/environment/opaoppcr_guide.htm.

4 PRODUCED WATER SAMPLING AND ANALYSIS REQUIREMENTS FOR OFFSHORE OIL AND GAS FACILITIES LOCATED IN THE UKCS

4.1 Offshore sampling requirements - general guidance

Produced water sampling requirements for offshore installations are detailed in the relevant OPPC permit schedule conditions. The sampling strategy followed will be partly influenced by the quantity of oil discharged to sea in the previous calendar year in so far as reference must be made to the previous year's EEMS returns to define whether or not an installation falls into the greater or less than two tonnes per annum category. Not all installations fall neatly into this classification and DECC has some degree of flexibility available although any changes to sampling strategies would only be allowed by submission of an OPPC permit variation. Should an operator wish to propose an alternative sampling strategy, they should contact their Environmental Inspector. The following information is a summary of typical produced water sampling schedule requirements.

Additional information on produced water sample handling and treatment may also be found in the ISO 9377-2 and ISO 5667-3 standards. The following guidelines are specific to the offshore oil and gas industry:

In certain situations where small amounts of oil are being discharged to sea, e.g. discharging less than two (2) tonnes of dispersed oil per annum and/or for unmanned installations where it may be impractical to take two samples per day; it may be more practical to ship samples directly onshore for analysis. Where samples are shipped onshore for analysis, it is recommended, that at least one sample, plus two duplicate spare samples i.e. three (3) bottles in total, should be taken for each sampling occasion (refer to Section 5.9 – Taking duplicate produced water samples). The duplicate samples need only be analysed should there be some doubt about the reliability of the first sample (e.g. first sample has a higher/lower than expected value), or if sample bottles are lost in transit or break. This arrangement should be discussed with DECC and detailed when applying for an OPPC produced water discharge permit.

4.2 Offshore installations discharging >2 tonnes of dispersed oil to sea per annum

- (a) Manned installations: at least two samples per day are required to be taken and analysed in order to comply with permit schedule conditions. These samples will be taken at approximately equal intervals, using the sample points described in section 5.
- (b) Unmanned installations: at least one set of produced water samples should be taken during each visit to the installation. Should the installation be temporarily manned for more than 48 hours, additional samples shall be taken every 48 hours for analysis.

4.3 Offshore installations discharging <2 tonnes of dispersed oil to sea per annum

- (a) Manned installations: a set of produced water samples should be collected and analysed at least once per calendar month.

- (b) Unmanned installations: one set of produced water samples shall be taken during each planned visit.

4.4. Offshore installations – produced water injection/re-injection

For installations injecting or re-injecting produced water, samples should be collected and analysed at least once per calendar month using a DECC approved method. *Note: visual estimation of high OIW concentration samples is not an approved method, but may be considered after discussion with a DECC Environmental Inspector.*

4.5. Offshore installations – produced water batch-wise discharge

For installations that discharge produced water in a batch-wise fashion, a sufficient number of representative sample(s) of each batch discharged must be taken and analysed. If the batch discharge continues for more than 12 hours, it should be sampled at least twice per day, at approximately equal intervals of time.

4.6. Offshore installations – displacement water discharge

For installations discharging displacement water, samples should be collected and analysed in the same way as per 4.2(a) & 4.3(a) as appropriate.

4.7. Compilation of monthly dispersed oil in produced water figure

ALL oil in water analysis results from a permitted discharge point must be included to calculate the overall monthly oil in water figure. It is not acceptable to ‘cherry-pick’ the best analysis results out of a suite of test results if, for example, monthly sampling is the required OPPC permit condition. If more analyses have been carried out then they must all be included in the compilation of the overall oil in water monthly figure. The monthly dispersed oil in produced water figure must be compiled and submitted to the department by the 16th of each calendar month via EEMS. Failure to do so is a breach of the permit conditions.

4.8. Training Requirements for personnel

It is a condition of the OPPC permits for discharge of oil to sea that personnel carrying out oil in water sampling and analysis methods must be provided with sufficient information, instruction and training to ensure the analysis is carried out correctly. Training records and any competence assessments of personnel should be kept on the installation where practical and made available to the Department on request. As a minimum, personnel conducting the analytical methods should be trained to a level of competency allowing personnel to perform the analysis correctly, manage routine verification, calibration, documentation and quality control test requirements without supervision. Operators must determine at what frequency periodic assessment or retraining of personnel is required in order to maintain levels of competency. This is particularly important where personnel do not routinely carry out the analytical procedures.

Note: DECC does not provide approval of training courses or assessments offered by operators or third party vendors. It is the responsibility of the operator to ensure that personnel are adequately trained to meet the requirements of the OPPC permit, their own requirements and the requirements of these Guidance Notes.

5 PRODUCED WATER SAMPLE POINTS AND SAMPLING

5.1 Produced water sample point location

The sample point for the collection of produced water samples should conform to the following criteria:

- (a) The sampling point should be immediately after the last item of treatment equipment in, or downstream of, a turbulent region, and in any case before any subsequent dilution. The sample point should also be downstream of any installed produced water volume meter (though see also 5.4b).
- (b) The location of the produced water sample point must be agreed with DECC and must not be changed without written permission. Failure to request permission to change the location of a sample point is a breach of the permit conditions and will require that an OPPC non-compliance be submitted.

5.2 Design of a produced water sample point

The design of the sample point should conform to the following criteria:

- (a) Vertical up-flow is the preferred orientation for installation of a produced water sample point. Under certain circumstances sample probes installed on downward flowing pipes may be acceptable provided that the flow velocity and mixing is adequate [see ISO 3171 for further details].
- (b) Where practicable, a centre line pitot should always be used. These are available commercially and can be of such a design that they can be withdrawn for inspection. Pitots can also be made very easily using stainless steel tubing or other suitable materials. The pitot should be of at least ½" bore and the edges of the pitot should be smoothed off prior to use. Where installation of centre line pitots may prove difficult, sidewall sampling may be used together with a suitably designed sample valve/tubing configuration.
- (c) For sample points in horizontal pipework, sample points should be located at a point where the flow velocity is high enough to provide adequate turbulent mixing. If centre line pitots are not available, sidewall sample points should be in the horizontal positions. Sidewall sample points on the top or bottom of horizontal pipe work is not recommended and should be avoided.
- (d) For external valving at the sample point, there will normally be a requirement for double block and bleed valving, although this may vary according to operator.
- (e) The distance between the sample probe and the sample valving should always be minimised, as the longer the sample line, the greater the chance of unrepresentative samples being collected. For example, where a sample point has not been flushed properly, there is a possibility that oil residue retained within the sample line will introduce an artificially high result.
- (f) Sample tubing requires no special guidelines but the material used should be compatible with the fluids being sampled. Generally, stainless steel is the preferred material of choice offshore, although special alloys may be required subject to fluid characteristics and safety implications. Plastic or rubber tubing must not be used.

5.3 Produced water sampling when using online oil in water monitors

Wide ranges of online oil in water monitoring technologies are commercially available and can vary significantly in terms of both their detection principles and

methods of sampling. Some systems operate using a side-stream taking produced water from the main process system, whilst others can be installed directly into the main produced water discharge pipe. Some general guidelines can, however, be applied to the installation of online systems so that representative sampling can be achieved.

- (a) Where online systems require a side-stream feed to the monitor, the feed should be provided by a dedicated sample connection. A centre line pitot should be used, in conjunction with vertical up flow (refer to Section 5.2a) to ensure that the sample is representative. Subject to the available pressure and the monitor flow requirements the sample may need to be pumped to the monitor.
- (b) The distance between the sample point and any external online monitor should be minimised as far as practically possible.
- (c) Where online systems require the installation of a probe into the main produced water flow line, the location should ensure that the probe is exposed to representative flow conditions, as detailed within ISO 3171.

5.4 Produced water flow rate and sample point condition

The use and condition of the sample point should conform to the following criteria:

- (a) Discharges of produced water to sea from sample points are a permitted activity under OPPC.
- (b) To assist in obtaining a representative sample, the sample point can be allowed to flow continuously if the sample point is downstream of the produced water meter. If the sample point is upstream of the produced water meter, the sample point must not be allowed to flow continuously between sampling occasions.
- (c) If sample points are not in continuous use, hydrocarbons and/or solids can collect within the probe and sample line. It is therefore essential that adequate flushing be carried out prior to a sample being taken. As a minimum, the sample point should be flushed for one minute prior to a sample being taken or until the line approximately reaches process temperature (i.e. the temperature of the vessel from which the fluid is being removed), whichever is the greater.
- (d) The sample point should be maintained in good working order.
- (e) Where the produced water flow rate is low and there are concerns about possible stratification, installation of an orifice plate to restrict flow and maintain turbulence should be considered.

5.5 Offshore produced water sample bottle requirements

The requirements relating to sample bottles used for dispersed oil in produced water analysis are as follows:

- (a) Clean borosilicate glass (high temperature) bottles of 500ml capacity should be used for the collection of produced water samples. Sample volumes of 1000ml may be required for analysis of low oil in water concentrations and with certain analysis methods. The ISO 5667-3 standard specifies 1000ml samples for hydrocarbon analysis.
- (b) Bottle caps must have an inert insert, as this will prevent contamination from the plastic bottle cap.
- (c) All sample bottles should be solvent washed prior to use and must be free of residual TTCE and excess water.

- (d) Plastic bottles should not be used under any circumstances, as plasticizers can leach in to the solvent and affect the analysis results.
- (e) Metal containers must not be used.
- (f) For sample shipment, sample bottles should be stored and transported in suitable sealed containers, which prevent ingress of light.

5.6 Labelling requirements for sending samples for onshore analysis

For samples to be sent onshore, it is essential that sample bottles be clearly labelled with the following minimum information:

- (a) Date and time sample was taken;
- (b) sample point location;
- (c) name of installation; and
- (d) type and amount of preservative added e.g. 2.5ml or 5ml HCl depending upon the volume of sampled water.

5.7 Sample collection and treatment following sampling

The following steps are requirements with regard to the collection and subsequent treatment of all produced water samples taken for analysis by either the IR method or OSPAR Reference Method:

- (a) Run the sample point as per 5.4.
- (b) Fill the sample bottle, taking care not to overfill it. If the temperature of the produced water sample is hot, heat protective gloves should be worn when collecting the samples. If the bottle is overfilled the sample must be discarded and the process repeated using a fresh, clean sample bottle.
- (c) Cap the bottle.
- (d) Acidify the sample with a 1:1 hydrochloric acid-water mixture to a pH <2, noting the volume of acid used. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to ensure that the pH is 2 or lower. Do not use immersion type pH probes to measure the pH of samples.

Warning: Produced water may contain sulphide compounds that when acidified may release hydrogen sulphide, which is extremely toxic, into the atmosphere. Acidification of the produced water sample must be carried out in an operational fume cupboard.

- (e) Cool the sample to lab ambient temperature (approx. 15°-20°C, but no more than 20°C) prior to the analysis being carried out. Other temperatures may be selected but only if they are specified in either a recognised analysis method or are recommended by the instrument manufacturer. The cap should be loosened during the cooling process and once cool, tightened securely.
- (f) Sample temperature can typically be determined using an IR or laser thermometer, or another method which avoids immersing a thermometer into the sample. The accuracy of the selected method should be checked on a 6 monthly basis. This can be carried out, for example, by a cross check against an alcohol thermometer with a certificate of conformity. Taking a temperature measurement of a liquid, both thermometers should read within $\pm 3^{\circ}\text{C}$ of each other. If the IR thermometer does not pass this check it should be replaced or recalibrated. The results of cross checks should be recorded in the oil in water logbook.

- (g) Sample sparging using nitrogen (or any other gas), is no longer permitted and should not be used under any circumstances unless it has been discussed and agreed with the Department.
- (h) Samples should be stored in a refrigerator (4°C to 8°C) if they are not going to be analysed within twelve hours. Prior to any analysis being carried out they must be warmed to laboratory ambient temperature or another specified temperature (see (e) above).

5.8 Sample analysis and storage times

For a variety of reasons it may not be possible to analyse the sample immediately (e.g. waiting on a replacement analyser, samples to be sent onshore for analysis), in which case samples must be acidified with a 1:1 hydrochloric acid-water mixture to a pH <2 and stored in a refrigerator (4°C to 8°C) until analysed. Samples sent onshore for analysis should be stored at or below in a refrigerator (4°C to 8°C), once received, until analysed. Preserved samples must be analysed within seven (7) days of collection. Where analysis within seven (7) days is not possible, an explanation must be provided to the appropriate DECC Environmental Inspector. For installations where samples are returned to shore for analysis on the same day as sampling, and where acid is unavailable, samples should be acidified on arrival at the onshore laboratory.

5.9 Taking duplicate produced water samples

When taking duplicate produced water samples mark duplicate sample bottles at 1/3, 2/3 and 3/3 volume measurement and then fill the sample bottles 1/3 at a time in turn until all bottles are full.

5.10 Florisil

Where there are concerns that polar components such as fatty acids may interfere with the analysis/detection method, the use of 1-2g of activated Florisil to treat the produced water sample extract is recommended. If used correctly this should ensure that polar components are removed from the sample extract prior to quantification. Note that un-activated florasil will not effectively remove polar and/or VFA components from the sample, possibly resulting in higher OIW results. Florisil containers must be securely sealed and must be stored in a desiccator when not in use. Florisil must be activated (16 hours at 140°C) prior to use, which may be carried out before being shipped offshore or activated offshore if suitable facilities exist. Whilst being shipped offshore, the activated Florisil must be kept dry. Activated Florisil, once opened and if stored correctly in a desiccator, will remain activated for 30 days. Larger amounts of Florisil may be used under exceptional circumstances but such use would be subject to DECC approval.

Where there is no facility to activate / reactivate florasil offshore, smaller volume containers e.g. 100g, of florasil should be considered so as to minimise or avoid unnecessary waste.

Note: For florasil to be effective, it must be activated and the solvent must be slowly passed through the florasil. Flooding the filter paper, such that the bulk of the solvent absorbs through the filter paper and runs down the side of the filter funnel without passing through the florasil, will not be effective and may result in higher results.

6 MEASUREMENT OF DISPERSED OIL IN PRODUCED WATER USING INFRARED ANALYSIS METHOD - DECC IR METHOD

(DECC Infrared / Tetrachloroethylene Method)

This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health procedures and to comply with relevant UK health and safety legislation.

6.1 Scope

This method is intended for the determination of the oil content within produced water, drains and other discharge streams. The method includes the measurement of most light oil fractions, although some loss of volatile components will occur during extractions.

The method has a nominal working range from 0 to 80mg/l and 0 - 0.8 A (absorbance units). The lower level of detection can be improved to 0.1mg/l by using longer path-length cells. The upper limit of the method can be extended at least to 1,000 mg/l by preparing dilutions of the sample extract.

Note: Although this procedure seeks to address all aspects of the analysis method, it is not equipment specific. It is the responsibility of the user to ensure that suitable local operating procedures are in place, for the specific equipment in use, in order to ensure that the analysis is carried out correctly.

6.2 Summary of Method

A sample of the discharge water to be analysed is acidified to a low pH (<2), extracted with two volumes of Tetrachloroethylene (TTCE) or an alternative solvent approved by DECC, and the IR absorbance measured using an infrared analyser with a fixed wavelength of 2930cm⁻¹. The oil content of the sample is determined by comparison of the infrared absorbencies of the extract against a calibration graph prepared using a series of standards containing a known mass of crude oil.

6.3 Apparatus

6.3.1 Glass separating funnel, 500ml or 1000ml volume, with PTFE stopcock.

6.3.2 Infrared spectrophotometer, preferably with fixed wavelength.

6.3.3 Cells, stoppered - 5mm path-length, sodium chloride or infrared grade quartz with a minimum of 80% transmittance at 2,930 cm⁻¹. The 5mm path-length is recommended as being convenient for monitoring levels normally encountered. Longer path-lengths may be used.

6.3.4 50ml class A volumetric flask with Teflon[®] stopcock.

6.3.5 Filter paper, medium grade, 12.5cm.

6.3.6 Glass sample bottles, 500ml or 1000ml with caps containing inert inserts.

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6.3.7 Glass Filter funnel, 10cm or 15cm diameter.

6.3.8 500ml or 1000ml measuring cylinder (5ml graduations).

6.3.8 IR or Laser Thermometer – used to determine temperature of samples and standards. The thermometer should be such that the temperature of the fluid can be determined without immersing the thermometer into the fluid itself.

Note: The thermometer should be maintained in a suitable manner to ensure accurate temperature measurement – refer to section 5.7 (f).

6.3.10 Lens cleaning tissue

6.3.11 Lab Fridge – used to store correlation standards and maintain them at 4°C to 8°C.

Note: All vessels likely to come into contact with extractant should be made of glass.

6.4 Reagents

6.4.1 Hydrochloric acid, 1:1 (HCl). Analytical reagent grade (36-38% AR or SG1.18 AR). Prepare by adding equal volumes of concentrated HCl to distilled water.

6.4.2 Sodium chloride - Reagent Grade.

6.4.3 Activated Florisil: 30 - 60 or 60 – 100 mesh B.S.S. (or equivalent). Also refer to section 5.10.

6.4.4 Tetrachloroethylene (TTCE). The solvent used must be free from contaminants or stabilisers, which may interfere with infrared absorption at the wavelength used.

Note: TTCE is harmful by inhalation, ingestion and skin absorption. All handling of TTCE should be carried out within an operational fume hood as far as possible.

Note: Whilst Tetrachloroethylene is the current DECC approved extraction solvent, DECC will allow the use of the proprietary solvent S-316 (a dimer/trimer of chlorotrifluoroethylene) as a direct replacement for tetrachloroethylene in the DECC IR method.

6.5 Method of Calibration

The series of standards required for calibration should be prepared by introducing a known mass of the particular stabilised crude involved into a known volume of distilled or deionised water followed by extraction, and preparing further standards by successive dilution of the extract. On installations where movement or motion prevent the generation of calibration standards using a weighed sample of crude, a fixed volume of crude can be used instead, by using a calibrated micropipettor or syringe

and dispensing the required volume of crude. The volume of the sample can then be converted back into mass by multiplying the volume of sample by the crude density at the temperature at which the calibration is carried out. Calibration should be carried out at lab ambient temperature (approx. 15°C - 20°C), but no more than 20°C.

6.5.1 Oil Reference: A fresh, stabilised crude oil or crude oil blend that is representative of the produced waters being processed should be selected and used. Typically a dry export crude sample will be suitable, though if export crude is a blend of the host installation and an imported crude, which is not processed on the host installation, then a crude sample should be taken from upstream of where the two different crude streams co-mingle. The well configuration at the time of sampling the crude should also be recorded. Operators should endeavour to obtain crude samples for calibration when the process is stable. Significant variation in well configuration may affect the overall oil composition and hence, calibration of the IR analyser. In these cases, recalibration of the IR analyser and correlation to the onshore GC may be required. It is the responsibility of the Operators to assess if variation in well configuration has such an impact.

Note: Well configuration data that should be recorded as a minimum are, the wells which are flowing at time of sampling, well production rates and water cut.

6.5.2 Stock Reference Standard: Accurately weigh about 300 mg (approx. 350µl if using a fixed volume) of reference oil and add to 1 litre of distilled / deionised water in a separating funnel. Add 5g of sodium chloride and shake well. Extract as per Section 6.7 below in 100 ml of solvent to form a stock reference standard.

6.5.3 Calibration Standards: Prepare a series of dilutions by pipetting volumes of stock reference standard into 100ml class A volumetric flasks and diluting to volume with solvent. A convenient series of volumes for dilution is 1, 5, 10, 15, 20 and 25ml of stock solution. Calculate the exact equivalent concentrations of oil in water of the dilutions in mg/l for each prepared standard.

6.5.4 Determine the IR absorbance of each standard and plot a best fit straight line graph of absorbance vs. oil in water concentration (mg/l). The correlation coefficient of the straight line should be calculated and, for IR instruments following this method, should be ≥ 0.98 . For other instruments or alternative methods, e.g. U.V. Fluorescence, lower coefficients may be acceptable. In these cases, or if an R^2 value of ≥ 0.98 for an IR method cannot be achieved, the operator should contact the relevant DECC Environmental Inspector to discuss.

Note: Should the best fit line of the graph result in low absorbance readings producing negative oil in water concentrations, then negative results should be reported as zero.

6.5.5 If the calibration of the alternative instrument has been carried out by an onshore laboratory, a portion of each of the calibration standard solutions, as well as the blank solution, must accompany the calibrated alternative

instrument offshore. On arrival, two standard solutions (at approximately 20% and 80% of the instrument range) used in the generation of the calibration graph, must be analysed offshore immediately. It should be confirmed with the onshore laboratory whether the analysis results lie within 95% of the calibration graph confidence limits to confirm that the calibration graph is still valid following shipment

- 6.5.6** If calibration solutions are prepared onshore but the calibration of the alternative instrument is to be carried out offshore, the calibration solutions, as well as a blank solution, must be clearly labelled with oil concentration (mg/l) and date generated prior to shipment. On arrival of the calibration solutions offshore, the solutions should be allowed to warm to lab ambient temperature and the IR instrument must be zeroed with the blank solution provided and the absorbance of the six calibration solutions determined. A graph of oil concentration vs. absorbance can then be generated (either offshore or by the onshore laboratory).
- 6.5.7** When a calibration curve is supplied, it must be signed and dated with the instrument serial number, analyst's name, and the correlation coefficient clearly recorded. Where calibration standards have been prepared based on oil volume and the mass calculated by oil density, the density of the oil at the calibration temperature must also be recorded.
- 6.5.8** Recalibration must be carried out every 6 months or sooner if the current calibration is found to be no longer valid during monthly validation checks.
- 6.5.9** During the 6 month period, at least one calibration validation check must be carried out each month following the month of calibration. This is achieved by analysing a standard solution that has been used in establishing the original calibration curve (Refer to Section 8.4.4 for full details).
- Note:** The standard solutions must be stored in a fridge (4°C to 8°C) and be kept tightly sealed when not in use. Standard solutions should not be kept for longer than six months.
- 6.5.10** If the calibration of an IR graph results in a non-linear graph this may prove problematic if trying to correlate the IR method against the OSPAR Reference Method. In many cases it is possible to obtain a graph that is linear in the 0-80mg/l range. If not the following questions should be addressed:
- (a) Is the correct determinand being used? e.g. transmission being used instead of absorbance;
 - (b) Is the optical band width too wide? Can it be adjusted? This may be the case with some filter instruments; and
 - (c) Is too high a concentration being measured? Diluting the solvent extract or reducing the optical path length can overcome this. In some cases other calibration ranges may be more appropriate e.g. 0-40mg/l if a non-linear response is being obtained.

If points (a) to (c) are addressed and a non-linear response is still obtained, it may be necessary to select a different instrument or analysis method.

6.6 Method of Sampling

Refer to Section 5.7 of these guidance notes for details regarding sampling & sample treatment.

6.7 Extraction

6.7.1 Cool the sample to lab ambient temperature (approx. 15°C - 20°C, but no more than 20°C).

6.7.2 Add 2.5ml of 1:1 hydrochloric acid to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the inside of the cap to ensure that the pH is 2 or lower. Add more acid if necessary to reduce the pH to 2 or lower. In cases where the presence of process chemicals results in an emulsion layer at the water/solvent boundary, additional acid may be added to break up the emulsion. Where additional acid is added, the total volume of acid used should be noted and deducted from the sample volume when calculating oil concentration (see section 6.9).

Note: It should be noted that unless there is a significant change in well fluids, which may also change produced water pH, the pH of produced water will not vary significantly. Once it has been established that a given volume of HCl will reduce pH to <2, then it is not necessary to check this with pH paper for every analysis. This check will only be required to be carried out periodically or should well fluids change.

Note: In exceptional circumstances, emulsions of TTCE and water may form. In some cases the addition of sodium hydroxide may be more effective at breaking this emulsion. Operators wishing to do this must first discuss this with DECC.

6.7.3 Pour the sample into a clean, dry separating funnel.

6.7.4 Add exactly 25ml solvent to the sample bottle.

Note: If dispensers are used to measure out volumes of solvent, then periodic checks that the dispenser is accurately measuring the required volume should be carried out.

6.7.5 Cap tightly and thoroughly shake the bottle for about 15 seconds to rinse the inside and cap. Transfer the solvent into the separating funnel and extract by shaking vigorously for 2 minutes, venting regularly to remove any pressure build-up.

6.7.6 Allow the mixture to stand for a period of at least five minutes in order for the TTCE to fully separate.

6.7.7 If required, place 1-2g of activated powdered florisil into a solvent moistened filter paper. Larger amounts of Florisil can be used if it can be demonstrated that this is required to remove larger than normal amounts of polar compounds from the produced water sample. Approval for the use of increased amounts of

Florisil must be obtained from a DECC Environmental Inspector. If desired, the Florisil may be placed in a thin glass column rather than onto filter paper. The use of florisil to treat the sample is recommended.

- 6.7.8** Drain the solvent layer slowly through a glass funnel containing solvent-moistened filter paper (and 1-2g of florisil if used) into a 50ml class A volumetric flask, avoiding overfilling or flooding the paper.
- 6.7.9** Repeat steps 6.7.4 – 6.7.6 with an additional 25ml portion of fresh solvent and drain the solvent layer through the filter paper, combining all solvent in the volumetric flask.
- 6.7.10** Rinse the tip of the separating funnel with a small portion of solvent and collect the rinsings in the volumetric flask. Adjust the extract volume up to 50ml with solvent by running additional solvent through the florisil and filter paper and stopper the flask. **Mix well.**
- 6.7.11** Drain the water layer into a 500 ml graduated cylinder and measure the sample volume to the nearest 2.5 ml.

6.8. Infra-Red Spectroscopy

- 6.8.1** Prepare the infra-red spectrophotometer according to the manufacturer's instructions.
- 6.8.2** Rinse a cell thoroughly and ensure that it is clean and oil free both outside and inside. Fill with clean solvent and place in the instrument. Adjust the meter to zero and ensure that the reading is steady.
- 6.8.3** Rinse a cell with two volumes of the extract to be measured and then fill the cell. Place the cell in the meter and note the absorbance reading.

6.9. Calculation and Results

- 6.9.1** Using the calibration graph, determine the oil concentration in the sample in mg/l.
- 6.9.2** If the absorbance reading is outwith the range of the linear calibration graph, a portion of the sample extract must be diluted. Using a clean, dry glass pipette withdraw 10ml of extract and transfer to a clean, dry 50ml volumetric flask. Make up to the mark with fresh TTCE and determine the oil concentration of the diluted sample extract as above.

- 6.9.3** Correct the observed oil concentration (mg/l) for sample volume, acid added and any dilutions using the following calculation (the analytical method assumes a 500mL sample volume):

$$\text{Corrected oil concentration (mg/l)} = \frac{\text{oil concentration (from 6.9.1)} \times 500\text{ml} \times \text{DF}}{\text{(Actual sample volume - vol. acid added)}}$$

Where,

DF = dilution factor = (volume extract diluted to / volume of extract to be diluted).

For example 10mls of extract is diluted to 50mls. Dilution factor = (50/10) = 5. If no dilution of the extract has occurred the dilution factor is 1.

- 6.9.4** Report results to nearest 0.1 mg/l for levels below 100mg/l. For results above 100mg/l report to the nearest 1mg/l.
- 6.9.5** For produced water measurement (only) the IR result obtained above must be correlated to the OSPAR Reference Method as detailed within Section 8.4.

6.10 Annex A

DECC IR Method for Determination of Oil on Sand/Scale/Solids

This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health procedures and to comply with relevant UK health and safety legislation.

A.1 Background

To comply with a Permit to discharge oil on sand under the Oil Pollution Prevention and Control Regulations 2005 (OPPC), representative samples and calculated estimates of the weight of discharged solids are required. The oil content of each discharge should be less than the OPPC permitted limit for that installation. These limits vary for each installation. Details of the sand washing and discharge process along with sample regime and analysis must be described within the OPPC application.

Any material to be discharged must first be cleaned to ensure that free oil is removed and recovered. This can be by an online cleaning system or an offline mobile washing tank/vessel. Upon leaving the washing phase the solids must be sampled before discharge (and commonly macerated to <1mm verifiable particle size). Discharge to sea should only commence upon authorization by the installation operator.

Compliance with OPPC can only be confirmed by hydrocarbon analysis, with results determined in an onshore laboratory, though preliminary analysis may be carried out offshore in order to give an indication that sand cleaning has achieved the required permit conditions and to allow discharge rather than wait for onshore results (this would require duplicate samples).

There are three main types of method used in the offshore oil & gas industry:

- Online & Offline in-process washing
- Online & Offline mobile washing
- Offshore decontamination chambers

A.1.1 Online & Offline in-process Washing

For installations that have solids cleaning systems as part of the process, the sample points will be installed as part of the washing unit. The sampling frequency will be entirely dependent on the design of the system and the operator should define the regime in order to make the samples 'representative'.

Installed meters can be used to estimate solids mass per discharge and a mass should be assigned against each sample to calculate the monthly and annual discharge. If no metering is installed to measure the mass of solids discharged to sea, then calculations should be made from solids production estimates or process system designs specifications to then allocate mass to each sample.

A.1.2 Online & Offline Mobile Washing

Probably the most common method of solids disposal is to remove the solids and route them to a mobile washing vessel. In most cases this is done by a third-party specialist cleaning contractor. The mobile washing vessels usually have sampling points installed on them, and if not samples can be taken at the outflow to the macerator.

The mass of each batch of solids can either be measured by instrumentation attached to the mobile wash vessel, or by estimation of the solids mass added to each batch wash.

Representative samples should be taken after each batch wash and the mass of each batch estimated and recorded. It is critical to ensure these two figures are assigned against each other correctly as many samples may be taken during a cleaning campaign with varying hydrocarbon composition in each wash, as well as varying mass per wash.

A.1.3 Offshore Decontamination Chambers

In some cases equipment can be cleaned & decontaminated offshore in a dedicated container/chamber/habitat. It is acceptable to accumulate material in the sump of the chamber and to take representative samples of that material. Before being routed to a macerator for disposal to sea, solids should be collected in the sump in the chamber, or at the macerator, and representative samples should be taken.

A.1.4 Sample Size

Solids samples should contain a minimum 50g of solid material. Free water should be poured off. The solid component should be placed into a suitable glass bottle, with water-tight cap and inert inserts, which has been solvent washed prior to use and free of oil and excess solvent. Plastic and metal sample containers should not be used. Wide necked glass bottles are recommended for ease of sub-sampling.

Sample bottles for despatch onshore must be fully labelled, for example: Sample ID, Installation, date & time, discharged mass, etc.

A.1.5 Final Discharge (online or offline)

Operators must have procedures in place to ensure that discharges are authorised by a responsible person. All results for oil on sand/scale/solids discharge must be recorded and kept available for inspection by DECC, preferably at the offshore location.

A.2 Scope

This method uses the DECC IR method as the basis for a method to determine the concentration of oil on sand/scale and provides amendments to that procedure. This method requires some additional analytical equipment and it may not be possible to carry this out on all installations (e.g. FPSO's where operation of a balance is impractical).

Note: Although a balance is required in order to carry out the above procedure, it may be possible to carry out this method based on volume of sand and using a suitable density factor for the sand. It would be necessary for operators to determine sand density via onshore analysis and some comparison of results over a number of samples made between onshore and offshore analysis to demonstrate suitability of the density factor. Any such approach should be discussed with a DECC inspector during the OPPC application process.

A.3 Summary of Method

A sample of the sand/scale/solids to be analysed is collected and a known weight of sub-sample is extracted in TTCE. The resultant extract is analysed by IR to determine the oil content. A calculation is then performed to determine the oil on sand/scale concentration in mg/kg. This analysis is carried out in triplicate on a composite sample obtained by taking a number of sub-samples from different points of the overall sand to be analysed prior to discharge. The average of the results obtained is used for reporting to DECC for each batch discharge.

Note: The oil on sand/scale is determined using IR and is NOT to be correlated to a GC-FID equivalent result as per produced water.

A.4 Apparatus

The additional equipment required to carry out this method are:

A.4.1 Analytical balance, 1 decimal place.

A.4.2 Filter Funnel, 100mm minimum.

A.4.3 Filter paper, to fit filter funnel.

A.4.4 Spatula.

A.4.5 100ml wide necked Duran Bottle or equivalent.

A.5 Reagents

No additional reagents beyond those used for the DECC IR Method are required to carry out this method.

A.6 Method of Sampling

- A.6.1** Sampling of the sand/scale/sludge must be performed in a manner to ensure that, as far as practically possible, representative samples are obtained.
- A.6.2** For sampling from mobile wash vessels at the outlet of the washing-vessel or macerator, as a minimum 3 samples must be taken per batch wash, evenly split across the batch (e.g. start, middle and end of discharge). These samples may be taken into the same sample bottle as a composite for the batch. If analysis is to be carried out both onshore and offshore, duplicates of each sample or composite will be required or sufficient sample taken so as to be able to split the sample to send onshore and offshore.
- A.6.3** For sampling from drums, skips or other vessels where bulk sand is stored prior to disposal, it is recommended that a minimum 50g composite sample is obtained by taking samples from the accumulated sand at a number of evenly spaced points and depths. Samples should not all be taken from the surface of the accumulated sand. The composite sample should then be mixed, before a sub-sample is taken for analysis.
- A.6.4** For sampling from in-process washing systems a representative sampling strategy must be defined within the OPPC application and agreed with DECC.
- A.6.5** All sample bottles must be solvent washed prior to use and be in a clean, dry condition. Plastic and metal bottles must not be used. Wide necked glass bottles are recommended for ease of sub-sampling.

A.7 Method of Calibration

The current, valid IR calibration graph is used for this analysis.

A.8 Extraction

- A.8.1** Weigh a clean, dry 100ml glass bottle to 1 decimal places. Using a spatula, transfer approximately 10g (or equivalent volume based on sand density) of the sludge/scale to the bottle and record the weight of the sub-sample to 1 decimal place.
- A.8.2** Measure 25ml of TTCE into the bottle containing the 10g sub-sample. Ensure the lid is tightly closed and shake vigorously for 1 minute. Carefully vent any gas by opening the lid slowly once the TTCE has settled.
- A.8.3** Place the 100mm filter funnel, containing a 1PS filter paper, into the top of a 500ml or 1000ml separating funnel and pour the solvent from the bottle into the separating funnel, ensuring the outlet valve on the separating funnel is closed.
- A.8.4** Repeat steps A.8.2 & A.8.3 three further times until all the TTCE has been transferred to the separating funnel. The sand should be trapped in the filter paper in the filter funnel so as to avoid blocking the stopcock of the separating funnel.

A.8.5 If required, place 1-2g of activated powdered florisil into a solvent moistened filter paper beneath the separating funnel.

A.8.6 Drain the solvent layer through a glass funnel containing solvent-moistened filter paper (and 1-2g of florisil if used) into a 100ml class A volumetric flask.

A.8.7 Rinse the tip of the separating funnel with a small portion of solvent and collect the rinsings in the volumetric flask. Adjust the extract volume up to 100ml with solvent by running additional solvent through the florisil and filter paper and stopper the flask. **Mix well.**

Note: Some installations will have an IR calibration graph based upon 50ml standards. As a result of using 100ml in this extraction step, the concentration of oil in the resultant extract using this procedure will be half what it should be. This will be taken into account in the calculation at the end.

A.9 Infra-Red Spectroscopy

A.9.1 Rinse a cell thoroughly and ensure that it is clean and oil free both outside and inside. Fill with clean solvent and place in the instrument. Adjust the meter to zero and ensure that the reading is steady.

A.9.2 Perform a x10 dilution of the extracted TTCE using a suitable volumetric flask and pipette which have been solvent washed prior to use. Note the dilution factor.

A.9.3 Rinse a cell with two volumes of the diluted extract to be measured and then fill the cell. Wipe the outside of the cell and place the cell in the meter and note the absorbance reading. If the absorbance is over the analytical range of the graph, further dilutions must be made, similar to section 6.9.2 of the IR method above.

A.10 Calculation and Results

A.10.1 Using the calibration graph, determine the oil concentration in the sample in mg.

Note: The IR calibration graph reports in mg/l but treat this as mg of oil in the sample for these purposes.

A.10.2 Correct the observed oil concentration (mg) for sample volume and any dilutions using the following calculation:

$$\text{oil concentration (mg/kg)} = \frac{\text{oil concentration (from A.10.1)} \times 1000 \times \text{DF} \times 100}{\text{sample weight (g)} \times Y}$$

Where,

DF = dilution factor = 10 plus any further dilutions required.

Y = normal IR calibration standard solution volume (ml).

For example: For a 10g sample, after diluting the initial extract by x10 a further x2 dilution is required to bring the extract concentration in range of the calibration graph. The final analysis result for the diluted oil concentration was 12mg. The total dilution factor is $10 \times 2 = x20$ dilution. The IR graph was also created using 100ml standards. The calculation is therefore:

$$\text{oil concentration (mg/kg)} = \frac{12 \times 1000 \times 20 \times 100}{10\text{g} \times 100} = 24,000\text{mg/kg}$$

A.10.3 Report results in mg/kg.

A.10.4 Do not correlate the IR result to the OSPAR Reference Method as total petroleum hydrocarbons are to be reported not just dispersed oil.

7 MEASUREMENT OF DISPERSED OIL IN PRODUCED WATER USING INFRARED ANALYSIS METHOD - DECC TRIPLE PEAK METHOD

Determination of the oil content of effluent water – Extraction and infra-red spectrometric method (Modified from the IP 426/98 method)

| |
|---|
| <p>This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health procedures and to comply with relevant UK health and safety legislation</p> |
|---|

7.1 Scope

Due to the presence of dissolved aromatics often found in high quantities in produced water samples obtained from gas/gas-condensate facilities, the measured oil in water figures using the DECC IR method may overestimate the dispersed oil content. If using IR analysis as an alternative method to the OSPAR Reference Method for analysing produced water samples taken from gas or gas-condensate installations it is recommended that the DECC Triple Peak Method (a modified version of the IP 426/98 method) be used. This method will allow total hydrocarbons, aliphatic hydrocarbons, and aromatic hydrocarbons to be calculated. This method is also the recommended method for the bi-annual analysis for oil in water analysis which requires reporting of total aliphatics, total aromatics and total hydrocarbons (refer to Section 11). Should this method be used as an alternative method for dispersed oil in produced water reporting, the total aliphatic hydrocarbons result should be correlated against the OSPAR Reference Method.

This standard specifies a method for the determination of the hydrocarbon oil content of water effluent, in the milligram per litre range.

NOTE 1: Calibration involves the solving of simultaneous equations and is suitable for instruments with computer control. In addition, procedures are given for both single and double beam instruments.

7.2 Principle

A known volume of produced water is acidified with hydrochloric acid and extracted with tetrachloroethylene (TTCE). The extract is eluted through a chromatographic column packed with an activated magnesium silicate to remove polar material, and magnesium sulphate to remove traces of moisture.

The treated extract is placed in a 10 mm silica infra-red (IR) cell and the absorbances of the peaks at 3030 cm^{-1} , 2960 cm^{-1} and 2930 cm^{-1} are measured in a scanning infra-red spectrometer. These absorbance values are used to calculate the oil content of the produced water sample.

Note 2: The absorbance of the peak at 3030 cm^{-1} measures aromatic or alkenic C-H stretch, the absorbance of the peak at 2960 cm^{-1} measures $\text{CH}_2\text{-H}$ /methyl C-H stretch and the absorbance of the peak at 2930 cm^{-1} measures CH-H/methylene C-H stretch.

7.3 Reagents

7.3.1 During the analysis, unless otherwise stated, use only reagents of recognized analytical reagent grade and only water conforming to grade 3 of ISO 3696.

- 7.3.2** Hydrochloric acid, HCl, concentrated [35.4% (m/m)].
- 7.3.3** Sodium chloride, NaCl
- 7.3.4** Magnesium sulphate MgSO₄, dried for 4 hours at 500°C, cooled to 200°C in a furnace and then placed in a desiccator and cooled to room temperature.
- 7.3.5** Column packing, an activated magnesium silicate of 250 µm diameter to 500 µm diameter (30 mesh to 60 mesh) dried for 4 hours at 500°C, cooled to 200°C in a furnace and then placed in a desiccator and cooled to room temperature.

Note 3: Florisil® has been found to be satisfactory

Florisil® is an example of a suitable product available commercially. This information is given for the convenience of users of this standard and does not constitute an endorsement by DECC of this product.

- 7.3.6** Tetrachloroethylene (TTCE), the solvent used must be free from contaminants, which may interfere with infrared absorption at the wavelengths used. Alkyl phenol stabilised TTCE solvent is recommended.

7.4 Calibration Reagents

- 7.4.1** Toluene
- 7.4.2** Hexadecane
- 7.4.3** 2,6,10,14-Tetramethylpentadecane (TMPD)

7.5 Preparation of stock solutions

Prepare nominal 200mg/l stock solutions in TTCE of each of the calibration reagents by weighing 0.20g of each of the calibration chemicals to the nearest 0.1 mg into separate 1L flasks (7.6.8). Dilute to the mark with TTCE and record the exact concentration to the nearest 0.1 mg/l on the flask.

7.6 Apparatus

- 7.6.1** Chromatography column, nominal diameter of 12 mm to 25 mm, and nominal length 100 mm.
- 7.6.2** Magnetic stirrer and follower, approximately 25 mm in length.
- 7.6.3** Separating funnel, nominal capacity 500 ml.
- 7.6.4** Measuring cylinder, 50 ml capacity.
- 7.6.5** Infra-red spectrophotometer, dispersive type or Fourier transform type, covering the range 4000 cm⁻¹ to 2500 cm⁻¹, with a dedicated computer for data manipulation.

- 7.6.6** Silica cells, matched IR grade 10 mm.
- 7.6.7** Stoppered glass conical flasks, nominal capacity 50 ml.
- 7.6.8** Volumetric flasks, one mark 500 ml and 50 ml capacities, conforming to class A of ISO 1042
- 7.6.9** Burette, 50 ml capacity, conforming to class A of ISO 385.
- 7.6.10** Graduated pipettes, conforming to class 1 of ISO 835. 10 ml, 30 ml and 50 ml capacity.
- 7.6.11** Analytical balance, with a weighing accuracy of 0.1 mg.

7.7 Sampling

Refer to Section 5.7 of these guidance notes for details regarding sampling & sample treatment.

Note: If oil concentration is expected to be very low, then sample volume may be increased to 1000ml to compensate for the additional solvent volume used.

Note: Produced water samples analysed by the DECC Triple Peak Method must not be sparged to remove volatile hydrocarbons prior to sample analysis since this will remove a significant portion of the total hydrocarbons (dissolved and dispersed oil) in the produced water sample.

7.8 Preparation of the chromatographic column

Fill the chromatography column (7.6.1), to almost capacity, with TTCE. Add column packing (7.3.5) to the column to a depth of approximately 30 mm. Add magnesium sulphate (7.3.4) to the column to a depth of 10 mm above the column packing. Drain the TTCE from the column until it is approximately 2 mm above the magnesium sulphate layer. Ensure that the column packing remains under TTCE throughout its use.

7.9 Infra-red spectrometer calibration

Set up the infra-red spectrometer in accordance with the manufacturer's instructions. Follow the procedure given in annex B.

Note 4: The calibration method involves solving the factors of three simultaneous equations, using the three calibration standards (7.5) individually, in accordance with annex B. The method can be performed on any type of infra-red spectrometer but the calibration method set up for a given spectrometer should be used only with that spectrometer

7.10 Procedure

7.10.1 Preparation of TTCE extract

7.10.1.1 Add approximately 2.5 ml of hydrochloric acid if the sample has not already been acidified and 100 ml of TTCE to the effluent in the sample container.

Insert a magnetic follower and place onto the magnetic stirrer and stir for 30 min±1 min at approximately 1500 rev/min.

7.10.1.2 Elute approximately 50 ml of fresh TTCE through the column and collect in a stoppered conical flask for use as a blank. Drain the TTCE from the column until it is approximately 2 mm above the column packing.

7.10.1.3 Decant the contents of the sample container into a 500 ml separating funnel. Allow to settle and run off the TTCE extract layer into a clean glass beaker.

7.10.1.4 Elute two portions of approximately 25mls of TTCE extract through the packed column, draining to within 2mm of the packing column after each elution. Discard the eluents.

7.10.1.5 Elute approximately 50ml of TTCE extract through the packed column and collect the treated extract into a 50 ml glass stoppered conical flask..

7.10.1.6 Drain off the water to a 500 ml measure cylinder, and read the volume to the nearest 2.5 ml.

7.10.2 Acquisition of spectral data for a single beam instrument

Fill one of the 10 mm silica cells (7.6.6) with TTCE blank (see 7.10.1.2). Place the cell in the beam of the spectrometer and scan to cover the range 3400cm⁻¹ to 2600 cm⁻¹. Ensure that the instrument conditions are the same as those when producing data for the calibration graph. Either record the spectrum of the blank or set the instrument to deduct the spectrum of the blank from the spectra of the following samples.

Remove the cell, empty and dry with clean dry air. Fill the cell with the TTCE extract (see 7.10.1.5). Place the cell in the beam of the spectrometer and scan over the range 3400cm⁻¹ to 2600 cm⁻¹ to obtain either the direct spectrum of the extract, from which the spectrum of the blank is deducted, or the spectrum of the extract after the automatic deduction of the spectrum of the blank.

7.10.3 Acquisition of spectral data for a double beam instrument

Fill one of the 10 mm matched pair silica cells (7.6.6) with the TTCE to be used as a blank (see 7.10.1.2). Place the cell in the reference beam of the spectrometer. Fill the other 10 mm silica cell with TTCE extract (7.10.1.5). Place the cell in the sample beam and scan over the range 3400cm⁻¹ to 2600 cm⁻¹.

7.11 Calculation of oil content

Calculate the oil content of the sample in accordance with Annex C.

7.12 Expression of results

Report the oil content of the effluent to the nearest 0.1 mg/l

7.13 Annex B (Normative)

Method of calibration and calculation by solving simultaneous equations using instruments with computer control

B.1 Calibration

B.1.1 Acquisition of spectral data for a single beam instrument

Fill one of the 10 mm silica cells with the TTCE to be used as a blank. Place the cell in the beam of the spectrometer and scan to cover the range 3400 cm^{-1} to 2600 cm^{-1} . Either record the spectrum of the blank or set the instrument to deduct the spectrum of the blank from the spectrum of following samples.

Remove and empty the cell. Dry the cell using clean dry air and the fill sequentially with the nominal 200 mg/l toluene, hexadecane and 2,6,10,14-tetramethylpentadecane calibration standards, washing the cell by filling with TTCE at least three times and drying using clean dry air, between each standard. Place cell in the beam of the spectrometer and scan to obtain either the direct spectrum of the standard, from which the spectrum of the blank is deducted, or the spectrum of the standard after automatic deduction of the spectrum of the blank.

B.1.2 Acquisition of spectral data for a double beam instrument

Fill one of the 10 mm matched pair silica cells with the TTCE to be used as a blank. Place the cell in the reference beam of the spectrometer. Fill the other 10 mm silica cell with one of the calibration standards, place the cell in the sample beam and scan over the range 3400 cm^{-1} to 2600 cm^{-1} . Empty and wash the sample cell in accordance with B.1.1 and repeat the procedures for the other two calibration standards.

B.1.3 Spectral measurements

Make measurements using spectra in absorbance mode. Measure the absorbance at 2930 cm^{-1} , 2960 cm^{-1} and 3030 cm^{-1} for each of the three stock solutions. Calculate the factors for the instrument by solving the following simultaneous equations for each standard, arising from the following equation:

$$C = [X(A_{2930})] + [Y(A_{2960})] + [Z(A_{3030} - A_{2930} / F)]$$

Where

C is the concentration of the hydrocarbons in the calibration standard;
 A_{2930} , A_{2960} and A_{3030} are the absorbance at 2930 cm^{-1} , 2960 cm^{-1} and 3030 cm^{-1} respectively;
F is A_{2930}/A_{3030} for hexadecane standard.

For the hexadecane standard the Z term is zero and for the TMPD standard the Z term can be assumed to be zero. Thus the three simultaneous equations become:

$$C_{\text{toluene}} = [X(A_{2930\text{toluene}})] + [Y(A_{2960\text{toluene}})] + [Z(A_{3030\text{toluene}} - A_{2930\text{toluene}} / F)]$$

$$C_{\text{TMPD}} = [X(A_{2930\text{TMPD}})] + [Y(A_{2960\text{TMPD}})]$$

$$C_{\text{hexadecane}} = [X(A_{2930\text{hexadecane}})] + [Y(A_{2960\text{hexadecane}})]$$

Where

C_{toluene} , C_{TMPD} and $C_{\text{hexadecane}}$ are the exact concentrations of the stock solutions. (see 7.4.1, 7.4.2 and 7.4.3)

Solve for the factors X, Y, Z

If the standards are too concentrated for the instrument, re-run using 50 mg/l standards made up from the nominal 200 mg/l standards suitably diluted with TTCE.

B.2 Calculation

Calculate the oil content of the sample, C_{Total} , in milligrams per litre, using the following equation.

$$C_{\text{Total}} = \{ [X(A_{2930})] + [Y(A_{2960})] + [Z(A_{3030} - A_{2930} / F)] \} \frac{10vD}{VL}$$

Where

X, Y and Z are factors calculated in accordance with A.1.3;

V is the volume of produced water sample (see 7.10.1.6), in millilitres;

D is the dilution factor (if the sample is not diluted, D=1, see note 5 below);

v is the volume of TTCE used to extract the produced water sample, in millilitres;

A is the absorbance at the specified frequencies;

F is A_{2930}/A_{3030} for hexadecane standard;

L is the cell path length, in millimetres.

Note 5: If the oil content is found to be greater than 25 mg/l it is recommended that a duplicate sample is tested and original TTCE extract diluted 50:50 with TTCE used as the blank and the result doubled.

B.3 Procedures to obtain aliphatic and aromatic hydrocarbons

Use the following equations to calculate aliphatic and aromatic hydrocarbons:

$$C_{\text{aliphatic}} = \{ [X(A_{2930})] + [Y(A_{2960})] \} \frac{10vD}{VL}$$

$$C_{\text{aromatic}} = C_{\text{total}} - C_{\text{aliphatic}}$$

7.14 Annex C

Procedure for Calibration Check and Analysis

These analyses can be carried out either onshore or offshore.

C.1 Apparatus – see Section 7.6

C.2 Reagents – see Section 7.4

C.3 Sampling and Extraction – see Section 7.7 & 7.10

C.4 Infra-Red Spectroscopy

C4.1 Prepare the infra-red spectrophotometer according to manufacturer's instructions.

C4.2 The solvent should be tested for purity prior to use. It is also recommended that a purity test be carried out regularly in order to detect possible contamination of the solvent from external sources, particularly when different batch numbers are supplied.

C4.3 Carefully rinse with solvent the outside and inside surfaces of the photometric cells used for sample and blank. Fill the sample cell with the solvent and place the cell in the light path of the photometer with the empty blank cell as a reference. Record a spectrum between about 3,200 - 2,700 cm^{-1} . The absorption peak at 2930 cm^{-1} should not exceed 1 per cent unit. If it is in excess of this, the solvent should be rejected since ideally there should be a straight baseline without peaks.

C4.4 Prepare a calibration plot of net absorbance vs. mg of oil per litre of sample using the response of the standards.

C4.5 Rinse a cell with two volumes of the solution to be measured; then completely fill the cell with solution. Place a matched cell containing the solvent used in the reference beam.

C4.6 Scan samples and standards from 3,200 cm^{-1} to 2,700 cm^{-1} .

Note: Single beam and non-scanning spectrophotometers can be used for this test. Follow manufacturer's instructions and measure the absorbance directly at or near 2,930 cm^{-1} .

C4.7 Construct a straight baseline under the hydrocarbon band as illustrated in Figure 1. If the scan is recorded on absorbance paper, read the absorbance of the peak maximum at 2,930 cm^{-1} and subtract the absorbance of the baseline at that point. If the scan is recorded on transmittance paper, the net absorbance is:

$$\text{Log } \frac{\% \text{ T (baseline)}}{\% \text{ T (peak maximum)}}$$

C4.8 If the net absorbance of a sample exceeds 0.8 of the linear range of the instrument as determined by the calibration plot, prepare a dilution of the sample by pipetting an appropriate volume of the extract into a volumetric flask and diluting to volume. If the absorbance is less than 0.1, more accurate results can be obtained by using a longer path-length cell.

C5. Calculation and Results

C5.1 Using the calibration plot, determine the oil concentration in the sample. The calibration should give the concentration in mg/l of sample.

C5.2 The analytical method assumes a standard volume of sample of 500 ml.

$$\text{mg oil/l sample} = \text{mg/l (from B2 \& B3)} \times \frac{\text{Standard Volume}}{\text{Actual Volume}}$$

C5.3 Report results to nearest 0.1 mg/l for levels below 100 mg/l.

8 IMPLEMENTATION OF THE OSPAR REFERENCE METHOD

8.1 Introduction

OSPAR has published a document entitled 'Oil in Produced Water Analysis – Revised Guideline on Criteria for Alternative Methods Acceptance and General Guidelines on Sample Taking and Handling – OSPAR Agreement 2006-6'. The UK guidance note draws upon much of the content of the OSPAR document, as well as findings from Round Robin tests carried out in the UK. There may be some slight differences between the two documents since the OSPAR document has to be suitable for use in all OSPAR countries and these guidance notes are specific for use in the UK only. In the first instance, the UK guidance notes should be used but if any doubt or confusion arises then DECC should be contacted for clarification.

The new reference method requires the use of a gas chromatograph equipped with a flame ionisation detector and requires the use of n-pentane as an extraction solvent. Note that n-pentane is a highly flammable solvent with a low boiling point. Use of this solvent offshore is subject to offshore health and safety legislation.

The following points should be considered if it is intended to directly implement the OSPAR Reference Method offshore:

- (a) cost and complexity of GC-FID equipment;
- (b) cost of specialist laboratory personnel;
- (c) level of equipment maintenance;
- (d) time taken to report 'official' analysis results;
- (e) no need to transport samples to shore for OSPAR Method; and
- (f) no need to establish correlation graph for OSPAR Method.

If an operator wishes to implement the OSPAR Reference Method directly offshore, DECC would welcome such an initiative.

Some operators may prefer to use a simpler analysis method offshore that has already been correlated against the OSPAR Reference Method in an onshore laboratory. Therefore, the DECC IR analysis method (or other analysis methods) may be accepted as an 'alternative' analysis method but only if it is correlated against the OSPAR Reference Method.

8.2 Using the OSPAR Reference Method directly offshore

Operators who intend to use the OSPAR Reference Method directly to analyse produced water samples for dispersed oil must closely follow the procedure in the method as given in section 8 of these guidance notes.

DECC is not responsible for the technical correctness of the OSPAR Reference Method or the content of its associated guidance notes. If errors are noted or there are queries regarding the OSPAR Reference Method or its associated guidance notes, DECC will be happy to note such queries and pass them onto the relevant competent authority. In certain instances an addendum (specific to the UK) may be compiled to summarise any recommended changes to the official method. Analysts are advised to check the DECC

website periodically in order to capture any updated guidance. All correspondence must take place through the offshore.inspectorate@decc.gsi.gov.uk mailbox.

Onshore laboratories involved in calibrating alternative methods will need to closely follow the OSPAR Reference Method detailed in section 8 & 9 of this guidance and they will also need to validate the method by checking parameters such as linearity, sensitivity, discrimination, etc. The validation process and calibration checks will have to be documented so that they can be inspected by DECC upon request. Onshore laboratories should note that DECC reserves the right to carry out periodic inspections of their in-house method in order to ensure that the OSPAR Reference method is being implemented correctly.

8.3 Use of alternative oil in water analysis methods to the OSPAR Reference Method

8.3.1 Acceptance criteria for alternative analysis methods

For an alternative analysis method to be accepted, DECC must be satisfied that the alternative method will produce results statistically equivalent to the OSPAR Reference Method.

8.3.2 Methodologies to demonstrate equivalent results

For analysis of dispersed oil in water concentrations using an alternative analysis method, the establishment of a valid correlation between the alternative method and the OSPAR Reference Method by using linear regression is required.

As of the 1 January 2007 only the OSPAR Reference Method is used to determine the reportable value of the dispersed oil content of produced water. Any analysis results for produced water obtained by alternative analysis methods must not be reported directly to DECC or through EEMS, but must be first correlated against the OSPAR Reference Method before being reported.

If it has been decided to use an alternative analysis method offshore, it is mandatory to establish a correlation between the alternative method and the OSPAR Reference Method. It is also mandatory to demonstrate the validity of the correlation over time in a way that can be accepted by DECC.

8.4 General approach on how to correlate an alternative analysis method

When considering the use of alternative oil in water analysis methods in conjunction with the OSPAR Reference Method, there are two variations on a method that can be used. There is not necessarily one 'best' method and care must be taken by analysts to select the most appropriate method for each individual situation.

Note: Methods A1 & A2 previously proposed, which involved correlation of duplicate samples analysed by both IR and the OSPAR reference method, and described in earlier versions of these Guidance Notes, have now been removed, as there are no operators in the UK taking this approach. The

previous Methods B1 & B2 are now referred to as Method A1 & A2 respectively in these guidelines. If operators wish to use the previous Method A1 or A2 approach they can refer to OSPAR Agreement 2006-6 guidance on the OSPAR website at <http://www.ospar.org/> and/or discuss this with DECC.

8.4.1 Method A1 - Correlation using laboratory prepared standard oil in water solutions when the alternative analysis method uses a solvent other than n-pentane.

8.4.2 Generation of Correlation Graph

Using this method, a standard oil in water stock solution is prepared in the laboratory and used to generate a series of standard solutions.

8.4.3 Correlation standards preparation

- (a) Select an alternative oil in water analysis method that is likely to yield a linear response and procure the appropriate bench top analyser / instrument.
- (b) Calibrate the analyser according to the manufacturer's instructions. Note that this can be carried out either offshore or onshore.
- (c) If an instrument is calibrated onshore and shipped offshore, two standard solutions (at 20% and 80% of the instrument range) used in the generation of the original calibration graph must be analysed offshore and the analysis results must lie within 95% of the calibration graph confidence intervals to confirm that the calibration graph is still valid following shipment.
- (d) Procedures specified in the DECC IR method (see section 6) on how to prepare standard solutions from a stock solution should be used. Note that two stock solutions (and two series of correlation standard solutions) will have to be generated since two different solvents will be used.
- (e) Fresh, crude oil samples that are representative of the blend of produced waters being treated should be selected for use.
- (f) Six or more correlation standard solutions covering a concentration range from 0-80 mg/l or other specified concentration range (see 6.5.10(c)) should be prepared from the standard stock solution by using the specified back extraction technique. The concentrations of the correlation standards should be evenly spaced.
- (g) The correlation standards used may be the same standards as used to calibrate the IR instrument, but must be remeasured using the new calibration graph.
- (h) Preparation of standards by direct injection of oil into the solvent is not permitted. Where use of a balance is unavailable e.g. due to vessel movement, crude oil density can be used to determine the mass of oil from a volume of oil used in the stock solution. Under certain circumstances (e.g. limited laboratory facilities) this procedure may be acceptable but it would require the consent of the appropriate DECC Environmental Inspector.
- (i) If it is intended to use a blank sample in the correlation graph e.g. as one of the six standards, this should be prepared as per (d) above. It is

not acceptable to include a 0,0 data result (origin) unless this is the experimentally obtained result.

- (j) Should the best fit line of the correlation graph result in low absorbance or IR readings producing negative oil in water concentrations, then negative correlated results should be reported as zero.
- (k) The correlation standard solutions must be stored in a fridge (4°C to 8°C) and kept tightly sealed when not in use. Standard solutions should not be kept for longer than six months.
- (l) A portion of each of the calibration standard solutions must accompany the calibrated alternative instrument offshore.

8.4.4 Validation, re-calibration and re-correlation requirements

Note: As a change to the previous guidance notes, the monthly validation check is to be carried out on the IR calibration graph, not the IR : GC correlation graph.

- (a) Validation must be carried out once per calendar month following generation of a new calibration graph. It is not necessary to validate the calibration graph the month it is generated. Validation can be achieved by analysing one of the calibration standard solutions by the appropriate analysis method.
- (b) The corresponding result is checked against the original IR calibration graph and if the result lies within the 95% confidence intervals, the calibration is considered to be valid.
- (c) If the result lies outside the 95% confidence intervals, a second sample should be analysed by the appropriate analysis method.
- (d) If the second result lies inside the 95% confidence intervals, the calibration is considered to be valid.
- (e) If the second result lies outside the 95% confidence intervals, then a new calibration graph, and correlation graph must be prepared using fresh standards. If possible, system checks on the instrument should also be carried out to determine if the instrument is still functioning correctly.
- (f) Whilst waiting for all validation test results, analysts are required to use the current calibration & correlation graphs.
- (g) Where a calibration or correlation graph cannot be established, or there are circumstances that prevent a calibration or correlation graph being prepared, produced water samples must be taken and shipped to shore for analysis by the OSPAR Reference Method (GC-FID) within seven (7) days of the sample being collected, or samples refrigerated until a replacement instrument can be shipped offshore and calibrated. and the samples analysed. In this case, a DECC Environmental Inspector must be immediately notified.
- (h) A new IR calibration or correlation graph must be prepared if there have been notable changes in the make up of the discharged produced water. This may be caused by, for example, new wells coming on stream. If in doubt, contact a DECC Environmental Inspector.
- (i) New calibration & correlation graphs should be implemented and made available to offshore personnel as soon as possible and certainly

before expiry of existing graphs. Failure to maintain valid calibration and correlation graphs must be reported to DECC as an OPPC non-compliance.

- (j) A check on the equation of the correlation line for each new 6-monthly correlation graph generated should give no more than a 20% difference in the correlated GC result from the previous 6-monthly correlation graph for a given alternative analysis method result (mg/l) unless there has been a significant change in the make up of the oil in the produced water. If a change greater than 20% is found, it should be determined whether there has been a significant change in the make up of the oil in produced water and if not, a DECC Environmental Inspector must be notified.
- (k) A calibration check must be carried out if the alternative instrument has been serviced, damaged, repaired or interfered with (see 8.4.3(c)). If the results do not fall within the 95% confidence interval, then a new calibration graph must be established.
- (l) Calibration and system checks for the instrument used in the alternative oil in water analysis method must be carried out in accordance with either the manufacturer's instructions or recommended analysis methods.
- (m) The results of all validations must be recorded and made available to the department on request. If possible, these results should be held offshore.

8.5 Method A2 – Correlation using laboratory prepared standard oil in water solutions when the alternative analysis method uses n-pentane as the solvent

- (a) Some alternative analysis methods utilise n-pentane as the solvent to extract oil from the sample solution. If the extraction procedure follows the steps of the OSPAR Reference Method (excluding the addition of any internal standard), the need for calibration of the alternative method is reduced to doing a correlation study between instruments/methods.
- (b) If using Method A2, Method A1 should be followed, substituting the word n-pentane for the word solvent. Only one set of calibration standards need be prepared when using Method A2 and care should be taken to ensure that there is sufficient volume of the calibration standards available to permit calibration analysis and monthly validations for the alternative method. Care should be taken to analyse the samples as quickly as possible and to prevent loss of solvent if transporting the samples to shore.

Summary Table of Calibration / Correlation Requirements

| Requirement | Frequency | # of Standards / Samples |
|--|-----------|--------------------------|
| Alternative Instrument Calibration (e.g. IR) | 6 Monthly | 6 |
| Correlation Graph | 6 Monthly | 12 (six IR & 6 GC) |
| Calibration Graph Validation | Monthly | Check 1 sample |
| Bi-Annual Samples | 6 Monthly | See Section 11 |

8.6 Dealing with alternative method analyser instrument breakdown

- (a) If the offshore alternative analyser currently in use fails, availability of a back-up or replacement analyser within 48 hours is essential as measurement of oil in produced water is a requirement for OPPC regulatory compliance.
- (b) Note that alternative analysers can be calibrated either onshore or offshore using the existing calibration standards, and correlated to the OSPAR Reference Method in the same manner as the original instrument. Details of the analyser breakdown and change of instrument must be recorded in the oil in water logbook.
- (c) While availability of the newly calibrated/correlated alternative analyser is awaited, if coming from onshore, produced water samples should be taken on a daily basis in line with the OPPC permit schedule conditions and preserved as per 5.7. These samples should be analysed as soon as the newly calibrated/correlated alternative analyser is available, which should be no longer than seven (7) days from sampling. In this instance, the appropriate DECC Environmental Inspector should be contacted.
- (d) If a pollution event or suspected pollution event occurs before the replacement analyser arrives, DECC must be notified immediately by the submission of a PON1 or OPPC Non-Compliance form giving an estimate of the discharge. Samples must also be collected at the time of the event and preserved as per 5.7. The PON1 or OPPC non-compliance form can then be updated or retracted depending upon subsequent analysis of the preserved samples.

8.7 General correlation issues covering methods A1 & A2.

8.7.1 Preparation of correlation graphs and statistical analysis

Preparing correlation graphs and interpreting statistical analysis results can be difficult and often there is more than one 'correct' way of doing this. It is intended that these guidance notes adhere to the best practice as outlined in the document "Preparation of Calibration Curves - A Guide to Best Practice" which has been published by the Laboratory of the Government Chemist (LGC) [3]. The LGC document sets out in a user friendly fashion the best ways of constructing calibration/correlation graphs and how best to use statistical analysis in the preparation of graphs.

8.7.2 Labelling of axis

The X-axis will normally be the OSPAR Reference Method and is assumed to represent the 'true' dispersed oil in water content.

8.7.3 Straight line graphs

Responses of GC instruments and instruments used in alternative analysis methods are expected to be linear within the concentration range of 0-80mg/l, or other specified concentration range. It is therefore necessary that a positive, straight-line correlation graph be constructed when correlating an alternative method against the OSPAR Reference Method.

8.7.4 Correlation graph going through the origin

The correlation line must not be forced through the origin.

8.7.5 Reporting of oil in water values to the DECC

It is important that the correct oil in water values be reported to DECC. Reporting of oil in water values should always be in terms of the OSPAR Reference Method and not in terms of an alternative analysis method.

8.7.6 Use of Accredited Laboratories

It is no longer a requirement that onshore laboratories carrying out oil in water analysis by the OSPAR reference method be UKAS (ISO17025) accredited, though it is encouraged. It is recommended that onshore laboratories work to the requirements of ISO17025 or GLP standards. Furthermore, operators who should all have an EMS in place, must assure themselves of the quality of work being carried out by contract laboratories on their behalf. Laboratories which, prior to 1 January 2010, have not carried out analysis by the OSPAR Reference method or correlation activities for offshore operators are required to contact DECC to advise them of their intention to do so.

8.7.7 Other correlation procedures

Other correlation procedures may be considered if it can be demonstrated that a valid correlation between the alternative method and the OSPAR Reference Method can be established. However, under normal circumstances DECC would expect Methods A1 & A2 listed above to be more than adequate.

9 OSPAR REFERENCE METHOD (ISO 9377-2 As Modified by OSPAR)

Note:

This method has been downloaded from the OSPAR website (www.ospar.org). It is inserted here only for convenience. Whilst DECC does not assume any responsibility for errors contained within this method, it will forward any errors or comments to the relevant OSPAR contact. Please send any feedback to the offshore.inspectorate@decc.gsi.gov.uk mailbox.

Please note that the page number on the content page of the original document has been omitted, as they are no longer valid in this document. Anyone who wishes to obtain a copy of the method in the original OSPAR format should visit the OSPAR website as listed above.

**9 OSPAR Reference Method of Analysis for the Determination of the
Dispersed Oil Content in Produced Water
(Reference number: 2005-15)**

Contents

Page

- 1 Scope
- 2 Normative references
- 3 Term and definition
- 4 Interferences
- 5 Principle
- 6 Reagents
- 7 Apparatus
- 8 Sampling and sample preservation
- 9 Procedure
- 10 Test report
- 11 Precision

Annex A (informative) Example of a column

Annex B (informative) Examples of gas chromatograms of mineral oil standard and water samples

Annex C (informative) Determination of boiling range of a mineral oil from the gas chromatogram

Bibliography

Determination of the content of dispersed mineral oil in produced water using gas chromatography with flame-ionization detection

1 Scope

This document specifies the OSPAR reference method for the determination of the content of dispersed mineral oil in water by means of gas chromatography. The method is designed for produced water and other types of waste water discharged from gas, condensate and oil platforms and allows the determination of the dispersed mineral oil content in concentrations above 0.1 mg/l. The method is a modification of ISO 9377-2 in order to include the determination of certain hydrocarbons with boiling points between 98°C and 174°C.

NOTE 1: The mass concentration of animal and vegetable fat in the test sample should not exceed 150 mg/l, because at higher values the adsorption capacity of the clean-up column packing may not be sufficient.

NOTE 2: In the case of highly polluted waste water, especially if containing a high amount of surfactants, a loss in recovery may occur.

2 Normative references

The following normative documents contain provisions, which, through reference in this text, constitute provisions of this document. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this document are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 5667-3:2003, *Water quality - Sampling - Part 3: Guidance on the preservation and handling of samples.*

ISO 8466-1:1990, *Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics - Part 1: Statistical evaluation of the linear calibration function.*

3 Term and definition

For the purposes of this document, the following term and definition applies.

3.1 Dispersed mineral oil content by GC-FID

The sum of the concentrations of compounds extractable with n-pentane, not adsorbed on Florisil and which may be chromatographed with retention times between those of n-heptane (C₇H₁₆) and n-tetracontane (C₄₀H₈₂) excluding the concentrations of the aromatic hydrocarbons toluene, ethyl benzene and the three isomers of xylene.

NOTE 3: Substances complying with this definition are long-chain or branched aliphatic, alicyclic, and (alkyl-substituted) polycyclic aromatic hydrocarbons, with boiling points between 98 and 525 °C.

4 Interferences

Compounds of low polarity (e.g. halogenated hydrocarbons) and high concentrations of polar substances may interfere with the determination. Surface-active substances may interfere with the extraction step.

5 Principle

The water is extracted with *n*-pentane. Polar substances are removed by clean-up on Florisil. The purified aliquot is analysed by capillary gas chromatography using a non-polar column and a flame ionisation detector (FID). The total peak area between *n*-heptane and *n*-tetracontane is measured. The peak areas of the aromatic hydrocarbons toluene, ethyl benzene and the three isomers of xylene are subtracted from the total peak area. The concentration of mineral oil is quantified against an external standard consisting of a mixture of two specified mineral oils, and the content of dispersed mineral oil is calculated.

It should be investigated whether and to what extent particular problems will require the specification of additional marginal conditions.

6 Reagents

All reagents shall be reagent grade and suitable for their specific purpose. The suitability of the reagents and solutions shall be checked by carrying out a blank test.

- 6.1 Water for the preparation of solutions, distilled water, or water from a generator of purified water capable of removing organic traces, for example using activated carbon, shall be used.
- 6.2 *n*-Pentane, C₅H₁₂
- 6.3 Sodium sulfate, anhydrous, Na₂SO₄.
- 6.4 Magnesium sulfate heptahydrate, MgSO₄·7H₂O.
- 6.5 Mineral acid, e.g. hydrochloric acid, $c(\text{HCl}) = 12 \text{ mol/l}$ ($\rho = 1,19 \text{ g/ml}$).
- 6.6 Acetone, C₃H₆O
- 6.7 Florisil, grain size 150 μm to 250 μm (60 mesh to 100 mesh), heated to 140°C for 16 h and stored in a desiccator.
- 6.8 Mixture of mineral oils, Type A & Type B
Type A should show discrete peaks in the gas chromatogram. An example is diesel fuel without any additives. See EN 590 for further information. Type B should have a boiling range higher than that of type A and should have unresolved signals in the gas chromatogram. An example of this type is a lubricant without any additives, boiling range 325°C to 460°C.
- 6.8.1 Standard¹ mixture
Weigh accurately equal amounts of two different types (type A and type B, both containing no additives) of mineral oil and add enough extraction solvent (6.11.2) to give a total hydrocarbon concentration of about 10 mg/ml.

¹ Standards are available from

Fachgruppe 1.2
Bundesanstalt für Materialforschung und -prüfung
Richard-Willstätter-Strasse 11
D-12489 Berlin, Germany

This information is given for the convenience of users of this document and does not constitute an endorsement by OSPAR of these products.

6.8.2 Calibration mixture

Prepare at least five different calibration solutions by diluting aliquots of standard mixture (6.8.1) with the extraction solvent (6.11.2). The following concentrations may be suitable:

0 (blank), 0.2 mg/ml, 0.4 mg/ml, 0.6 mg/ml, 0.8 mg/ml and 1.0 mg/ml.

Higher concentrations may be advisable for other applications.

Store the calibration mixture tightly sealed in a refrigerator (4°C to 8°C). The calibration mixtures are stable for up to six months.

6.8.3 Quality Control (QC) standard

Prepare a standard solution according to 6.8.1 in acetone (see 6.6) with a mass concentration of e.g. 1 mg/ml. The exact concentration should be about a thousand times the desired application range.

NOTE 4: When using a lubricant for QC, the stock solution is easily prepared in extracting agent (6.2), which is further diluted in acetone about tenfold before spiking the QC water.

Store the solution tightly sealed in a refrigerator (4°C to 8°C). It is stable for up to six months.

6.9 Standard mixture of *n*-alkanes for system performance test

Dissolve *n*-alkanes with even carbon numbers (C₂₀, C₄₀ and at least three further *n*-alkanes) in extracting agent (6.2) to give concentrations of approximately 50 µg/ml of the individual components. It may be necessary to use a different solvent, e.g. heptane, for the first solution; in this case dilute this first solution with extracting agent (6.2).

Store the standard mixture tightly sealed in a refrigerator. It is stable for up to six months.

NOTE 5: This solution is used to verify the suitability of the gas chromatographic system for the resolution of *n*-alkanes as well as for the detector response.

NOTE 6: This solution is used to give information on the retention times of the *n*-alkanes to characterize the hydrocarbons in the sample.

6.10 Reference compounds

6.10.1 *n*-Heptane, C₇H₁₆

6.10.2 *n*-Tetracontane, C₄₀H₈₂

6.10.3 *n*-Eicosane, C₂₀H₄₂

6.10.4 Toluene, C₇H₈

6.10.5 Ethyl benzene, C₈H₁₀

6.10.6 *o*-Xylene, C₈H₁₀

Formatada: Português (Portugal)

Formatada: Português (Portugal)

6.10.7 m-Xylene, C₈H₁₀

6.10.8 p-Xylene, C₈H₁₀

Formatada: Inglés (Estados Unidos)

6.11 Extraction solvent containing reference compounds

6.11.1 Extraction solvent stock solution

Dissolve 20 mg of *n*-tetracosane (6.10.2) in *n*-pentane (6.2). Then add 20 µl of *n*-heptane (6.10.1) and dilute with *n*-pentane to 1 000 ml.

Store the solution tightly sealed in a refrigerator. It is stable for up to six months.

NOTE 7: *n*-Tetracosane is only moderately soluble in *n*-pentane. Slight warming or treatment with ultrasonics accelerates the dissolution process.

6.11.2 Extraction solvent standard solution

Immediately prior to use, dilute the stock solution (see 6.11.1) with tenfold extracting agent.

6.12 Stearyl stearate test solution, C₃₆H₇₂O₂

Dissolve 200 mg of stearyl stearate in 100 ml of extraction solvent standard solution (6.11.2).

NOTE 8: This solution is used to check the efficiency of the clean-up procedure. Store the solution tightly sealed in a refrigerator. It is stable for up to six months.

7 Apparatus

7.1 Usual laboratory glassware. Clean all glassware by the usual procedures for this type of analysis and check for purity (measurement of blank). If necessary, rinse the glassware with extracting agent (6.2) and re-check the blank.

7.2 Gas chromatograph, equipped with a non-discriminating injection system and a flame ionization detector. The injection system shall allow injections up to a volume of at least 50 µl.

7.3 Column for gas chromatography, fused silica, with one of the following stationary phases:

non-polar, immobilized 100 % dimethylpolysiloxane, or 95 % dimethyl-/5 % diphenylpolysiloxane, or modified siloxane polymer and typical dimensions:

| | |
|--------------------|--------------------|
| length: | 5 m to 30 m |
| internal diameter: | 0.25 mm to 0.53 mm |
| film thickness: | 0.25 µm to 1.2 µm |

For an example, see annex B.

It is recommended to use a precolumn (e.g. 2 m, 0.53 mm i.d., deactivated fused silica).

- 7.4** Data system, suitable for integrating the total area of the gas chromatogram and suitable for compensating for 'column bleeding' and for re-integrating after drawing a new baseline.
- 7.5** Sampling bottles, glass, with ground glass stopper, capacity 250 ml and 1 000 ml, or with screw cap, lined with PTFE (polytetrafluoroethene).
- The sampling bottle shall allow direct extraction from the bottle.
- 7.6** Centrifuge.
- 7.7** Centrifuge tubes, of capacity 100 ml, with suitable (screw)cap.
- 7.8** Microseparator, or other suitable device for phase separation.
- 7.9** Clean-up columns, made from glass, with frit of sinter porosity 2, for example see Figure A.1.
- 7.10** Magnetic stirrer with bar, of length suitable to ensure thorough mixing.

8 Sampling and sample preservation

Sampling and storage shall be in accordance with ISO 5667-3 and other OSPAR documents².

Fill the sampling bottle (7.5) to approximately 90 % with the sample, seal tightly and weigh (*m*). Keep the sample at about 4°C and extract the sample as soon as possible, but in any case within four days.

If necessary, preserve the sample by acidifying with mineral acid (6.5) to pH 2.

NOTE 9: If formation of emulsions or a concentration of animal and vegetable oils > 150 mg/l is expected; it is advisable to withdraw additionally a smaller sample volume in a 250 ml sampling bottle.

9 Procedure

9.1 Blank test

Carry out blank tests with each series of tests in accordance with 9.3, including all reagents and glassware in the same way as the samples.

9.2 Determination of the recovery

Determine the recovery at regular intervals, preferably in each series of tests, using 900 ml of water (6.1) to which 1,0 ml of the QC standard (6.8.3) has been added. Perform the test starting with 9.3 and calculate the recovery. Ensure that the recovery is between 80 % and 110 %

² OSPAR Agreement 2006-6: Oil in produced water analysis – Guideline on criteria for alternative method acceptance and general guidelines on sample taking and handling.

9.3 Extraction procedure

Cool the sample to about 10°C, if necessary, to prevent losses of the extracting agent by volatilization.

Acidify the sample to pH 2 by adding mineral acid (6.5), if this has not been done in the field (see clause 8).

Add about 80 g of magnesium sulfate (6.4) per 900 ml of sample to avoid emulsions.

NOTE 10: The addition of magnesium sulfate is not necessary if samples are known not to form emulsions.

Add 50 ml of extraction solvent standard solution (6.11.2) and a magnetic stirrer bar, close the bottle and stir vigorously for 30 min on the magnetic stirrer (7.10).

Remove the stopper and replace it by the micro separator (7.8).

Add enough water (6.1) to allow withdrawal of the extracting-agent layer from the micro separator, transfer it to the clean-up column (7.9) and proceed according to 9.4.

When transferring the organic phase to the clean-up column, take care to avoid the transfer of water, as this will incrust the surface of the sodium sulfate. It is recommended to transfer the organic layer in several steps using a pipette, or, when using the micro separator (7.8) (Figure A.2), to position the meniscus below the cock.

In the case of strong emulsions, centrifuge the extract as follows. Transfer the extracting-agent phase together with the emulsion into a 100 ml centrifuge tube (7.7) and close the tube. Break the emulsion by centrifuging the extract.

NOTE 11: Centrifugation for 10 min to 15 min is usually sufficient.

Extraction by shaking may be adequate, but verify the efficiency.

9.4 Clean-up procedure

Transfer the *n*-pentane phase (see 9.3) to a small column (see Figure A.1) filled with 2 g of Florisil (6.7) and covered with a layer of 2 g of sodium sulfate (6.3).

NOTE Pre-rinsing of the column with a few milliliters of *n*-pentane (6.2) can be useful to prevent the formation of channels.

Let the *n*-pentane phase (see 9.3), followed by an additional 10 ml of *n*-pentane (6.2), run through the column into a 50 ml volumetric flask until the liquid reaches the 50 ml mark.

NOTE 12: Other procedures using the same amount of Florisil for cleaning the extract, e.g. shaking the total extract with 2 g of Florisil during 30 min on a shaking apparatus, may be used as an alternative, provided the results are equivalent to the column testing of Florisil (see 9.6).

9.5 Concentration

External apparatus for concentrating the purified *n*-pentane extract is not allowed. The gas chromatograph (7.2) is equipped with an injection system that allows an injection of at least 50 µl of *n*-pentane. Injection of 50 µl is only required for low mineral oil

contents, i.e. at levels near the limit of determination. Depending on the range of concentrations normally measured, a **fixed injection volume**, e.g. 25 or 50 μl , shall be used both for the calibration and for the measurements of the extracts.

Leave the empty sample bottle to drain for 5 min. Close the bottle with the cap used previously and determine its mass (m_2) to an accuracy of 1 g.

9.6 Suitability testing of Florisil

Check the suitability of Florisil at regular intervals and each time a new batch of dried Florisil is used, as follows:

For this purpose, use a test solution of stearyl stearate (6.12) and a calibration solution of mineral oils (6.8).

Perform the clean-up procedure (9.4) with 10 ml of the stearyl stearate solution, then add extracting agent (6.11.2) to a volume of 25 ml. Transfer an aliquot of the purified solution to a septum vial and analyze by gas chromatography (9.7). Measure the peak areas of stearyl stearate after Florisil treatment. Dilute 0,5 ml of stearyl stearate solution with extracting agent (6.11.2) to 25 ml and analyze by gas chromatography. Calculate the ratio of the peak areas for stearyl stearate in the treated and in the untreated solutions. This ratio should be less than 1. If not, activate the Florisil according to 6.7.

Perform the clean-up procedure (9.4) with 10 ml of 2 mg/ml calibration solution of mineral oils (6.8), then add extraction solvent standard solution (6.11.2) to a volume of 25 ml. Transfer an aliquot of the purified solution into a septum vial and analyze by gas chromatography.

Determine this mineral oil recovery on the basis of the peak area between C_{10} to C_{40} in the treated (with Florisil) and untreated calibration solutions. It should be at least 80 %. If this criterion is not met, wash out the Florisil batch with ample water and activate the Florisil as given in 6.7. If the repeated test shows again that the criterion is not met, try another batch of Florisil with a different batch number.

9.7 Determination by gas chromatography

9.7.1 Adjusting the gas chromatograph

Select a capillary column with one of the stationary phases specified (see 7.3 and annex B) for gas chromatographic analysis. Adjust the gas chromatograph until optimum separation is obtained. The peaks in the gas chromatogram of the standard mixture of n-alkanes (6.9) shall be baseline-separated. The relative response (peak area) of n-tetracontane ($C_{40}H_{82}$) compared with n-eicosane ($C_{20}H_{42}$) should be at least 0,8. If not, the discrimination of the injection system is too high and the injection system shall be optimized or replaced.

9.7.2 Calibration

9.7.2.1 General

For calibration a distinction is made between initial calibration, working calibration and checking of the validity of the calibration curve. Initial calibration determines the

working range and the linearity of the calibration function according to ISO 8466-1. Perform this calibration when the apparatus is used for the first time.

In the next step establish the final working range and perform the routine calibration. Repeat this calibration after maintenance (e.g. replacement of the capillary column), after repair of the gas chromatographic systems, and in case the system has not been in use for a longer period of time, or if the validity criteria cannot be met. Check the validity of the initial calibration with each series of samples to be analyzed.

Correct all chromatograms for column bleeding, for this purpose run blank chromatograms (chromatograms with solvent only) and use these for baseline correction.

9.7.2.2 Initial calibration

Establish the preliminary working range by analyzing at least five dilutions of the calibration standard mixture (6.8). Test for linearity in accordance with ISO 8466-1.

9.7.2.3 Routine calibration

After examining the final working range, analyze a minimum of five dilutions of the standard calibration mixture (6.8). Calculate a calibration function by linear regression analysis of the corrected peak areas. The actual sensitivity of the method may be estimated from the calculated regression function.

9.7.2.4 Check of the validity of the calibration function

Check the validity of the calibration function from the routine calibration with each batch of samples by analysis of one standard solution after every ten samples. The concentration of this standard solution shall lie between 40 % and 80 % of the working range. Make sure that the individual results do not deviate by more than 10 % of the working calibration line. **If this criterion is met, assume the calibration to be valid.** If not, recalibrate in accordance with 9.7.2.3.

For large batches of samples the number of analyses of the standard solution may be reduced, provided that at least three measurements are obtained for calculating the mean result.

9.7.3 Measurement

Measure the sample, the calibration solutions and the blank solution in the gas chromatograph.

At regular intervals record a gas chromatogram (blank chromatogram) by injecting extracting agent (6.2) and analyze under the same conditions as for the sample. Use a chromatogram of extracting agent to correct the areas of the chromatograms of the samples.

NOTE 13: An increase in "column bleeding" may indicate contamination of the injection system or the column.

9.7.4 Integration parameters

Integrate the gas chromatogram between *n*-heptane and *n*-tetracontane. Start the integration just after the *n*-heptane peak at the signal level in front of the solvent peak

(S in Figure B.3). End the integration just before the beginning of the *n*-tetracontane peak on the same signal level (E in Figure B.3).

Check all chromatograms visually to ensure correct integration. Draw a straight line from S to E. Mark the beginning and end of the integration on the chromatogram.

Identify the peaks of the aromatic hydrocarbons toluene, ethyl benzene and the three isomers of xylene. Integrate these peaks separately and subtract their peak areas from the total integrated area.

NOTE 14: For examples of chromatograms, see annex B.

The presence of peaks between solvent peak and *n*-heptane indicates that the sample probably contains low-boiling, volatile hydrocarbons.

Discrete peaks or an increased level of the baseline at the end of the chromatogram (retention time greater than that of *n*-tetracontane) indicate that the sample probably contains hydrocarbons with a high boiling point. This should be mentioned in the test report.

NOTE 15: The range of the carbon numbers of n-alkanes present in the sample is determined by comparing the gas chromatogram of the sample extract with that of n-alkane standard solution (6.9). The corresponding boiling range can be derived from annex C.

9.8 Calculation

Calculate the hydrocarbon oil index using the equation:

$$\rho = \frac{(A_m - b) \cdot f \cdot V \cdot w}{a \cdot (m_1 - m_2)}$$

where

- ρ is the content of dispersed mineral oil, in milligrams per liter;
- a is the slope of calibration function, in liters per milligram;
- A_m is the integrated peak area of the sample extract, in instrument-dependent units;
- f is any dilution factor of the sample extract;
- m_1 is the mass of the filled sampling bottle, in grams;
- m_2 is the mass of the empty sample bottle, in grams;
- w is the density of the water sample, in grams per millilitre (for fresh water 1,00 g/ml may be used);
- V is the volume of the final extract, in milliliters;
- b is the intercept of the y-axis in instrument-dependent units.

9.9 Expression of results

Express the concentration of mineral oil in water as hydrocarbon oil index, in milligrams per litre, to two significant figures.

Examples

Dispersed mineral oil 15 mg/l
Dispersed mineral oil 2.9 mg/l

10 Test report

The test report shall refer to this document and contain the following details:

- a) identity of the sample;
- b) the content of dispersed mineral oil, in milligrams per liter;
- c) any peculiarities observed during the test;
- d) any actions not specified in this document, which may have influenced the result. In addition, the following qualitative information can be provided in the test report:
- e) the boiling range of the mineral oil detected on the basis of the relative retention time versus the boiling point of the calibration mixture of *n*-alkanes;
- f) any presence of volatile hydrocarbons;
- g) any presence of hydrocarbons with a high boiling point.

11 Precision

At the moment precision and accuracy data from an interlaboratory trial are not available.

The instrumental part of this method has been checked in a small ring test.

Four laboratories in four countries (Denmark, the Netherlands, Norway and the United Kingdom) have analysed two standard solutions of hydrocarbons in the range C7 – C40 with different levels of toluene, ethyl benzene and xylenes. Each laboratory analysed the standards in triplicate on two different days.

The results are given in Table 11.1, expressed as the ratio between the measured and the true values

Table 11.1: Ring test results for the OSPAR reference method

| | Day | Lab 1 | Lab 2 | Lab 3 | Lab 4 |
|----------|-----|-------|-------|-------|-------|
| Low TEX | 1 | 0.95 | 1.01 | 0.98 | 1.21 |
| Low TEX | 2 | 0.93 | 1.01 | 0.87 | 1.09 |
| High TEX | 1 | 0.96 | 1.06 | 1.01 | 1.35 |
| High TEX | 2 | 0.92 | 1.02 | 0.90 | 1.13 |

In addition the laboratories were asked to determine also the content of mineral oil according to ISO 9377-2, i.e. only the hydrocarbons in the range C10 – C40. These results are given in table 11.2, expressed as the ratio between the measured and the true values.

Table 11.2: Ring test results for ISO 9377-2

| | Day | Lab 1 | Lab 2 | Lab 3 | Lab 4 |
|----------|-----|-------|-------|-------|-------|
| Low TEX | 1 | 0.97 | 1.04 | 1.06 | 1.31 |
| Low TEX | 2 | 0.93 | 1.03 | 0.93 | 1.18 |
| High TEX | 1 | 0.97 | 1.08 | 1.08 | 1.43 |
| High TEX | 2 | 0.91 | 1.04 | 0.96 | 1.19 |

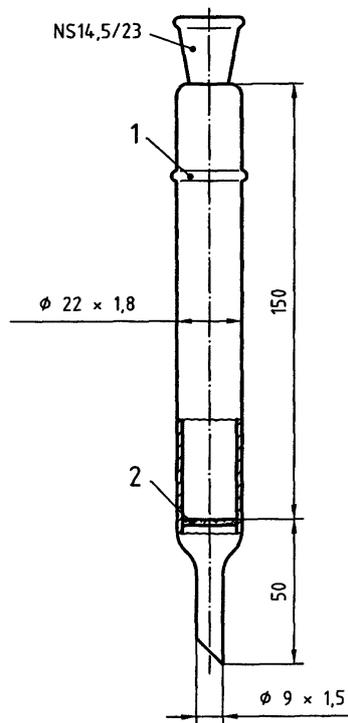
The results of Lab 4 differ from the results of the other laboratories. Lab 4 did not use a large volume injection system, resulting in a too low signal.

The results of the other three laboratories show that modification of ISO 9377-2 by extending the range of hydrocarbons to C7 – C40 and excluding the aromatic hydrocarbons toluene, ethyl benzene and the isomers of xylene, have little or no effect compared to ISO 9377-2.

Annex A
(informative)

Example of a column and a micro separator

Dimensions in millimeters



Key

- 1 Glass bulb
- 2 Fritted glass filter

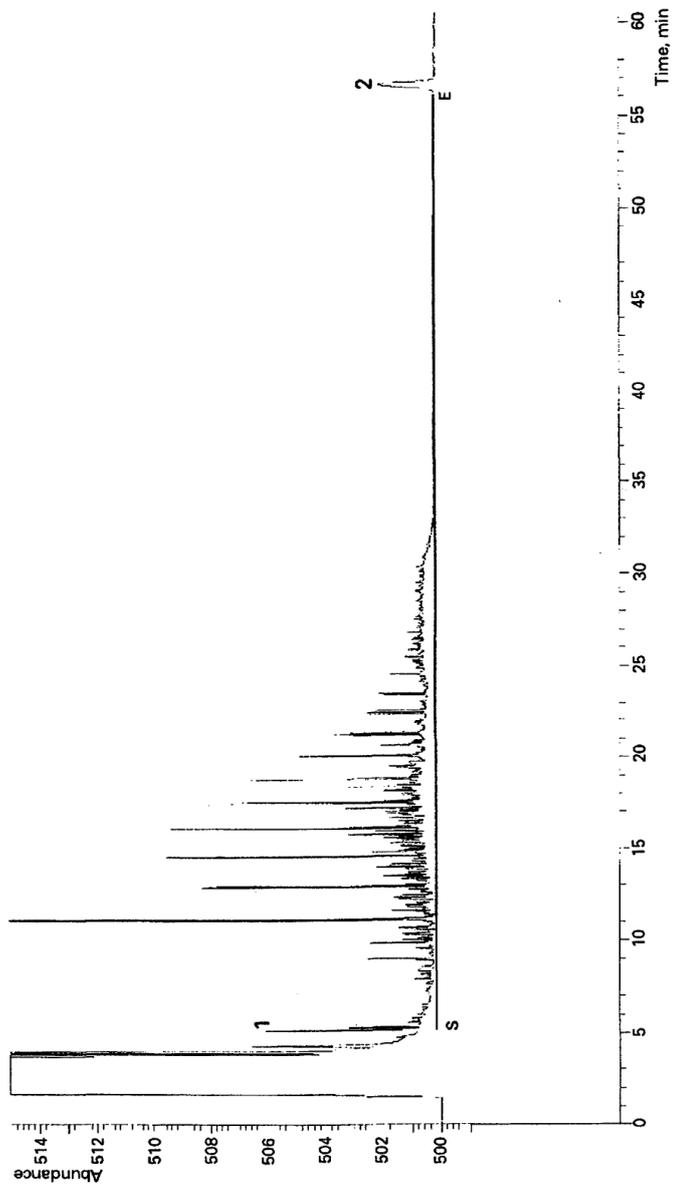
Figure A.1 – Example of a column

Annex B
(informative)

Examples of gas chromatograms of mineral oil standard and water samples

The gas chromatograms have been recorded under the following conditions:

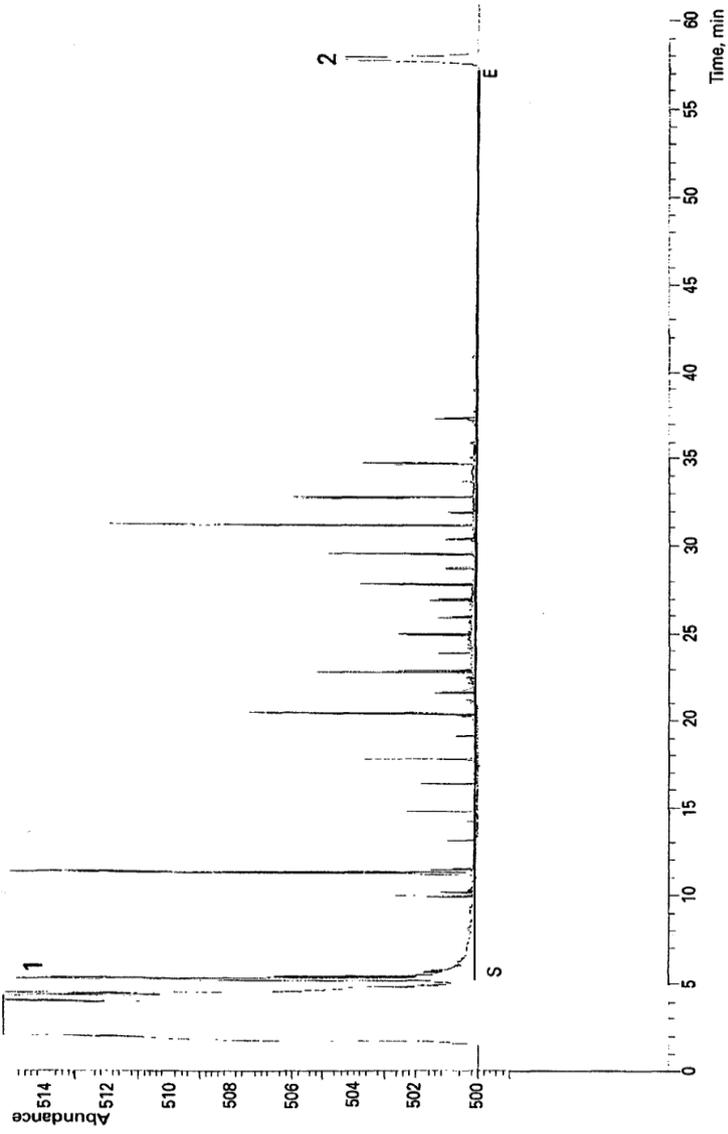
| | |
|-----------------------------|---|
| Injection technique: | programmed temperature vaporization (PTV) |
| Injection temperature: | 50 °C to 300 °C |
| Injection volume: | 1 µl |
| Column length: | 30 m |
| Column internal diameter: | 0.25 mm |
| Liquid phase: | DB 5 MS |
| Film thickness: | 0.25 µm |
| Pre-column: | deactivated fused silica capillary |
| Carrier gas: | hydrogen |
| Carrier gas pressure: | 0.8 bar |
| Oven temperature programme: | 40 °C for 5 min, 10 °C/min to 300 °C, 300 °C for 20 min |
| Detector: | flame ionization detector |
| Detector temperature: | 300 °C |
| Make-up gas: | nitrogen |
| Make-up gas flow: | 25 ml |



Key

- 1 *n*-Heptane
- 2 *n*-Tetracontane

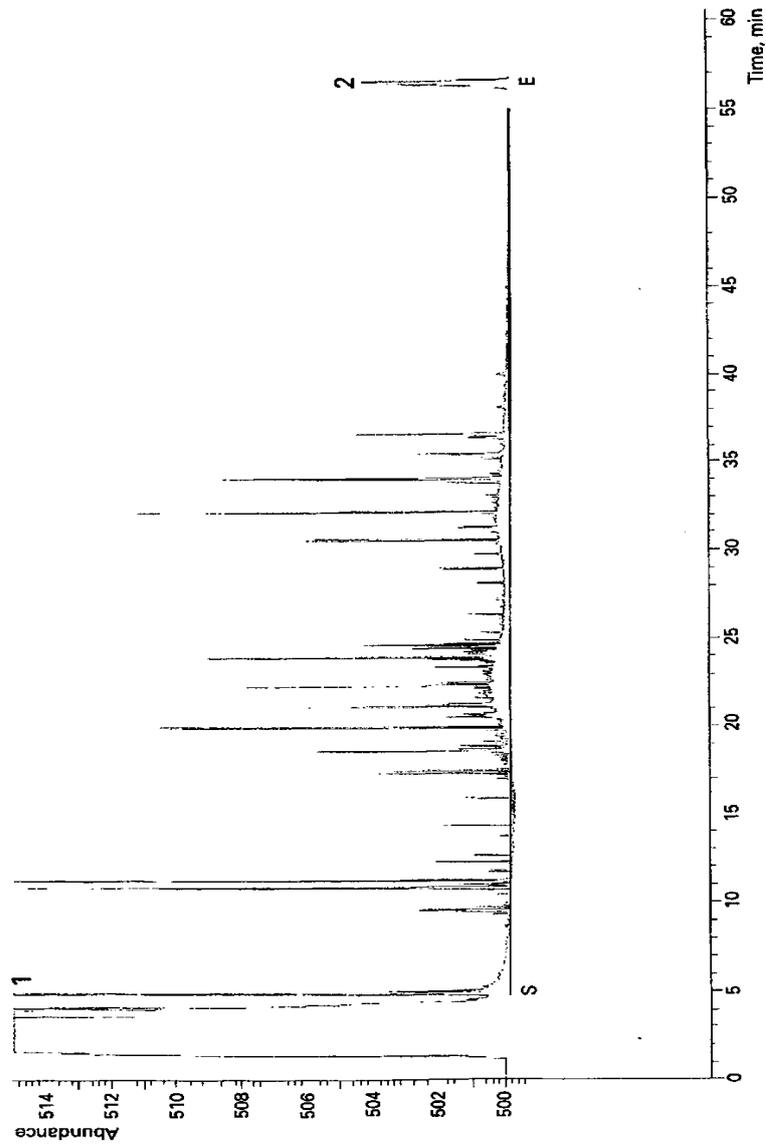
Figure B.1 – Gas chromatogram of a standard solution (0.5 mg/l)



Key

- 1 *n*-Heptane
- 2 *n*-Tetracontane

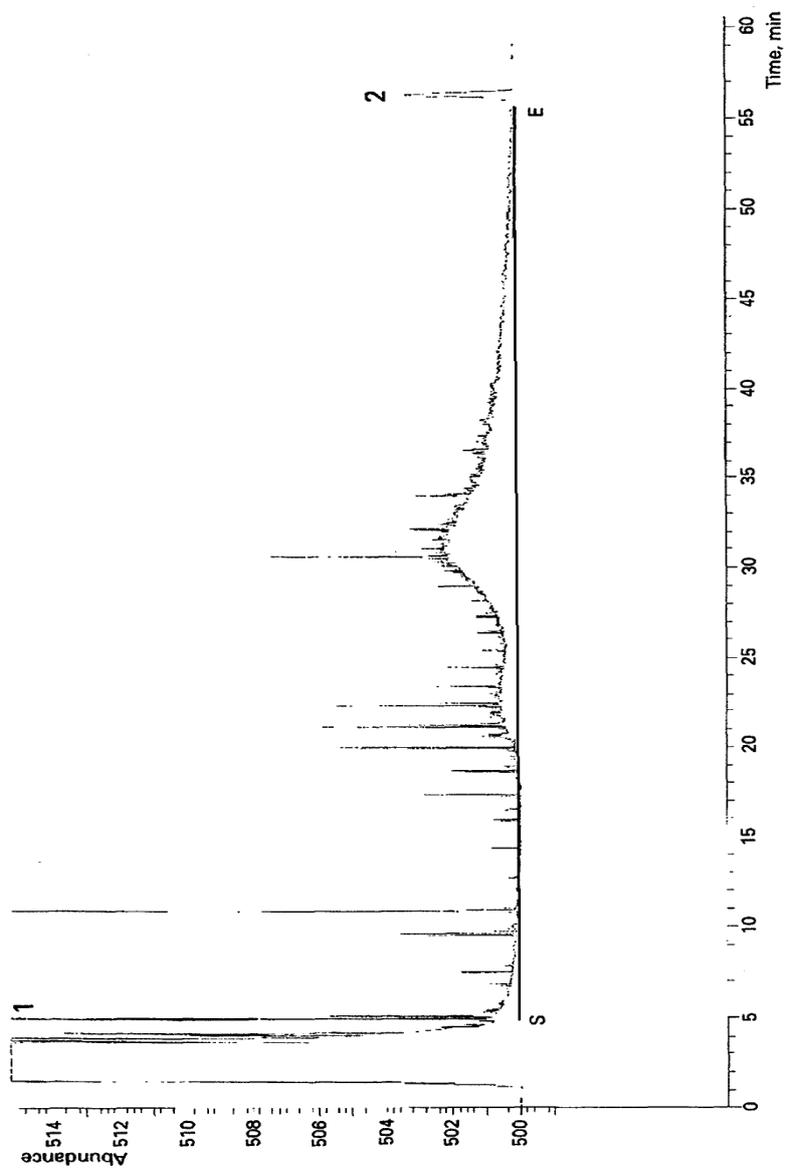
Figure B.2 – Gas chromatogram of a surface water contaminated with fuel oil



Key

- 1 *n*-Heptane
- 2 *n*-Tetracontane

Figure B.3 – Gas chromatogram of a waste water



Key

- 1 *n*-Heptane
- 2 *n*-Tetracontane

Figure B.4 – Gas chromatogram of a waste water contaminated with lubricating oil

Example of the instrumental conditions for the determination of dispersed oil in produced water by gas chromatography

Apparatus and conditions

- Gas chromatograph: Trace GC 2000
- Precolumn: 10m * 0.53mm Fused silica coupled with 5m * 0.53mm * 0.5 μ m CP-SIL 8CB
- Analytical column: CP-SIL 5CB (25m * 0.32mm * 0.4 μ m)
- Carrier gas: Helium
- Flow rate: 3.0 ml/min (constant flow)
- Injection volume: 50 μ l
- Injection speed: 4 μ l/sec
- SVE time: 0.05 min
- Extraction liquid: *n*-pentane

Formatada: Inglés (Estados Unidos)

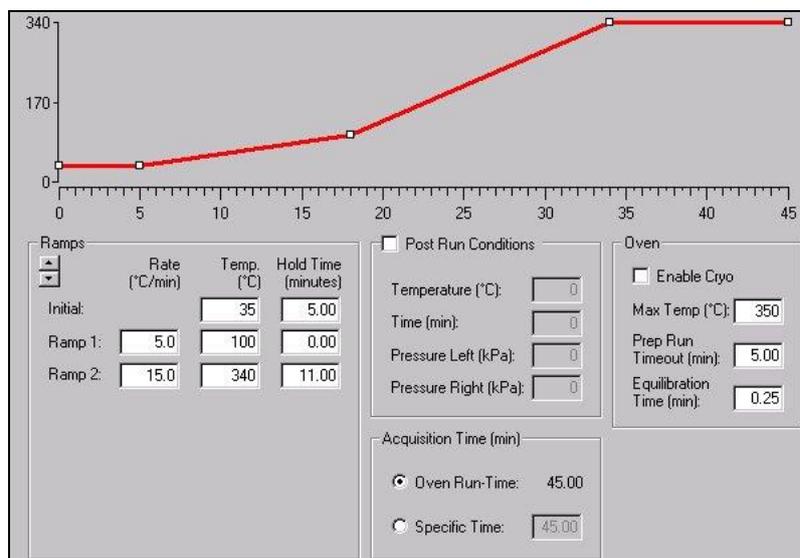
Formatada: Inglés (Estados Unidos)

Temperature programme

n-Heptane and benzene (if possible) shall be fully separated from the extraction solvent *n*-pentane.

The following programme has been used:

Fig B.5 Temperature programme



Identification

Fig. B.6 Standard solution of BTEX

Solutions of individual BTEX-compounds have been used for allocation of retention times.

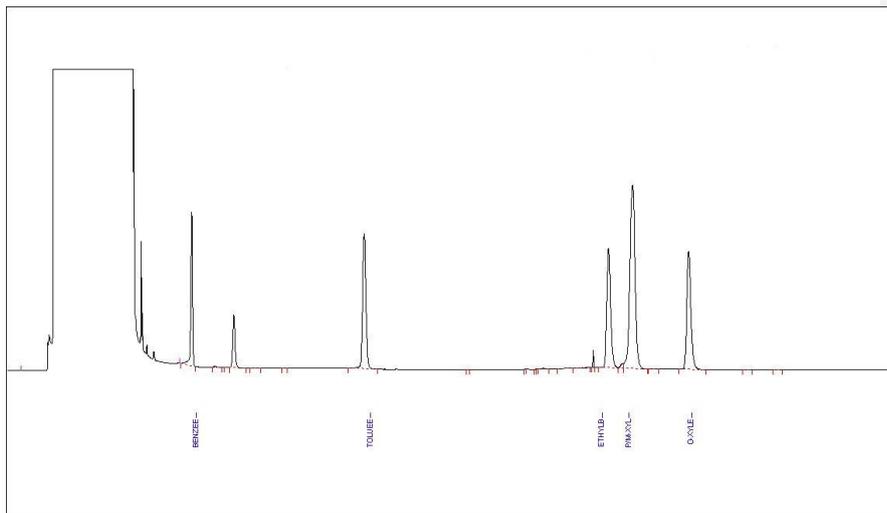


Fig B.7 Calibration mixture of Mineral Oil, including C7, C10 and C40 internal standards

(Calibration mixture from National Institute for Public Health and the Environment – The Netherlands)

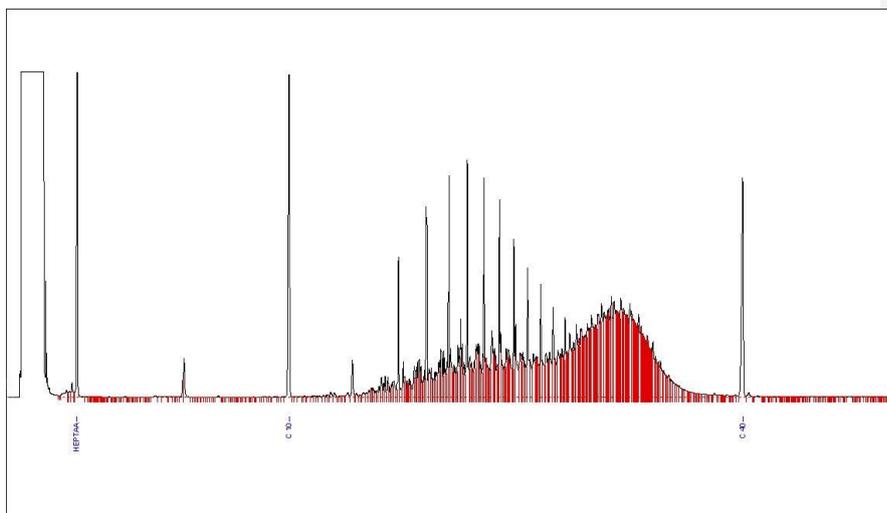
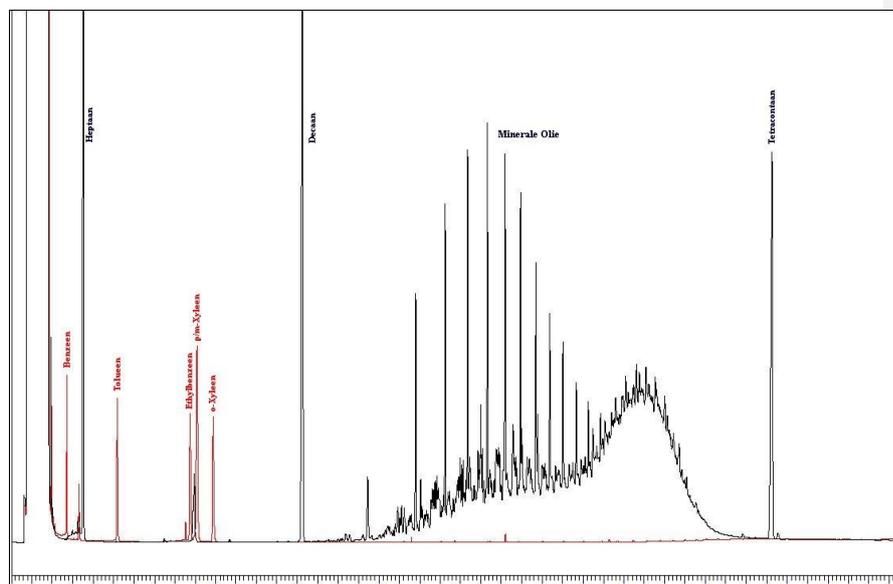


Fig B.8 Overlay of standard solution of BTEX and calibration mixture of Mineral Oil including C7, C10 and C40 internal standards



Annex C
(informative)

Determination of boiling range of a mineral oil from the gas chromatogram

Table C.1 shows the boiling points of the *n*-alkanes containing between 2 and 44 carbon atoms (up to and including C₄₄). Using these boiling points, it is possible to determine the boiling range of the mineral oil by comparing the gas chromatogram of the calibration mixture of *n*-alkanes with that of the sample extract.

Table C.1 - Boiling points of n-alkanes

| Number of carbon atoms | Boiling point °C | Number of carbon atoms | Boiling point °C |
|------------------------|------------------|------------------------|------------------|
| 2 | -89 | 23 | 380 |
| 3 | -42 | 24 | 391 |
| 4 | 0 | 25 | 402 |
| 5 | 36 | 26 | 412 |
| 6 | 69 | 27 | 422 |
| 7 | 98 | 28 | 432 |
| 8 | 126 | 29 | 441 |
| 9 | 151 | 30 | 450 |
| 10 | 174 | 31 | 459 |
| 11 | 196 | 32 | 468 |
| 12 | 216 | 33 | 476 |
| 13 | 235 | 34 | 483 |
| 14 | 253 | 35 | 491 |
| 15 | 271 | 36 | 498 |
| 16 | 287 | 37 | 505 |
| 17 | 302 | 38 | 512 |
| 18 | 317 | 39 | 518 |
| 19 | 331 | 40 | 525 |
| 20 | 344 | 41 | 531 |
| 21 | 356 | 42 | 537 |
| 22 | 369 | 43 | 543 |
| | | 44 | 548 |

Bibliography

- [1] EN 590:1998, *Automotive fuels - Diesel - Requirements and methods of test.*
- [2] KVERNHEIM A.L. *et al.*, Development of a new hydrocarbon index for oil-in-water. *Chemosphere*, 39, 1999, pp. 2707-2722.

Annex D

UK Comments on the OSPAR Reference Method

While the OSPAR Reference Method is the standard to which laboratories must base their in house method, it is recognised that the reference method has been implemented differently by laboratories while still conforming to the principles of the reference method. The following comments or recommendations are based upon discussions with laboratories who took part in the DECC Round Robin and may provide information to allow laboratories to improve on their in house methods.

Note: Numbered references below refer to the section number within the OSPAR Reference method.

6 Reagents

6.8.1 Mixture of Mineral Oils, Type A & Type B

A variety of mineral oil mixtures are currently being used, some ready-made with 50:50 gravimetric concentrations and some gravimetrically prepared in house³. Either is acceptable.

Some labs are spiking the standard solution with individual TEX components so as to better identify these peaks and remove them from the overall integration.

7 Apparatus

7.3 Column for Gas Chromatography

Columns typically used in the UK are:

25 or 30m length
0.32mm Internal diam.
0.25µm, 0.4µm or 0.52µm film thickness

Pre-columns are not always used, but where they are 5m, 0.53mmID deactivated silica ones are used.

³ In addition to details provided within the OSPAR method, Standards are also available from:

Chiron AS
Stiklestadveien 1
NO-7041 Trondheim
Norway

Sigma-Aldrich Company Ltd.
The Old Brickyard
New Road
Gillingham
Dorset
SP8 4XT
UK

This information is given for the convenience of users of this document and does not constitute an endorsement by DECC of these products.

7.8 Microseparator

The microseparator as shown previously in Figure A.2., Annex 2 of the Reference Method does not work in the configuration shown and has been removed from this copy of the guidance notes. Although one UK laboratory has corrected the design of the microseparator to work, the majority of laboratories decant the mixed solvent/water sample to a separating funnel and running off the water. This is acceptable to DECC.

9.3 Extraction Procedure

The OSPAR method calls for 30 minute stirring using a magnetic stirrer, though no guidance on stirring speed is provided. Laboratories have opted to set the stirring speed such that the vortex reaches the bottom of the sample bottle as long as stirring is steady. Some laboratories vigorously hand shake the sample bottle with pentane for 2 minutes. Either option is acceptable to DECC, though there is some feedback from laboratories that vigorous hand shaking gives higher recoveries than using a magnetic stirrer. Laboratories are required to demonstrate that extraction efficiency is >90% for whichever method is taken.

Additionally, some labs are cooling samples prior to extraction, and during extraction to minimise solvent / light end losses.

9.4 Clean-up Procedure

A variety of actions are being taken from use of clean-up columns as described to pre-charged florisil cartridges to filter paper with florisil. There appears to be no impact on option chosen, though use of a clean-up column or pre-charged florisil cartridges will ensure better contact between the solvent and florisil. It should be ensured that the florisil used is activated.

9.7.4 Integration Parameters

Unlike normal gas chromatography where integration is typically from baseline to baseline, the OSPAR reference method requires integration of the chromatogram in a different manner.

To be compliant with the OSPAR method, integration of the chromatogram, for both calibration standards and samples, should be from just after the *n*-heptane peak and end at the start of the *n*-tetracontane peak. Additionally, the integration must be at the signal level in front of the solvent peak (pentane) and be at the same signal level when integration finishes just before the beginning of the *n*-tetracontane peak.

Previously, Annex B of the OSPAR Method (and these Guidance Notes) showed a number of chromatograms from the original ISO 9377 method used for C10 - C40 analysis, hence S (solvent peak) is indicated incorrectly for the ISO 9377-2 mod method.

These chromatograms have now been adjusted for purposes of these Guidance Notes, to correctly identify S as the heptane peak. Integration should start at the end of the

heptane (C7) peak, at the signal level before the pentane peak, and continue until the start of the *n*-tetracontane (C40) peak, at the same signal level.

For removal of the TEX components from the chromatogram, the TEX peaks should be assumed to extend to the baseline of the signal level before the pentane peak.

10 USE OF ONLINE OIL IN WATER ANALYSERS

10.1 Introduction

The use of online monitors for analysis of oil in produced water can offer many benefits to operators of offshore oil and gas platforms. These include:

- (a) Knowledge of the 'true' extent of oil to sea discharges.
- (b) Continuous process information on oil in produced water (as opposed to relying on twice daily analysis results).
- (c) The possibility of 'real time' monitoring of discharged quantities of oil if linked to a produced water volume meter.
- (d) Reduction in the usage of, and analyst exposure to, solvents.
- (e) Allowing an operator to spot process upsets quickly, therefore minimising oil to sea pollution events.
- (f) Reduction in sampling and analysis work for offshore laboratory personnel.

Should approval be sought for the installation of an online monitor for reporting purposes, the following sections are intended to provide operators with guidance on what information DECC requires. Other strategies may be acceptable but would be subject to DECC approval.

10.2 General approach

A DECC approved alternative oil in water analysis method (see Section 6 and 7) must be selected before an online monitor is fitted on an offshore installation.

10.2.1 Requirement for Calibrated Alternative Analyser

A calibrated bench top based alternative method that has been correlated against the OSPAR Reference Method will be required when considering using an online monitor. An alternative analysis method is needed for:

- (a) Reporting / monitoring purposes whilst an online analyser is in the process of being approved.
- (b) Correlating the alternative method against the online monitor.
- (c) Validating the performance of the online monitor.
- (d) Use as a back-up system in case the online monitor breaks down or fails to produce valid results.

10.2.2 Procedure for the implementation of an online monitor:

- (a) Select and procure a suitable online monitor.
- (b) Install the monitor in accordance with manufacturer and/or vendor's instructions.
- (c) Establish a correlation by analysing duplicate field samples by both the online monitor and the calibrated alternative method.
- (d) Check correlation on a weekly basis.
- (e) Update correlation graph on a monthly basis.
- (f) Collect and process data for reporting purposes.

10.3 Specific Issues

10.3.1 Installation

Online oil in water analysers should only be installed where they can be easily accessed. It is important that where online systems require the installation of a probe into the main produced water flow line, the location ensures that the probe is exposed to representative flow conditions. If the online monitor is installed on a by-pass line, then the length of the sampling line should be kept to a minimum (see also sections 5.2 & 5.3).

10.3.2 Sampling

It is important that there is an appropriate sampling device fitted so that parallel produced water samples can be collected (see 5.2 & 5.9) and analysed by the calibrated offshore alternative method. Taking samples from the sampling device must not affect the online monitor's performance / analysis in any way.

10.3.3 Correlation

Following the installation and commissioning of an online monitor, correlation using field samples should be carried out. Refer to Appendix B as an example.

As a minimum, 10 correlation data points should be obtained over a discrete time period, at least one hour apart. For each of the 10 data points, samples should be taken in triplicate and analysed by the approved alternative method and an average value obtained for each data point. The average alternative analysis value for each data point is then compared to the average value that the online analyser reported over the time period during which each set of triplicate samples were taken.

If possible, samples should be taken to cover the typical range of oil in water concentration (0-40mg/l) and should be taken at a time when the process is expected to be reasonably steady.

10.3.4 Construction of a correlation graph

A correlation graph is generated by plotting the average readings from the online monitor against the average values from analysing the field samples using the approved method. Linear regression is carried out on the data points with the 95% confidence intervals calculated using a statistical software package.

A calibration graph with the 95% confidence intervals shown should then be printed out. The online monitor's serial number, the date of the calibration, correlation coefficients and analysts signature must be noted on the graph.

10.3.5 Re-correlation requirements

Re-correlation will be required after the alternative analysis instrument has been recalibrated. In addition, re-correlation is required if the online monitor has been serviced, damaged, repaired or interfered with. Re-correlation is also required if validation checks show this is required, as detailed in 10.3.6

below, or if there is a significant change in the composition of make up of the discharged produced water stream.

10.3.6 Validation

Validation of the online monitor's performance should be carried out on a weekly basis. This step is important as it gives an indication of any early drift or calibration problems.

A validation is carried out by taking three samples and analysing those using the approved method. An average reading is then obtained from the online monitor during the period when the corresponding samples were taken. The results are then plotted onto the correlation graph. If the results are within the 95% confidence interval, then it is acceptable to keep using the correlation graph. If not, another check must be carried out and if the latest point is within the 95% confidence intervals, then it is acceptable to keep using the correlation graph. If the latest point is outside the 95% confidence intervals, a new correlation graph must be established.

10.3.7 Monthly correlation graph update

At the end of each calendar month, a new correlation graph should be constructed by adding the latest validation data points to the original correlation data points and establishing new 95% confidence intervals. The reason for doing this is that over a period of time the correlation graph will cover a reasonably wide concentration range and it also partially addresses the issue of correlation graph validity against time.

10.3.8 Approval from DECC

Although it is expected that in the majority of cases, online analysers would be used for process monitoring, following the successful generation of a correlation graph, the operator may wish to seek formal approval from DECC to report oil in water figures obtained from an on-line monitor in lieu of manual sampling and analysis methods. Such approval will be granted on a case-by-case basis. Before an online monitor is approved by DECC, oil in water sampling and analysis should continue using the approved alternative method or OSPAR Reference Method until the reporting of data from the online monitor is deemed reliable by DECC.

10.3.9 Reporting of oil in water data from an online monitor

Online monitors gather data continuously. It is important that an accurate monthly average dispersed oil in water figure can be calculated. The oil in water figures reported to DECC must be in terms of the OSPAR Reference Method.

Day to day oil in water calculations may be complicated by the fact that it is the alternative analysis method that has been correlated against the OSPAR Reference Method and not the online monitor. In this instance it will be necessary to obtain (i) the oil in water concentration in terms of the alternative method using the online analyser / alternative analyser correlation graph, and (ii) the oil in water concentration in terms of the OSPAR Reference Method using the alternative analyser / GC-FID analyser correlation graph.

It is important to note that oil in water values greater than 100mg/l must be reported to DECC by submitting a PON1 or OPPC non-compliance form. An online analyser may record many values above 100mg/l during, for example, during ongoing periods of process plant upsets. Therefore, if an on-line analyser is used by an operator for reporting purposes, an agreement should be reached with DECC regarding reporting of produced water values exceeding 100mg/l.

10.3.10 Dealing with online monitor breakdown

If an online monitor breaks down, or is considered to be unreliable, there must be an immediate return to a DECC approved sampling and analysis programme as detailed in the OPPC permit schedule conditions.

10.3.11 Responsibility

It remains the responsibility of the OPPC permit holder to ensure that the correlation procedure is carried out correctly and adhered to.

10.3.12 Other correlation approaches

Other correlation approaches may also be used providing that it can be demonstrated that there is no statistically significant difference between the results obtained from the online monitor and those obtained from a DECC approved reference method.

A worked example that shows how to correlate online oil in water analysers against an alternative analysis method is given in Appendix B.

11 BI-ANNUAL PRODUCED WATER SAMPLING AND ANALYSIS

There is a requirement for sampling and analysis, on a bi-annual basis, of produced water samples for:

- (i) Total Aliphatics.
- (ii) Total Aromatics.
- (iii) Total Hydrocarbons.
- (iv) BTEX (Benzene, Toluene, Ethyl Benzene and Xylene).
- (v) NPD (Naphthalene, Phenanthrene and Dibenzothiophene, including C1-C3 Alkyl Homologues).
- (vi) 16 EPA PAH's (excluding Naphthalene and Dibenzothiophene).
- (vii) Organic Acids (Total Organic Acids, Formic, Acetic, Propionic, Butanoic, Pentanoic and Hexanoic Acids).
- (viii) Phenols (Total Phenols, C0-C3 Phenols, C1, C2, C3, C4, C5, C6, C7, C8, C9 Alkyl Phenols plus Homologues).
- (ix) Metals (Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Zinc).

11.1 Introduction

For the purposes of building up a database of information on the amounts of various constituents of produced water discharged to sea, a condition of certain OPPC permit schedules requires operators to carry out a bi-annual (twice yearly) sampling and analysis programme of produced water samples discharged from designated sampling points.

The following paragraphs specify how samples should be collected, what the recommended analysis technique is, what the detection limits are and how the results should be reported.

11.2 Bottles required for sampling

11.2.1 PAH analysis

A labelled acid washed sample bottles (1-litre acid washed amber glass bottle containing 1ml of 3% sodium thiosulphate solution). 5ml of 50% hydrochloric acid will also be required for acidification of the sample.

11.2.2 BTEX analysis

A labelled acid washed sample bottles (1-litre acid washed glass bottle.)

11.2.3 Metal analysis (other than Mercury)

A labelled 1-litre acid washed polyethylene bottle required for each sample. 5ml of 50% hydrochloric acid will also be required for acidification of the sample.

11.2.4 Mercury analysis

A 0.5 litre capacity glass sample bottle containing 10 ml of 0.1M potassium dichromate oxidising agent will be required to be supplied to each offshore location. 10-ml aliquots of sulphuric acid will also be required with each sample bottle for sample acidification.

11.2.5 Organic acid (or Volatile Fatty Acid – (VFA)) analysis

A 0.5 litre acid washed amber glass bottle.

11.2.6 Bottles for alkyl phenol analysis

A 1-litre acid solvent washed amber glass bottle.

11.2.7 Oil in water analysis

A 1-litre solvent washed glass bottle containing 5ml of 50% HCl will be required to be supplied to the offshore location.

11.3 Packaging

All bottles should be packaged in suitable containers that are in accordance with the relevant dangerous goods restrictions for airfreight. A suitably qualified person should complete the paperwork for transportation of the bottles by air.

11.4 Sampling Methods

11.4.1 General

Samples must be taken from sample points identified within the relevant permit schedule and in the same manner as described section 4.14 and as amended below. Sample bottles must not be rinsed out prior to sampling as some of the sample bottles may already contain small amounts of preservation reagents. All samples should be labelled to show details of the date, time, location and installation from which the sample was taken.

11.4.2 PAH analysis

A 1-litre acid washed amber glass bottle marked "PAH analysis" should be filled (leaving no air gap) with a representative sample from the discharge point. The entire contents of the hydrochloric acid ampoule should be added slowly to the sample, the lid should be secured and the bottle should be checked for leaks. The bottle should be inverted six times to ensure thorough mixing.

Note: *Appropriate safety precautions should be taken when adding the acid. (See chemical MSDS.) Always add acid to water, never water to acid.*

11.4.3 BTEX analysis

A 1-litre acid washed glass bottle marked "BTEX analysis" should be filled (leaving no air gap) with a representative sample from the discharge point. The lid should be secured and the bottle should be checked for leaks.

11.4.4 Metal analysis (other than Mercury)

A 1-litre polyethylene bottle marked "Metals Analysis" should be filled to the mark with a representative sample from the discharge point. The entire contents of the hydrochloric acid ampoule should be added slowly to the sample, the lid should be secured and the bottle should be checked for leaks. The bottle should be inverted six times to ensure thorough mixing. .

Note: *Appropriate safety precautions should be taken when adding the acid. (See chemical MSDS.) Always add acid to water, never water to acid.*

11.4.5 Mercury analysis

A 0.5 litre glass sample bottle marked "For Mercury Analysis" should be filled to the 0.5 litre mark with a representative sample from the discharge point. The entire contents of the sulphuric acid ampoule should be added slowly to the sample, the lid should be secured and the bottle should be checked for leaks. The bottle should be inverted six times to ensure thorough mixing. .

Note: *Appropriate safety precautions should be taken when adding the acid. (See chemical MSDS.) Always add acid to water never water to acid.*

11.4.6 Organic acid

A 0.5 litre acid washed amber glass bottle marked "VFA analysis" should be filled (leaving no air gap) with a representative sample from the discharge point. The lid should be secured and the bottle should be checked for leaks.

11.4.7 Alkyl Phenol analysis

A 1-litre solvent washed amber glass bottle marked "Alkyl Phenol analysis" should be filled to the 900ml mark with a representative sample from the discharge point. The lid should be secured and the bottle should be checked for leaks.

11.4.8 Oil in water

A 1-litre glass bottle marked "For oil in water" should be filled to the 1-litre mark with a representative sample from the discharge point. The entire contents of the hydrochloric acid ampoule should be added slowly to the sample, the lid should be secured and the bottle should be checked for leaks. The bottle should be inverted six times to ensure thorough mixing.

Note: *Appropriate safety precautions should be taken when adding the acid. (See chemical MSDS.) Always add acid to water never water to acid.*

11.5 Analysis Methods

11.5.1 PAH Analysis

PAH analysis to include:

Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benz(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Indeno(1,2,3-cd)pyrene

Other components to quantify:

Dibenzothiophene
1-methyl naphthalene
2-methyl naphthalene
9-Methylphenanthrene
4-Methylthiophene
2,6 Dimethyl naphthalene
9-Ethylphenanthrene
4-Ethylthiophene
Trimethylphenanthrene
2-Isopropylnaphthalene
1,2,6 - Trimethylphenanthrene
Other isomers as appropriate

Dibenz(a,h)anthracene
Benzo(g,h,i)perylene

When the on-shore laboratory receives the samples, they should be dosed with at least two internal standards that reflect the different number of rings present i.e. at least one two-ring and one three-ring internal standard should be used. The samples should then be solvent extracted, and the extract concentrated by evaporation and analysed by GC/MS/MS with the sample components separated, identified and measured by injecting an aliquot into a high-resolution fused silica capillary column. The method of analysis will be based on a draft ISO standard, ISO WD 14653-2:1997, "Water quality – Determination of Polynuclear Aromatic Hydrocarbons (PAH) – Part 1: Determination of 16 PAH in water by gas chromatography with mass spectrometric detection" or US EPA 610.

Further details on this method are available in OSPAR paper OIC 04/3-2 presented by Denmark at OIC 2004. See <http://www.ospar.org/eng/html/welcome.html> for further details, check the DECC website (<https://www.og.decc.gov.uk/>) or contact DECC for a copy.

The UK detection limit for PAH is 0.1 µg/l.

11.5.2 BTEX analysis (Benzene, Toluene, Ethyl Benzene, (o,m,p Xylene))

Analysis will be carried out by a headspace method based on GC/MS. The method is described in ISO method 11423-1- "Water-quality Determination of benzene and some derivatives. Part 1: Head-space gas chromatographic method". In addition it is recommended to use mass spectrometry as the detection technique and labelled internal standards for quantification. Further details on this method are available in OSPAR paper OIC 04/3-2 presented by Denmark at OIC 2004. See <http://www.ospar.org/eng/html/welcome.html> for further details, check the DECC website (<https://www.og.decc.gov.uk/>) or contact DECC for a copy.

The UK detection limit for BTEX is 1.0 µg/l.

11.5.3 Metals (Cd, Pb, Zn, Ni, As, Cr, Cu)

The samples will be filtered prior to analysis. The samples will be analysed using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Atomic Absorption Spectroscopy (AAS), Dynamic Reaction Cell Inductively Coupled Plasma Mass Spectroscopy (DRC-ICP-MS), High Resolution Inductively Coupled Plasma Mass Spectroscopy (HR-ICP-MS), Hydride Generation Atomic Absorption Spectroscopy (HG-AAS), or Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). The samples will be diluted with de-ionised water to reduce the sodium level; this may include a pre analysis to determine the Na content.

After dilution, the samples will be analysed using the appropriate element wavelengths, which are sensitive, free from interference and are linear in the calibration range. The latter will be assured by analysing a quality control sample, which is generally at mid point of the concentration range and prepared from an alternative batch to that of the standard.

Since the sample matrix is unknown, some samples may require different dilutions and so the detection limit can either be improved or eroded. If applicable, a combination of matrix matching of reference standards and dilution should be used to improve detection limits.

Voltammetry is another technique that may be suitable for the analysis of metal ions in produced water. It is well suited to saline matrices and can achieve lower detection limits than some of the ICP techniques since large dilutions are not required to eliminate salinity issues.

The UK detection limit for Cd is 0.5 µg/l.

The UK detection limit for Pb is 1 µg/l.

The UK detection limit for Zn is 5 µg/l.

The UK detection limit for Ni is 9 µg/l.

The UK detection limit for As is 1 µg/l.

The UK detection limit for Cr is 1.5 µg/l.

The UK detection limit for Cu is 10 µg/l.

11.5.4 Alkyl phenol content

C₁ – C₃, C₄ – C₅ and C₆ – C₉ alkyl phenols including isomers will be determined by GC-MS.

The UK detection limit for alkyl phenols is 0.1 µg/l.

11.5.5 Organic acid content

Formic, acetic, propionic, butanoic, pentanoic and hexanoic organic acids should be determined by GC-MS or by Ionic chromatography, isotachopheresis (ITP).

The UK detection limit for organic acid is 2 mg/l.

11.5.6 Mercury content

Mercury should be determined using ICP-AES, i.e. Elemental Hg will be generated using SnCl₂/Au-amalgamation, or Cold Vapour Atom Absorption Spectroscopy (CV-AAS). The method of standard addition should be used for this analysis.

As described in section 11.5.3 voltammetry is another technique that may be suitable for the analysis of Mercury in produced water.

The UK detection limit for Hg is 0.5 µg/l.

11.5.7 Oil in water content

The analysis should be carried out using the DECC Triple Peak method to provide total oil in water, aliphatic and aromatic content (for details please refer to Section 7 of these guidance notes).

11.6 Reporting of test results

The appropriate bi-annual analysis EEMS form must be completed for each discharge point and submitted to the processing authority by 1st September and 1st March of each year for the reporting periods 1st January – 30th June and 1st July – 31st December respectively. It is highly recommended that samples are collected during the middle part of each reporting period in order to avoid delays caused by unexpected process issues.

Late submission of returns is a non-compliance with the OPPC Regulations and must also be reported using an OPPC non-compliance form.

12 HYDROCARBON ANALYSIS OF NON-PRODUCED WATER DISCHARGE STREAMS

There are many potential non-produced water hydrocarbon discharge sources from an offshore installation and there is not always an agreed reference analysis method that can be recommended for these additional hydrocarbon sources. The following information is offered as 'best practice' and should be used wherever possible.

12.1 Measurement of Crude Oil on Water Based Mud Drill Cuttings

When drilling through the oil-bearing section of a reservoir using water-based mud, the drill cuttings could become contaminated with traces of crude oil. The measurement of crude oil on water based mud drill cuttings is therefore considered to be important, as this is a permitted activity under the OPPC regulations.

The retort analysis method is the current accepted UK analysis technique. Other techniques such as Gas Chromatography – Mass Spectrometry (GC-MS), Gas Chromatography Flame Ionisation Detection (GC-FID) or Fourier Transform Infrared Spectroscopy (FT-IR) may be used if it is not possible or practical to use the retort method.

12.2 Measurement of hydrocarbons on thermally treated Organo-Phase Fluid (OPF) drill cuttings

OSPAR Decision 2003/3 allows for the discharge of 1% or less of synthetic oil on OPF drill cuttings. The discharge of OPF cuttings that have been treated so that they contain 1% of oil or less, (w/w) is a permitted operation under The Offshore Chemicals Regulations 2002 (OCR).

Note: This is not a discharge normally covered by the OPPC regulations although an OPPC permit will be required for the discharge of fluids associated with any cuttings treatment, e.g. Rotomill, which contain reservoir hydrocarbons which is distinguishable from synthetic oil using a recommended analysis method shown below.

Details of the appropriate limits of treated OPF drill cuttings should be contained in the relevant section of the PON15 designated to cover chemical use and/or discharge operations for that particular operation. Further guidance on sampling, etc, is available from the DECC Environmental Management Team (emt@decc.gsi.gov.uk).

Following appropriate solubilisation of the OPF from drill cuttings, DECC recommends using either Gas Chromatography – Mass Spectrometry (GC-MS), Gas Chromatography – Flame Ionisation Detection (GC-FID) or Fourier Transform Infrared Spectroscopy (FT-IR) (or a combination of these techniques) as a means of quantifying the levels of synthetic hydrocarbons present on discharged OPF cuttings. These methods may also be suitable for determining the amount of reservoir hydrocarbons contained on the cuttings.

12.3 Measurement of crude oil on sand or scale

Schedules 6(a) to 6(c) of the OPPC permits cover the discharge of crude oil contaminated sand or scale to sea. DECC recommends that the DECC IR method be used for this type of analysis. The analyst will have to measure out a portion of the oily sand/scale and then use TTCE solvent to extract the oil phase retained on the sand/scale. Results should be reported in mg/kg. A representative sample of crude oil must be used when constructing the calibration graph. Refer to Annex A of the DECC IR Method (section 5) for details of oil on sand analysis. In actual laboratory testing of oil contaminated sand or scale, if the DECC IR Method is not suitable/available, other types of analysis using e.g. FT-IR or GC/MS or different solvent systems may prove more suitable. In this instance, the appropriate DECC Environmental Inspector should be contacted. Note that oil on sand analysis is not to be correlated to the OSPAR Reference method.

12.4 Measurement of oil in hazardous and non-hazardous drainage systems

Discharges of hydrocarbons from hazardous and non-hazardous drains caissons are a permitted activity under the OPPC regulations. Hydrocarbon discharges from drains must not contain more than 40mg of hydrocarbons per litre (40mg/l) in discharged water on a monthly average basis.

DECC recommends that samples taken for the purpose of measuring the oil content of discharges from hazardous and non-hazardous drains be analysed by the DECC IR Method. If the DECC IR Method is not suitable other types of analysis using e.g. FT-IR or GC/MS or different solvent systems may prove more suitable. In this instance, the appropriate DECC Environmental Inspector should be contacted. Note that analysis of oil in drains systems is not to be correlated to the OSPAR Reference method.

12.5 Measurement of hydrocarbons in well-bore clean-up samples

Under the Prevention of Oil Pollution Act, (1971), exemptions from Section 3 of the Act were granted to allow for the discharge of hydrocarbon contaminated seawater, or brine, that resulted from the chemical cleaning of a well, prior to the addition of completion brines. Given that the hydrocarbons being removed in well clean-ups are either residual organo-phase fluids (OPF's), or some of the components of the original OPF used to drill the well, discharge of such hydrocarbons now falls under the auspices of OCR. However, an OPPC permit will be required for the discharge of well clean up fluids which contain reservoir hydrocarbons which is distinguishable from synthetic oil using a recommended analysis method shown below.

Details about appropriate limits for the discharge of hydrocarbons contained in contaminated seawater or brine should be contained in the relevant section of the PON15 designated to cover chemical use and discharge operations for that particular operation and analysts are again referred to the DECC Environmental Management Team (emt@decc.gsi.gov.uk) for further information on sampling, reporting, etc.

DECC recommends using either Gas Chromatography – Mass Spectrometry (GC-MS), Gas Chromatography – Flame Ionisation Detection (GC-FID) or Fourier Transform Infrared Spectroscopy (FT-IR) (or a combination of these

techniques) as a means of quantifying the levels of hydrocarbons present on discharged well cleanup samples. If no OPF's are expected within the well clean up fluids, then the DECC IR method may be used to quantify the level of reservoir hydrocarbons within the discharge samples.

Care must be taken, when analysing well bore clean-up returns, to remove all or most of the surfactants present as they may register as hydrocarbons in the overall analysis. This may be achieved by using recognised sample clean-up techniques utilising Florisil for example.

REFERENCES

- [1] OSPAR Agreement 1997-16 on "Sampling and analysis procedure for the 40 mg/l target standards" (www.ospar.org)
- [2] "OSPAR Recommendation 2001/1 for the management of produced water from offshore installations" (www.ospar.org)
- [3] Preparation of calibration curves – a guide to best practice, September 2003, LGC/VAM/2003/032 (www.nmschembio.org.uk/PublicationArticle.aspx?m=115&amid=472)

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IR method and
alternative met
- Plot the averag
the calibration

Data points
within 95%?

APPENDICES – WORKED EXAMPLES ILLUSTRATING CORRELATION METHODS DEVELOPED IN CHAPTER 8.

The data used in the worked examples below are hypothetical, and therefore do not represent real oil in water data. The examples have been created for the purpose of demonstrating the principles involved in correlating one method against another.

The calibration graphs with the 95% confidence intervals calculated in the worked examples below have been generated using a statistical software package called Minitab and Version 14 which was used by DECC for creation of this guidance note. Use of this software by DECC does not constitute a recommendation and analysts are free to use other suitable software packages that can carry out similar tasks. DECC experience on how to generate suitable graphs using Minitab is offered within this guidance document. However analysts would be well served in obtaining professional advice in this area and not just relying upon DECC experience.

Use of Minitab 14

Generating graphs correlating Alternative Analysis results against OSPAR reference results is quite straightforward using Minitab. Data can be copied from an Excel or Word document and pasted directly onto a Minitab worksheet. If you go to 'Stat' on the toolbar and select 'Regression' followed by 'Fitted Line Plot', this will take you into a Fitted Line Plot menu. OSPAR Reference Method analysis results go into the X (Predictor) axis and results for the Alternative analyses go into the Y (Response) axis. Under Options the box for the 95% Confidence Interval should be ticked. Once this has been done, select OK from the main Fitted Line Plot menu. A graph should appear that contains both the 95% Confidence Intervals and has the regression equation at the top.

Adding validation data is straightforward but it has to be remembered that all data in the columns will be used in the graph and in preparation of the regression equation. This is useful when generating a new plot after removing an outlier for example but can be awkward if trying to overlay validation data points to see if they fit into the existing graph.

A simple way of checking whether data is within or out with the 95% confidence interval is to go to the 'Editor' function and select 'Crosshairs'. It is then relatively easy to see whether data points lie within the 95% confidence intervals.

Any comments on the use of Minitab 14 or any other statistical package, in relation to these guidance notes, should be sent to offshore.inspectorate@decc.gsi.gov.uk

APPENDIX A

Correlating an Alternative Method against the OSPAR Reference Method using Laboratory Prepared Correlating Standards

It is October 2009 and EDU Limited has decided that they want to use an alternative oil in water analysis method to the OSPAR Reference Method on their offshore installation Atholl Bravo but they wish to use method A2.

The operator has decided that UK Central Laboratories should carry out the onshore correlation of the alternative method instrument against the OSPAR Reference Method. The alternative method instrument was despatched to the onshore laboratory together with a representative sample of stabilised crude oil.

For the alternative method, n-pentane is used as an extraction solvent.

(1) Correlation standards preparation

At the onshore laboratory, a stock solution of oil in water was prepared by introducing a known weight of stabilised crude oil into a known volume of saline water. This was followed by pentane extraction. A series of six calibration standards were then prepared by successive dilutions of the pentane extract using pentane.

(2) Analysis results

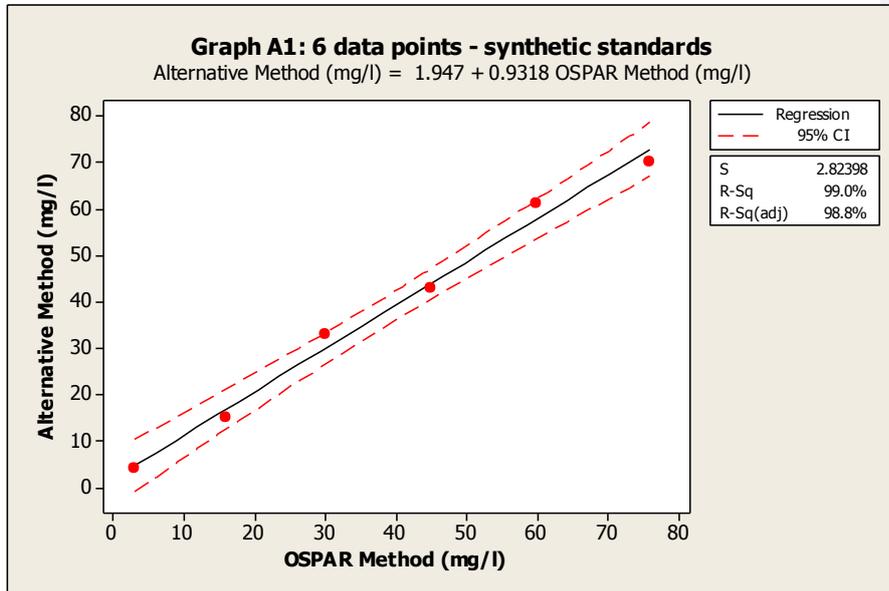
Correlation standards were then analysed by both the alternative method and the OSPAR Reference Method. Results obtained are shown in Table A1.

| | | | | | | |
|---------------------------|---|----|----|----|----|----|
| Alternative Method (mg/l) | 4 | 15 | 33 | 43 | 61 | 70 |
| OSPAR GC-FID (mg/l) | 3 | 16 | 30 | 45 | 60 | 76 |

Table A1: Analysis of correlation standards

(3) Correlation curve construction

A correlation graph was constructed by plotting the results shown in Table A1. The points were then fitted using linear regression with the 95% confidence intervals calculated using Minitab. The resultant graph – Graph A1 is shown:



Following the correlation, the alternative method instrument (along with a series of standard solutions) was returned to EDU Limited for use on installation Atholl Bravo. Upon delivery, two of the standard solutions were checked to ensure the instrument had not been damaged in transit, and were determined to be valid.

(4) Monthly Validation

To check if the original IR calibration is still valid, each calendar month a sample of one of the original IR standard solutions was analysed by the alternative method. The result obtained was checked and found to lie within the 95% confidence interval.

APPENDIX B

Correlating an Online Monitor against an Approved Alternative Method

Installation Atholl Charlie is owned and operated by EDU Limited and has been discharging more than 100 tonnes of dispersed oil to sea per annum for the last two years according to the EEMS figures.

In a desire to better control and monitor platform emissions, the operator has looked at various online monitoring techniques and decided to fit an online monitor to measure the dispersed oil in the discharged produced water. Currently two samples are taken daily at 06:00 and 18:00, and analysed by the DECC IR method. The DECC IR method has been correlated with the OSPAR Reference Method.

Following a factory calibration, the online instrument was shipped offshore and installed on the installation. The online monitor was installed on a produced water by-pass line that has been fitted with a “Y” shaped sampling device. This device allows samples parallel to the ones analysed by the online monitors be taken and analysed by the approved alternative method.

Note: It is important to make sure that taking parallel samples do not in any way affect the measurement of oil concentration by the online monitoring instrument.

(1) Correlation

Following installation of the online analyser, correlation against the alternative method analyser was carried out. The correlation, which was assisted by the instrument supplier, took 5 days, during which time 10 correlation data points were obtained.

For each correlation point, three samples were taken and analysed by the approved method. An average reading was then obtained from the online monitor during the time period when the corresponding samples were taken.

Note:

(a) Samples were taken over a wide concentration range. All the samples were taken at a time when the production process was reasonably steady.

The obtained calibration results are shown in Table B1.

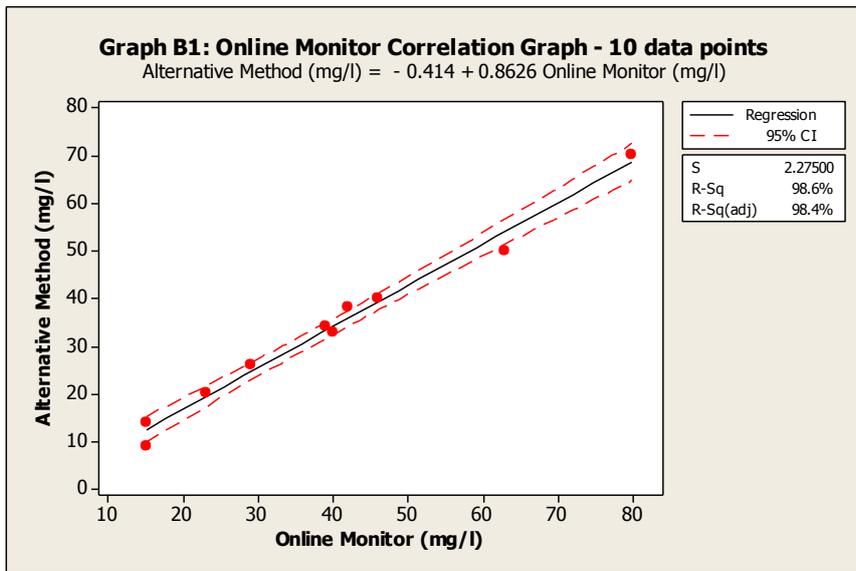
| | | | | | | | | | | |
|--|----|----|----|----|----|----|----|----|----|----|
| Alternative Method (Average result) (mg/l) | 9 | 20 | 38 | 26 | 34 | 40 | 50 | 14 | 70 | 33 |
| Online Monitor Value (mg/l) | 15 | 23 | 42 | 29 | 39 | 46 | 63 | 15 | 80 | 40 |

Table B1 Correlation results

(2) Correlation curve construction

A correlation graph was constructed by plotting the average values from analysing the field samples using the alternative method against the average readings from the online monitor. A correlation graph for the alternative method vs. OSPAR reference method is still also required. The points were fitted using linear regression with the 95% confidence intervals calculated using Minitab.

An example of the obtained correlation graph is shown in Graph B1.



(3) Validation

Each week a validation was carried out. The method of carrying out the check was identical to the way a validation data point was generated. This meant that three samples were taken and analysed by the approved method, an average reading obtained and an average reading obtained from the online monitor at the time when the corresponding samples were taken.

An example of the validation results obtained in the first calendar month is given in Table B2.

| | Cal 1-wk1 | Cal 2-wk2 | Cal 3-wk3 | Cal 4-wk3 | Cal 5-wk4 |
|--------------------|-----------|-----------|-----------|-----------|-----------|
| Alternative (mg/l) | 25 | 30 | 15 | 17 | 45 |
| Online (mg/l) | 28 | 36 | 25 | 23 | 55 |

Table B2 Weekly validation results

In this example, validation result Cal 1, Cal 2 and Cal 5 were found to be within the 95% confidence intervals. Validation result Cal 3 was found to be outside the 95% confidence intervals, but another check (Cal 4) which was done immediately after Cal

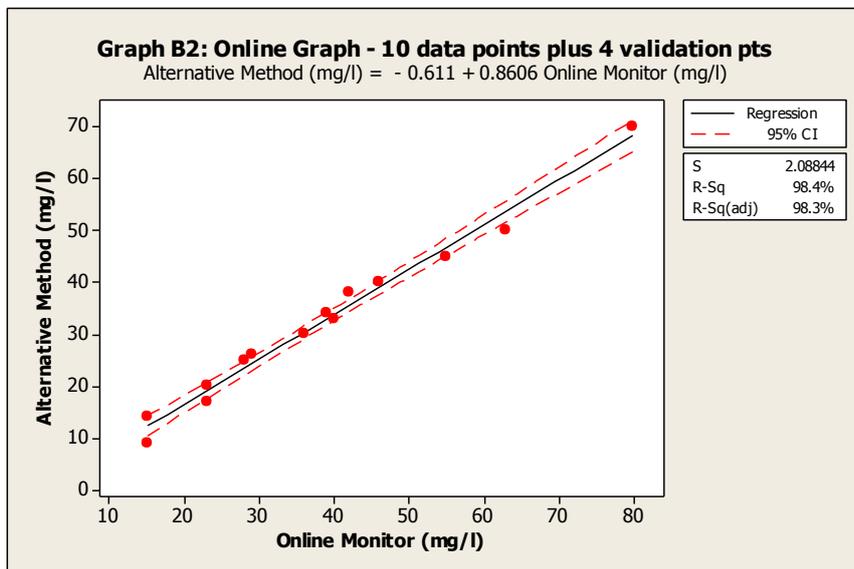
3 showed that the validation point was within the 95% confidence intervals. The use of the correlation was therefore continued.

Note: if Cal 4 point was also outside 95% confidence intervals, a re-correlation would have to have been carried out.

(4) Monthly correlation graph update

At the end of the first calendar month, a new correlation graph was constructed by adding the latest validation data points into the original set of data points. A new graph is drawn and new 95% confidence intervals are calculated.

In the above example, Cal 1, Cal 2, Cal 4 and Cal 5, i.e. those within the 95% confidence intervals, were added to the original correlation graph data points. A new correlation graph with new 95% confidence intervals was then produced as shown in Graph B2.



(5) Approval from the DECC

Following the successful generation of a correlation graph and two calendar months smooth operation, EDU Limited sought formal approval from DECC to use results from the online analyser for reporting purposes.

The following information was submitted to DECC:

- (i) Original correlation graph and the two monthly updated correlation graphs.
- (ii) Validation results (at least 4 sets of results each month for the first two month period following the establishment of a correlation graph), i.e. results obtained from the approved method and average results from the online analyser for each of the validation points.
- (iii) Methodology for calculating the monthly mass of oil discharged into the sea.