

# Chapter 2

## Measurement of Oil in Produced Water

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**Abstract** The measurement of oil in produced water is important for both process control and reporting to regulatory authorities. The concentration of oil in produced water is a method-dependent parameter, which is traditionally evaluated using reference methods based on infrared (IR) absorption or gravimetric analysis, although Gas Chromatography and Flame Ionisation Detection (GC-FID) have recently become more accepted. This chapter will give a brief overview of hydrocarbon chemistry and discuss the definition of oil in produced water and the requirement for its measurement. Reference and non-reference (bench-top and online monitoring) methods for the measurement of oil in produced water are reviewed. Issues related to sampling, sample handling and calibration, as well as methods of how to accept a non-reference method for the purpose of reporting, are discussed.

### 1 Introduction

Discharge of produced water from oil and gas productions is generally regulated. Historically one of the key parameters used for compliance monitoring is the oil concentration in produced water, is because it is relatively easy to measure.

Measurement of oil in produced water is required from an operational point of view, because process optimisation is increasingly being implemented by operators so that less oil is discharged, less chemicals are used, process capacity is increased, and oil and gas production is maximised.

Despite the importance of measuring oil in produced water, it is not widely understood what oil in produced water really is, or what the standard methods or field analyses are actually measuring. A very good example of this is the definition of the performance standard under OSPAR (Oslo-Paris Convention). The definition of 40 mg/L, which was reduced to 30 mg/L as of 1 January 2007, dealt with dispersed oil in produced water (OSPAR Recommendation 2001). However, what the old infrared-based OSPAR method measured was not just the dispersed oil. As a result, OSPAR faced a number of challenges in relation to the change in the method of measuring oil in produced water, in order to meet the OSPAR target of 15% reduction of year 2000 total oil by 2006.

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Oil in produced water is a method-dependent parameter. This point cannot be emphasised enough. Without the specification of a method, reported concentrations of oil in produced water can mean little, as there are many techniques and methods available for making this measurement, but not all are suitable in a specific application.

Other issues include sampling, calibration, and the acceptance of a non-reference method for the purpose of reporting. Sampling is often not addressed by an analytical method. However, sampling can lead to significant uncertainty in the final result, which can be important in terms of regulatory compliance and process optimisation.

While uncertainties associated with calibrations are often included in reference method precision data, if the calibration procedures are not strictly followed, they can produce quite different results. A good example showing such an effect was given by a study carried out by Statoil who confirmed an average of 19% reduction by using synthetic oil as a calibration oil compared to using a crude oil in a single wavelength method (Paus et al. 2001).

Also, as a reference method is not always suited for use in the field, alternative methods are used. For the purpose of compliance monitoring and reporting, acceptability of results from a non-reference method is of interest to many. Guidance for such acceptance is given.

## 2 Basic Hydrocarbon Chemistry

Oil in water is essentially petroleum compounds in water (Total Petroleum Hydrocarbon Criteria Working Group Series 1998). Petroleum compounds can be divided into two main groups: hydrocarbons and heteroatom compounds.

Hydrocarbons are usually measured as Total Petroleum Hydrocarbons (TPHs). These are molecules that only contain carbon and hydrogen. The heteroatom compounds are those that contain not only carbon and hydrogen but also heteroatoms such as sulphur, nitrogen and oxygen.

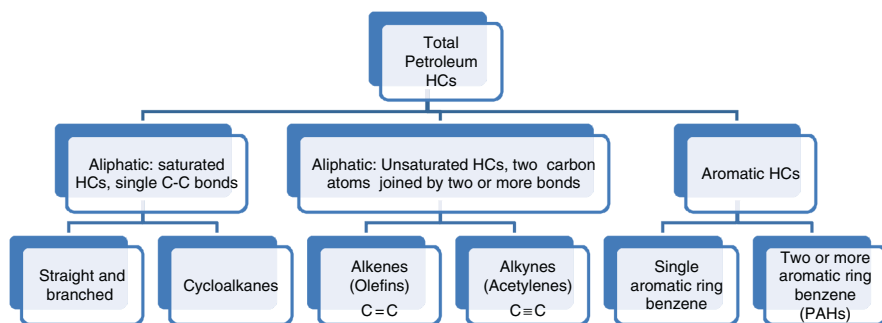
Hydrocarbons are in general grouped into three categories: saturated, unsaturated and aromatics.

*Saturated* hydrocarbons are characterised by single C–C bonds with all other remaining bonds saturated by H atoms. This group can be subdivided into aliphatic and alicyclic.

Aliphatic hydrocarbons are straight or branched with a general molecular formula:  $C_nH_{2n+2}$ . The common names for these types of compounds are alkanes and isoalkanes, which are often referred to by the petroleum industry as paraffins and isoparaffins respectively.

Alicyclic hydrocarbons are saturated hydrocarbons containing one or more rings with a general molecular formula:  $C_nH_{2n}$ . They are also called cycloalkanes or naphthenes or cycloparaffins by the petroleum industry.

*Unsaturated* hydrocarbons are characterised by two or more bonds (C=C for alkenes or C≡C for alkynes) between two carbon atoms. They are not usually found in crude oils, but are produced in cracking processes (converting large molecular



**Fig. 2.1** Hydrocarbon chemistry – total petroleum hydrocarbons (TPHs)

hydrocarbons to smaller ones). Unsaturated hydrocarbons can be sub-grouped into alkenes/olefins and alkynes/acetylenes.

Alkenes/olefins are those that contain two carbon bonds with a general molecular formula  $C_nH_{2n}$ .

Alkynes/acetylenes are those that contain three carbon bonds with a general molecular formula  $C_nH_{2n-2}$ .

*Aromatic* hydrocarbons are characterised by a benzene ring structure. The benzene ring contains six carbons; each carbon in the ring binds with one hydrogen. Depending on the number of rings that an aromatic hydrocarbon molecule contains, they are often further divided into single ring aromatics and polycyclic aromatics (containing two rings or more).

A summary of the different types of hydrocarbons is given in Fig. 2.1. Having an understanding of the basic hydrocarbon chemistry is useful. It will help with an appreciation of what is meant by oil in water, in particular, when covering topics such as aliphatic, aromatic hydrocarbons, dissolved and dispersed oils, solvent extract clean-up to remove the polar components, etc.

### 3 Definition of Oil in Produced Water

Oil in produced water is a general term. As shown in Fig. 2.2, it can mean different things to different people. Since the results are method dependent, without specifying the method used to determine the oil concentration, values reported for oil in produced water can be misleading.

*Dispersed oil* – usually means oil in produced water in the form of small droplets, which may range from sub-microns to hundreds of microns.

Dispersed oil will contain both aliphatic and aromatic hydrocarbons.

*Dissolved oil* – usually means oil in produced water in a soluble form. Aliphatic hydrocarbons in general have very low solubility in water. It is the aromatic hydrocarbons, together with things like organic acid that form the bulk of dissolved oil.

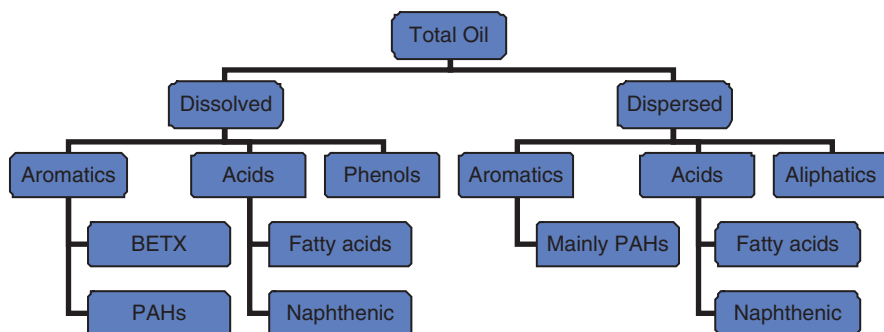


Fig. 2.2 Oil in produced water (Yang 2006)

### 3.1 Solubility of Hydrocarbons

The solubility of pentane, hexane, heptane, octane, nonane decane in water is given in Table 2.1. As the carbon number increases in a straight-chain saturated hydrocarbon molecule, solubility decreases rapidly. For *n*-octane, it is already around 1 mg/L, which becomes insignificant when compared to a performance standard such as that in the North Sea of 30 mg/L. This is why straight chain aliphatic hydrocarbons are generally ignored when discussing dissolved oil in a produced water sample.

Solubility of some of the single ring aromatic hydrocarbons is given in Table 2.2. It is quite clear that when they are present in a produced water sample, their concentration can be significant in comparison to a performance standard or discharge limit 30 mg/L.

### 3.2 Definitions

When produced water samples are taken and acidified, many of the organic acids and phenols are converted from water soluble (dissolved) to oil soluble (dispersed), which are then extracted into a solvent. Treatment of the extract using florisil before analysis usually removes them and they are not included in the oil measured.

In the OSPAR makes a distinction between total oil and dispersed oil. Total oil means total hydrocarbons (OSPAR Recommendation 2001). Dispersed oil means

**Table 2.1** Solubility of saturated straight chain aliphatic hydrocarbons (<http://home.flash.net/~defilip1/solubility.htm>)

Compound	<i>n</i> -pentane	<i>n</i> -hexane	<i>n</i> -heptane	<i>n</i> -octane	decane
Solubility (mg/L)	39	11	2	1	0

**Table 2.2** Solubility of BETX and other single ring aromatic hydrocarbons (Frintrop 2007)

Compound	Molecular formula	Solubility at 25°C (mg/L)
Benzene	C <sub>6</sub> H <sub>6</sub>	1790
Toluene	C <sub>7</sub> H <sub>8</sub>	526
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	169
<i>o</i> -xylene	C <sub>8</sub> H <sub>10</sub>	178
<i>p</i> -xylene	C <sub>8</sub> H <sub>10</sub>	162
<i>m</i> -xylene	C <sub>8</sub> H <sub>10</sub>	161
1,2,3-Trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	75
1,2,4-Trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	57
1,3,5-Trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	48
<i>p</i> -Ethyl toluene	C <sub>9</sub> H <sub>12</sub>	95
<i>o</i> -Ethyl toluene	C <sub>9</sub> H <sub>12</sub>	75
<i>m</i> -Ethyl toluene	C <sub>9</sub> H <sub>12</sub>	40
Iso-propyl benzene	C <sub>9</sub> H <sub>12</sub>	61
<i>n</i> -Propyl benzene	C <sub>9</sub> H <sub>12</sub>	52
<i>n</i> -Butyl benzene	C <sub>10</sub> H <sub>14</sub>	12

the hydrocarbons as determined according to the OSPAR reference method (OSPAR Agreement 2005). Currently, dispersed oil is defined as follows:

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<sub>7</sub>H<sub>16</sub>) and *n*-tetracontane (C<sub>40</sub>H<sub>82</sub>) excluding the concentrations of the aromatic hydrocarbons toluene, ethylbenzene and the three isomers of xylene.

In the USA, oil in produced water is referred to as “Oil and Grease”. It is defined as those materials that are extracted by *n*-hexane not evaporated at 70°C and capable of being weighed (<http://water.epa.gov/scitech/methods/cwa/oil/1664.cfm>).

Oil in produced water measured by the OSPAR method can be very different from what is quantified in the USA. This difference will also vary for the range of oily waters from the different types of oil and gas installations.

While there is an international standard method now available (ISO 9377-2 GC-FID method), for both historical and economic reasons, there is as yet no unified method for the measurement of oil in produced water.

## 4 Reference Methods

As oil in produced water is method-dependent, it is critical that a reference method is defined and available so that the data obtained from different installations can be directly compared. There are three main types of reference method available:

- Infrared absorption;
- Gravimetric;
- Gas Chromatography and Flame Ionisation Detection (GC-FID).

## 4.1 Infrared Absorption

In a typical infrared absorption based method, an oily water sample is first acidified, then extracted by a chlorofluorocarbon (CFC) solvent. Following the separation of the extract from water sample, the extract is then removed, dried and purified by the removal of polar compounds. A portion of the extract is placed into an infrared instrument, where the absorbance is measured. By comparing the absorbance obtained from a sample extract to those that are prepared with known concentrations, the oil concentration in the original sample can be calculated.

The fundamental principle of infrared based measurement is that of the Beer–Lambert law, which is given by the following equation:

$$A = \log I_0/I = ELc \quad (2.1)$$

where

$A$  is the absorbance;

$I_0$  is the incident light intensity;

$I$  is the transmitted light intensity;

$E$  is a constant;

$L$  is the path length;

$c$  is the hydrocarbon concentration in the sample extract.

There are two types of infrared-based reference method:

- Single wavelength infrared methods, and
- Triple peak or three wavelength methods.

In a *single wavelength* method, quantification (measurement of absorbance) is done by using a single wavelength, usually at around  $2930\text{ cm}^{-1}$ , which corresponds to the  $\text{CH}_2$  stretch vibration frequency. Several examples of single wavelength infrared reference methods are listed in Table 2.3.

In theory, a single wavelength method quantifies all of the  $\text{CH}_2$  contained in a sample extract. These include all of the aliphatic hydrocarbons and those that are contained in aromatic hydrocarbons such as ethylbenzene. The results will depend on how calibration is carried out and whether it uses a synthetic oil or field specific oil. The effect of using different calibration oils will be discussed in Section 7.

For a single wavelength infrared method, both fixed wavelength and scanning infrared instruments can be used. Many of the fixed wavelength instruments available on the market are portable, and easy to use, which offers advantages for offshore applications.

In a *triple peak or three wavelength* infrared method, instead of measuring the absorbance at one fixed wavelength, infrared absorbance at three different wavelengths is recorded. The three wavelengths are respectively related to the stretch vibration frequency of aromatic C–H at  $3030\text{ cm}^{-1}$ , methylene CH–H at  $2960\text{ cm}^{-1}$  and methyl  $\text{CH}_2$ –H at  $2930\text{ cm}^{-1}$ . Oil content is quantified by using an equation such

**Table 2.3** Examples of single wavelength reference methods

Reference method	Wavelength (cm <sup>-1</sup> )	Solvent used	Calibration	Status
Old OSPAR (OSPAR Agreement 1997)	2925	CCl <sub>4</sub> ; Freon; Tetrochloroethylene	Field specific oil	Superseded
USA EPA 413.2	2930	Freon	<i>n</i> -hexadecane + isooctane	Superseded
USA EPA 418.1	2930	Freon	<i>n</i> -hexadecane + isooctane	Superseded
ASTM 3921-85	2930	Freon	<i>n</i> -hexadecane + isooctane or oil in question	Superseded
ASTM D 7066-04 (2004)	2930	S-316	<i>n</i> -hexadecane + isooctane or oil in question	Still in use

as one shown in Eq. (2.2) below, which takes into account the absorbance obtained at the three wavelengths (DECC Guidance Notes 2010). The equation has three coefficients ( $X$ ,  $Y$ ,  $Z$ ) that will have been determined by measuring the absorbance at the same three wavelengths of known concentration calibration standards.

$$C_{\text{total}} = \{[X (A_{2930})] + [Y (A_{2960})] + [Z (A_{3030} - A_{2930}/F)]\} 10vD/VL \quad (2.2)$$

where

$C_{\text{total}}$  is the oil-in-water concentration;

$X$ ,  $Y$  and  $Z$  are factors calculated using absorbance obtained with known concentration calibration standards;

$v$  is the volume of extraction solvent;

$D$  is the dilution factor (if the sample is not diluted,  $D = 1$ );

$V$  is the volume of produced water sample;

$A$  is the absorbance at the specified wavelengths;

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

$L$  is the cell path length.

With a three wavelength method, the aromatic part of hydrocarbons in the samples is more properly quantified. Also such a method allows the calculation of aliphatic and aromatic hydrocarbons as given in the Eqs. (2.3) and (2.4).

$$C_{\text{aliphatic}} = [X (A_{2930})] + [Y (A_{2960})] 10vD/VL \quad (2.3)$$

$$C_{\text{aromatic}} = C_{\text{total}} - C_{\text{aliphatic}} \quad (2.4)$$

**Table 2.4** Examples of three wavelength based infrared methods

Reference method	Country	Solvent used	Calibration	Status
DIN Standard (DIN 38409 PT 18 English 1981)	Germany	Freon	No calibration, fixed coefficients	Superseded
Her Majesty's Stationary Office (1983)	UK	Freon	<i>n</i> -Hexadecane, pristane and toluene	Superseded
IP 426/98 (Energy Institute)	UK	Tetrachloroethylene	<i>n</i> -Hexadecane, pristane and toluene	Still in use
GB/T 17923-1999 (1999)	China	Carbon tetrachloride	<i>n</i> -Hexadecane, pristane and toluene	Still in use

For a triple peak method, while a fixed wavelength instrument may be used, in general a scanning infrared instrument is employed. There are several examples of three wavelength infrared methods shown in the Table 2.4.

It is important to realise that although three wavelength infrared methods quantify both aliphatic and aromatic hydrocarbons and allow the calculation of aliphatic, aromatic and total hydrocarbons, it does not mean that the results obtained from a three wavelength method will be higher than those obtained from single wavelength methods.

*Extraction solvents* play an important part in infrared reference methods. They are used to extract oil from a water sample. Obviously anything that is not extracted will not be included in the analysis.

A good solvent should possess a number of properties in addition to good extraction ability. These may include

- sufficient infrared transmission (infrared transparency)
- environmental friendliness,
- safe to use,
- heavier than water,
- reasonably priced and easily available.

Over the past 20 years, different solvents have been used in infrared based reference methods. These are given in the Table 2.5.

All these solvents are infrared transparent and have been known to be a good extractants for oil in water (Wilks 2001). They are all heavier than water which means that they can be easily separated from the water phase and drained from the extraction funnel.

Carbon tetrachloride was commonly used with infrared methods, but due to its carcinogenicity, it was replaced by Freon in the late 1900s. When Freon was found to be an ozone depleting substance, it was gradually phased out in the late 1900s



**Table 2.5** Commonly used solvents for infrared based methods (Yang 2002)

Solvent	Formula	Density at 25°C (g/mL)	Boiling point (°C)	Toxicity	Ozone depletion
Carbon tetrachloride	CCl <sub>4</sub>	1.59	77	Carcinogen	Yes
Freon	C <sub>2</sub> F <sub>3</sub> Cl <sub>3</sub>	1.56	49	Low	Yes
Tetrachloroethylene	C <sub>2</sub> Cl <sub>4</sub>	1.623	121	Moderate (suspected carcinogen)	No
S-316	CClF <sub>2</sub> CClF CClFCClF <sub>2</sub>	1.75	134	Low	Not sure

and early 2000s and was replaced by tetrachloroethylene and S-316. However people have been concerned with the fact that tetrachloroethylene is suspected to be carcinogenic and that S-316 is expensive.

In some developing countries, carbon tetrachloride is still used. The United Nations Industrial Development Organization (UNIDO Kortvelyssy 2008) has set up a series of workshops where alternatives to carbon tetrachloride have been discussed.

While infrared methods are excellent for the measurement of oil in water, they are being used less frequently now, mainly due to problems related to solvents.

## 4.2 Gravimetric

Gravimetric-based methods measure anything extractable by a solvent that is not removed during a solvent evaporation process and is capable of being weighed.

In a typical gravimetric-based method, an oily water sample is extracted by a solvent. After separating the solvent (now containing oil) from the water sample, it is placed into a flask, which has been weighed beforehand. The flask is placed into a temperature controlled water bath, and the solvent is evaporated at a specific temperature, condensed and collected. After the solvent is evaporated, the flask now containing the residual oil, is dried and weighed. Knowing the weight of the empty flask, the amount of residual oil can be calculated. Examples of gravimetric methods are shown in Table 2.6.

**Table 2.6** Examples of gravimetric based methods

Reference method	Country	Solvent used	Evaporation temperature (°C)	Status
ASTM D4281-95	USA	Freon		Superseded
Method 5520 B (2001)	USA	<i>n</i> -hexane	85	In use
EPA 413.1	USA	Freon	70	Superseded
EPA 1664 A ( <a href="http://water.epa.gov/scitech/methods/cwa/oil/1664.cfm">http://water.epa.gov/scitech/methods/cwa/oil/1664.cfm</a> )	USA	<i>n</i> -hexane	85	In use

Before the sample extract is placed into the flask for the evaporation process, it may go through a cleaning step to remove the polar components, e.g. organic acids, phenols.

The most widely used gravimetric method is probably the USA EPA Method 1664 A (<http://water.epa.gov/scitech/methods/cwa/oil/1664.cfm>). The method was developed following the phase-out of Freon. In the method a litre of water is acidified to pH less than 2 and then extracted using three volumes of *n*-hexane. The hexane extract is then combined and dried before it is distilled at 85°C. Depending upon whether the hexane extract undergoes a silica gel treatment (cleaning) process, the residual oil obtained is called either Hexane Extractable Material (HEM) or Silica Gel Treated – Hexane Extractable Material (SGT-HEM).

In the USA, HEM is synonymous with “Oil and Grease”. For regulatory compliance monitoring of the offshore oil and gas industry, it is this “Oil and Grease” as determined by the EPA Method 1664 A that is compared to the discharge limits of a monthly average of 29 mg/L and a daily maximum of 42 mg/L.

### 4.3 GC-FID

Unlike infrared and gravimetric methods, the use of GC offers the potential for obtaining details of the different types of hydrocarbons in the oil fraction. In general a typical GC-FID instrument will include the following components:

- Carrier gas supplier;
- Injector;
- Chromatographic column;
- Detector;
- Data handling system.

In a typical GC-FID method, an oily water sample is acidified and extracted by a solvent like other reference methods. The extract is then dried and purified before a small amount of the extract is injected into a GC instrument. With the help of a carrier gas and the chromatographic column, different groups of hydrocarbons will then leave the column at different times and be detected. Carrier gas is used to move the components through the column while the column acts to separate the different groups of hydrocarbons so that they leave the column and are detected at different times.

As hydrocarbons leave the column, they are burned and detected by a Flame Ionisation Detector (FID), which responds to virtually all combustible components. For oil-in-water analysis, it is the sum of all the responses within a specific carbon range or retention time that is related to the oil concentration by reference to standards of known concentrations.

Examples of GC-FID reference methods are shown in Table 2.7. The OSPAR GC-FID method, which is currently used as the reference method for measuring oil

**Table 2.7** Examples of reference GC-FID methods

Reference method	Country	Solvent used	Hydrocarbon index	Status
ISO 9377-2 (2000)	International	Boiling range (36°C to 69°C)	C <sub>10</sub> –C <sub>40</sub>	In use
OSPAR GC-FID (OSPAR Agreement 2005)	OSPAR countries	<i>n</i> -pentane	C <sub>7</sub> –C <sub>40</sub> minus TEX <sup>a</sup>	In use
TNRCC Method 1005 (2001)	USA	<i>n</i> -pentane	C <sub>6</sub> –C <sub>35</sub>	In use

<sup>a</sup>TEX stands for Toluene, Ethylbenzene and Xylene

**Table 2.8** Difference between the ISO 9377-2 and OSPAR GC-FID methods

	ISO 9377	OSPAR GC-FID
Solvent	<i>n</i> -Pentane/ <i>n</i> -hexane	<i>n</i> -pentane
Extract concentration step	Yes	No
Hydrocarbon index	C <sub>10</sub> –C <sub>40</sub>	C <sub>7</sub> –C <sub>40</sub> minus TEX
GC Column	No need to separate TEX, normal resolution GC	Must separate TEX from the rest, high GC resolution
Precision information	Yes	No

in produced water in North Sea countries, is a modified version of the ISO 9377-2. The key difference between the OSPAR GC-FID method and the ISO 9377-2 is summarised in the Table 2.8. Although the OSPAR GC-FID is the official reference method for the measurement of oil in produced water in the North Sea region, the use of GC-FID offshore for produced water analysis is still limited. To date only operators in the Norwegian sector are using it offshore. Most of the operators in other OSPAR nations either have collected the samples and sent them onshore for GC-FID analysis or have been using an alternative method that is correlated to the reference method.

#### 4.4 Discussion of Reference Methods

Reference methods are important. Without them, discharge limits or performance standards, like 30 mg/L in the North Sea become meaningless. The universal use of reference methods means that one can compare data obtained from various sources, regulators will be able to formulate future legislation based on sound information, and operators can establish appropriate policy towards produced water discharge. However, for historical reasons and the fact that produced water is a waste stream, there has never been an oil-in-water reference method intentionally accepted and adopted by regulators and operators alike.

It should be emphasised that different methods will produce different results; therefore, it is not really possible to compare results obtained from different reference methods. It should also be said that different methods will require different instruments and procedures, which affects costs (capital and operational), training, health and safety.

Generally speaking, infrared-based methods are very well established, commonly used and easy to deploy with portable fixed wavelength instruments. However, due to the use of CFC solvents, and the lack of compositional details, they are becoming less used. Gravimetric methods are simple and relatively cheap, but again they do not provide details of composition. Due to the evaporation procedures involved in gravimetric methods, there is some loss of volatile components. GC-FID methods do not need require CFCs, have no issues with the loss of volatiles, and have the potential to provide detailed information on composition, but they necessitate sophisticated instruments which require skilled operators.

## 5 Field Measurement Methods

While reference methods are essential for compliance monitoring, comparison of results and the development of future legislation, developments, they are not always user-friendly, and in some cases they may even be impossible to apply. Also, from an operational standpoint, one often requires results quickly. This is particularly true when a production process is being optimised. Analysis using some of the reference methods such as GC-FID and gravimetry, can be time consuming. Instruments and methods for use in the field that are easy, inexpensive and rapid, offer advantages and are often needed.

Field instruments and methods can be grouped into two major categories – laboratory bench-top and online monitors. Bench-top instruments and methods used for routine oil-in-water analysis may be correlated to the reference methods so that results can be submitted in compliance reports. Online monitors are used for process trending and detection of process deviation. They are advantageous in process optimisation.

### 5.1 Bench-Top

There are a significant number of bench-top instruments on the market for the measurement of oil in produced water. Techniques used include the following:

- Colorimetric;
- Fibre optical chemical sensor;
- Infrared
  - Horizontal Attenuated Total Reflection (HATR);
  - Using S-316 as an extraction solvent;
  - Using Supercritical CO<sub>2</sub> as an extraction solvent;

- Solventless;
- Using a non-conventional wavelength for detection;
- UV absorption;
- UV fluorescence.

### 5.1.1 Colorimetric

In a colorimetric method, oil in water is determined by extracting a sample with a solvent and then directly measuring the colour in the sample extract using a visible spectrophotometer at a wavelength, for example, of 450 nm. It is critically important that the oil in the contaminated water must show colour. A colourless oil is undetectable by this method. As a result for water samples collected from gas and gas condensate installations, such a method may not work properly.

A well-established colorimetric method is provided by Hach (Hach Method 8041), which has the measurement range of 0–80 ppm. But according to a comparison study (Lambert et al. 2001), such a method is best suited for water samples containing dark coloured oil in a concentration range of between 10 and 85 ppm. The colorimetric method is widely used by Petrobras in Brazil.

### 5.1.2 Fibre Optical Chemical Sensor

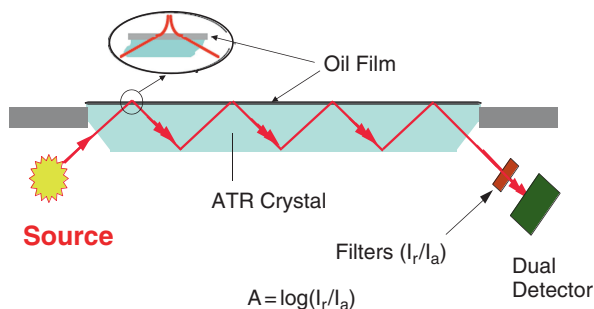
A fibre optical chemical sensor is essentially an optical fibre coated with a polymer that can absorb hydrocarbons. Such a sensor comes as a probe. When the probe is inserted into an oily water sample, hydrocarbons are absorbed by the polymer which can change its refractive index. By measuring the amount of transmitted light before and after the absorption of hydrocarbons and through calibration with known concentrations of hydrocarbons, it is possible to measure the oil concentration in an unknown water sample.

In principle it should work; however, measurements will depend on the types of oils and how easily the hydrocarbons are absorbed by the polymer. It is also equilibrium based, and as a result, it can take some time before a reading is taken. The probe must be cleaned and re-zeroed after each measurement. According to the manufacturer (Saini and Virgo 2000; <http://www.petrosense.com/products.html>), PetroSense PHA-100 WL systems have been used by oil operators in the Gulf of Mexico. It is uncertain how well the technology is able to cope with dispersed oil which can actually form the main phase of oil in produced water derived from oil and gas installations.

### 5.1.3 Infrared – Horizontal Attenuated Total Reflection (HATR)

In a conventional infrared method, oil concentration is quantified by measuring infrared absorbance after transmitting an infrared light through a cuvette containing sample extract. With HATR, infrared light is reflected at a crystal surface above which a layer of oil is deposited once the solvent has evaporated from the sample aliquot (Fig. 2.3). At each reflection, infrared light is absorbed in a similar way as

**Fig. 2.3** A schematic diagram of the HATR technique (Wilks 1999); ATR = attenuated total reflectance,  $A$  = absorbance,  $I$  = irradiance,  $r$  = reflected,  $a$  = attenuated



in the conventional infrared analysis. Therefore by calibration and comparing the absorbance obtained from a sample extract to that obtained from calibration standards with known concentrations, the oil concentration in the sample is determined.

This is a well-established technology with portable instruments available from Wilks Enterprise, Inc. These instruments are believed to be widely used by the offshore oil and gas industry. According to Wilks Enterprise, the measurement range is 4–1000 ppm. The sample extract requires evaporation before measurement. It is inevitable that some of the volatile components in the sample extract will be lost during the evaporation process. Therefore, such a method may be less suited for samples taken from gas and gas condensate installations, which may contain a significant amount of volatile hydrocarbons.

### 5.1.4 Infrared – Using S-316 and Horiba Instrument

This is a semi-automatic version of a conventional infrared analysis method. Small volumes of water sample and extraction solvent S-316 are injected into the Horiba instrument. Extraction and separation are then carried out automatically, and a portion of the extract is diverted to a measurement cell. Oil concentration is obtained by measuring the infrared absorbance.

The instrument (<http://www.qlimited.com/pdf/Horiba-OCMA-310-Q.pdf>) is believed to have been well established and widely used, especially in Asian countries. Although the measurement process is essentially the same as a conventional infrared-based reference method, it is not a reference method.

According to the instrument supplier, Horiba, the measurement range is 0–200 ppm. Key issues are the use of S-316, which is a CFC, and more importantly, the expens as discussed in the early sections.

### 5.1.5 Infrared – Using Supercritical CO<sub>2</sub> Extraction

In this method, one uses supercritical CO<sub>2</sub> as an extraction solvent to extract the oil from water samples. Infrared quantification is then carried out on the supercritical CO<sub>2</sub> that contains the extracted oil just like a conventional infrared method.

**Fig. 2.4** A picture of supercritical CO<sub>2</sub> IR technology (Private communication with Ed Ramsey of Critical Solutions Technology)



In theory it is easy to understand. In practice, however, the technology is more complicated as it involves pumping liquid CO<sub>2</sub> into a high pressure metal vessel in which a sample bottle is placed until it reaches a supercritical state. On reaching the supercritical state, a portion of the supercritical CO<sub>2</sub> (now containing oil) is diverted to a high pressure infrared cell for quantification. After analysis is carried out, CO<sub>2</sub> is vented directly to the atmosphere. An example of such an instrument is shown in Fig. 2.4. This interesting technology does not require the use of CFC. Although CO<sub>2</sub> has its health and safety issues, the technology does not produce CO<sub>2</sub>, therefore one can claim that it is environmentally neutral and friendly.

The author has tested such an instrument (Yang 2003) and found the results similar to those using other solvents, e.g. tetrachloroethylene. However, for water samples containing heavy oil, it was found that cleaning of the high pressure vessel after extraction can be time consuming.

### 5.1.6 Infrared – Solventless Approach

Recently a solventless approach has been developed (Martin et al. 2008). A sample of oil in water is filtered through a special membrane which can retain oil (dispersed). The membrane is dried before it is placed into the instrument, and infrared





**Fig. 2.5** Pictures showing the steps involved in the OSS solventless IR technology (Martin et al. 2008)

quantification is done just like a conventional infrared reference method. The steps involved are illustrated in Fig. 2.5.

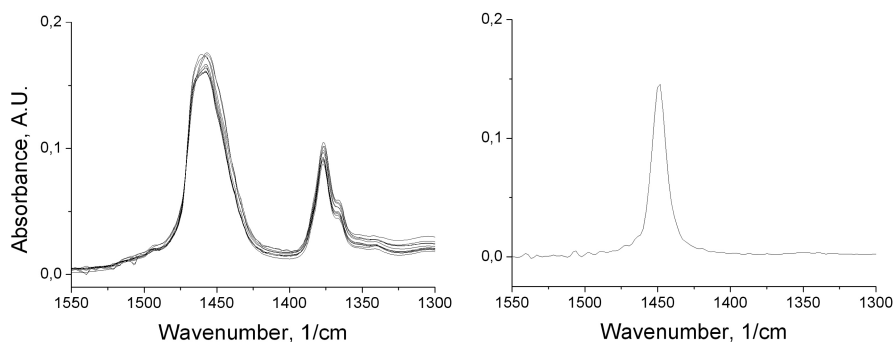
The key element is the membrane, which apparently can transmit infrared light. The technology is still being perfected before entering the market. One of the key issues will be the effect of solid particles that are often present in a produced water sample. Other issues are related to sample size, and the possible loss of oil (as oil can stick to the internal surface of an injection syringe). According to the supplier, a detection range from 3 to 200 ppm is covered (Smith and Martin 2008). Also it is believed that the supplier of the technology is working towards a single-laboratory validated method acceptable to ASTM.

### 5.1.7 Infrared – Using a Non-conventional Wavelength for Detection

This is a new technology based on Quantum Cascade Laser Infrared (QCL-IR) technology in which an oily water sample is extracted by a cyclic hydrocarbon, such as cyclohexane or cyclopentane. Quantification is then carried out by measuring absorbance at a wavelength in the region of  $1350\text{--}1500\text{ cm}^{-1}$  using mid-infrared spectroscopy that employs a Quantum Cascade Laser as a light source.

To illustrate the measurement principle, Fig. 2.6 shows attenuated total reflection (ATR) absorbance spectra for samples containing crude oil collected in the North Sea in comparison to that obtained from the extraction solvent cyclohexane. While the samples with crude oil show absorption in the region  $1350\text{--}1400\text{ cm}^{-1}$ , no absorption occurs in this range for the solvent cyclohexane. By exploring the difference and through calibration, one can calculate the oil concentration in a water sample. The technology is new. There is now an instrument available called “Eracheck” which according to the supplier has a measurement range of 0.5–1000 ppm.





**Fig. 2.6** FTIR absorbance spectra of different samples from the North Sea measured with the ATR technique (*left*) and that from the solvent cyclohexane (*right*) (Lendl and Ritter 2008)

### 5.1.8 UV Absorbance

Like aliphatic hydrocarbons which absorb infrared at certain wavelengths, aromatic hydrocarbons absorb ultraviolet (UV) light. Therefore by measuring the UV absorbance of a sample extract in a similar fashion to the reference infrared method, but using UV spectroscopy, one can quantify aromatic hydrocarbons in an oily water sample. Provided that the ratio of aromatic hydrocarbon content to that of the total hydrocarbon content remains relatively constant, the total hydrocarbon content can be obtained via calibration. The UV absorbance technique has not been widely used for oil in produced water measurement.

### 5.1.9 UV Fluorescence

When aromatic hydrocarbons absorb UV light, they emit fluorescent light at a longer wavelength. By measuring the intensity of the UV fluorescence light, one can determine the amount of aromatic hydrocarbons, which can be related to the total amount of hydrocarbons providing that the ratio of aromatics to total hydrocarbons remains relatively constant.

UV fluorescence instruments have been widely used by the oil and gas industry for the measurement of oil in produced water. Portable instruments are available on the market, for example, the TD-500 from Turner Designs Hydrocarbon Instruments (Brost 2008) and Fluorochek from Arjay Engineering (Reeves 2006). Both of these are handheld and easy to use.

The UV fluorescence technique is the second most widely used and accepted after infrared. It is very sensitive and requires no use of CFC solvents, but it is important to remember that should the ratio of aromatic to aliphatic (or aromatic to total hydrocarbons) change due to, for example, the inclusion of new oil streams from different fields, then a new calibration should be established before a measurement is carried out.

## 5.2 *Online*

There are many techniques that can be used for online oil in water monitors. A list of these techniques is given below.

- Focused ultrasonic acoustics
- Fibre Optic Chemical Sensors
- Image analysis
- Light scattering and turbidity
- Photoacoustic sensor
- UV fluorescence including Laser-Induced Fluorescence (LIF).

### 5.2.1 Focused Ultrasonic Acoustics

In this technique, a highly focused acoustic transducer is inserted directly into a produced water stream (Anaensen and Volker 2006). The transducer focuses and a time window determines the measurement volume. Any particles, such as oil droplets, solid particles and gas bubbles, that pass through the measurement volume will produce acoustic echoes. These signals are detected, classified and used to work out particle size and size distribution. Oil concentration is then calculated from the size and size distribution obtained.

A relatively new development of this technique is from TNO TDP. They had licensed the technology to Roxar who have built an online oil-in-water monitor that is being commercialised. According to Roxar, it has a measurement range of 0–1000 ppm.

### 5.2.2 Fibre Optical Chemical Sensors

This technique has been described in the previous sections (<http://www.petrosense.com/products.html>). Here a Fibre Optical Chemical Sensor probe is inserted into a produced water by-pass line. Because it is an equilibrium based technique, a back washing mechanism has to be arranged so that the probe can be cleaned and re-zeroed after each measurement. This cleaning and re-zeroing process means that only one measurement can be taken every hour or so. Therefore, although it is an online monitor, it cannot provide data on a minute-by-minute basis as others can.

### 5.2.3 Image Analysis

Image analysis instruments are based on using a high resolution video microscope to examine the content of a sample stream. Video images are captured in sequence. Particles on each of the images are then counted and analysed with their volumes calculated. To calculate the concentration of the particles, sample volume related to each of the images is determined by multiplying the image area (width by length) by the focal depth.

To distinguish oil droplets from solid particles, a shape factor is often used. For example, the ViPA (Visual Process Analyser) from Jorin (Butler et al. 2001), has the shape factor defined as  $4\pi \cdot \text{Area}/\text{Perimeter}^2$ . For a perfect circle (sphere), the shape factor is always 1. As the length of perimeter increases compared to the area enclosed, the shape factor value decreases very quickly. For a particle to be classified as an oil droplet, the shape factor has to be very close to 1. Gas bubbles that are often present in a produced water stream will be spherical too, but its optical property is markedly different from oil, so they can be easily recognised and excluded from oil droplet size and concentration calculation.

Over the past few years, several image analysis systems have been made available. In addition to Jorin, there are other commercial online monitors from J.M. Canty (O'Donoghue and Relihan 2009) and Fluid Imaging (Petersen and Ide 2008). Image analysis has been popular for produced water re-injection applications where knowledge of the size and size distribution of oil droplets and solid particles in addition to concentration is important. The instruments are increasingly being used for process optimisation (O'Donoghue and Relihan 2009; Iqbal 2009).

## 5.2.4 Light Scattering

Light scattering was probably the most popular technique for online measurement of oil in water. Ships above a certain size have to be fitted with a type-approved bilge water treatment system that must include an oil content meter to comply with the strict regulations of the International Maritime Organisation (IMO). The vast majority of these oil content meters are based on light scattering.

The technique involves passing visible light through an oily water sample. Due to the presence of particles (oil droplets, solid particles and gas bubbles), some light will be scattered, and a reduced amount will be transmitted. By measuring the amount of transmitted light together with the amount of light that is scattered at different angles, it is possible to distinguish the oil droplets from solid particles and gas bubbles, and determine the oil concentration.

There are many manufacturers who supply online light scattering based oil in water monitors. The best-known suppliers for the oil and gas industry include Deckma (Schmidt 2003) and Rivertrace Engineering ([http://www.rivertrace.com/products/industrial\\_applications](http://www.rivertrace.com/products/industrial_applications)).

## 5.2.5 Photoacoustic Sensor

The principle of the photoacoustic sensor is simple (Whitaker et al. 2001). A pulsed laser light is focused on to a small sample of oily water. Oil (dissolved and dispersed) will absorb the optical energy, which causes sudden local heating. The local heating produces thermal expansion which generates high frequency pressure waves. These pressure waves are detected and correlated with oil concentration.

When the sensor was first made, it was a probe type. Tests indicated that there was a linear response in concentration range of 20–2000 ppm. The development

work was focused on subsea separation and produced water re-injection applications. Despite extensive testing and development by AkerKvaerner, a commercial system is yet to emerge.

### 5.2.6 UV Fluorescence

The principle of UV fluorescence for oil-in-water measurement has been described in section 5.1.9. The key difference between an online monitor and a bench-top analyser is that no solvent extraction is required online. For online monitors, in addition to using a UV lamp as a light source, Laser Induced Fluorescence (LIF) has been developed and applied in recent years. With LIF, a probe type monitor is possible.

There are several manufacturers who supply UV fluorescence online monitors. The best-known ones that use lamps as a light source include Arjay Engineering ([http://www.arjayeng.com/arjayeng\\_oil\\_and\\_water.htm](http://www.arjayeng.com/arjayeng_oil_and_water.htm)), Sigrist (Rechsteiner and Schuldt 2007), and Turner Designs Hydrocarbon Instruments (Bartman 2002). These are well established and have traditionally dominated the market.

The best-known manufacturers, who apply LIF technology, are Advanced Sensors (Thabeth and Gallup 2008), ProAnalysis (Skeidsvoll et al. 2007) and Systekum (Bublitz et al. 2005). These are relative new-comers to the oil-in-water measurement market. Nevertheless, over the last 10 years the development and commercialisation of these monitors has been rapid.

Using LIF, a probe can be easily constructed, which delivers an advantage in that it can be inserted into a produced water stream or fitted inline. Other UV fluorescence monitors that use a lamp as a light source are generally fitted into a produced water by-pass stream. Having a by-pass runs the risk of non-representative sampling. The drawback comes during maintenance or instrument replacement, when an inline monitor can pose greater difficulty than one fitted to a by-pass line.

With the help of developments and commercialisation of the LIF-based monitors, UV fluorescence is now the most widely used technique for online measurement of oil in produced water.

## 5.3 Field Instrument Selection

As discussed in the previous sections, there are many different techniques and instruments to choose from when it comes to a specific application. For laboratory bench-top instruments, parameters to be considered may include the following:

*Purpose of measurement:* e.g. for process optimisation and control or for reporting. For process control and optimisation, repeatability is perhaps more important while for reporting, in addition to repeatability, accuracy also becomes very important.

*Property and characteristics of produced water:* e.g. oil colour, presence of chemicals and solid particles. Colour of oil is extremely important if one

is to use a colorimetric based method. Some production chemicals can be extracted together with oil and can affect UV methods. Solids will have a detrimental effect on the filtration infrared method. For methods involving evaporation, light components can be lost.

*The use of solvents:* if a solvent is used, one needs to check the method must be environmentally sound, and user friendly. Availability and cost must be considered.

*Calibration procedures:* what is involved in the calibration? What calibration check is required and at what frequency?

*Instrument compactness and ease of use:* for offshore operations, space is limited and, handheld or portable instruments are more welcome. Most bench-top instruments are easy to use with minimal training, and should not be an issue for a laboratory technician.

*Costs:* these include Capital Expenditure (Capex) and Operation Expenditure (Opex). Costs of instrument and measurement (operations) vary significantly. Costs associated with Opex may include the purchase of solvent and its disposal. Opex depends on the number of analyses involved.

*Maintenance and after-sale service:* this not only affects the operating costs, it can also have an impact on production.

For online monitors, most of these items apply. However, certain issues specific to online monitor applications may need to be carefully considered when it comes to instrument selection:

*Properties and characteristics:* in addition to those mentioned for bench-top methods, online monitoring requires consideration of things such as gas bubbles in the produced water stream.

*Issue of inline or online:* inline monitors require no sampling by-pass line, but may affect calibration and instrument retrieval when it comes to repair or maintenance. Online using a by-pass can be more easily isolated, and therefore facilitates instrument retrieval, but one has to verify that fluid in the by-pass line has the same property and concentration as in the main flow stream.

*Space available for fitting the instrument:* for online monitoring, instruments should be fitted downstream of a turbulent region where oil is well mixed with water. If a by-pass line is to be used, then the length of this line should be minimised. Online monitors come in a variety of configurations. Some even come with a sample pre-conditioning system to generate uniform dispersion. The amount of available space might determine the type of online monitor chosen.

*Previous applications and field test data:* although no two applications will be the same, it will be very useful if the instrument suppliers have already found similar applications and can provide test results.

*Others:* additional considerations include pressure, temperature, flow rate (minimum and maximum for by-pass line) and pressure rating.

## 6 Sampling and Sample Handling

Measurement methods are very important for obtaining good results, but if the samples that are analysed are not representative of the flow stream, the results obtained will be of little use regardless of how the samples are analysed. It is important to realise that a measurement method can only give a result as good as the sample can provide!

### 6.1 Sampling

To obtain a representative sample from a produced water stream, there are a number of aspects that one has to consider. These include:

- location of taking a sample;
- sampling devices;
- iso-kinetic sampling;
- sample bottles.

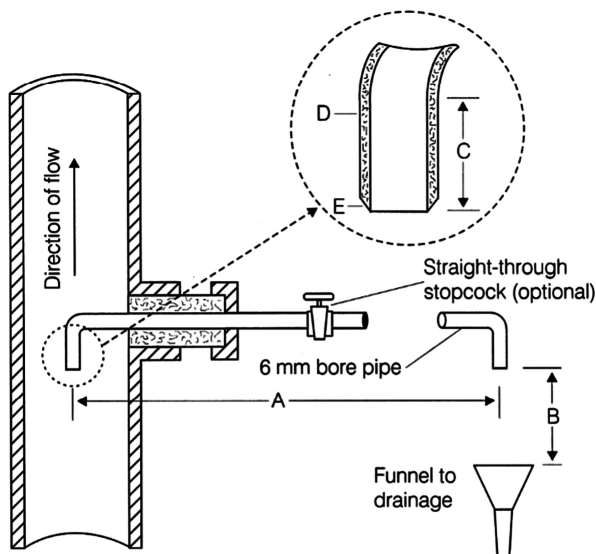
Sampling location will depend upon what is to be determined from the sample. For regulatory compliance monitoring, samples may have to be taken at specified locations. Without the approval from a regulatory body, one may not change such a location. For process control and optimisation, this may not be an issue, i.e. samples can be taken at any location. Generally speaking, when a produced water sample is taken for the purpose of measuring oil in water, the sample needs to be taken downstream of a turbulent region where oil is expected to have mixed well with the water. In an ideal situation, the sample should also be taken from a vertical pipe. In a horizontal pipe, stratification may take place.

Once a location is chosen, a sampling device is selected that will remove a section of the main flow for subsequent analysis. An example of a good sampling probe is shown in Fig. 2.7 (IMO Resolution MEPC.107(49) 2003). For produced water sampling, a half-inch (12.7 mm) sampling pipe is probably more appropriate than a quarter inch (6.35 mm) pipe.

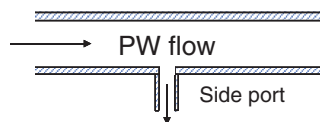
A side wall sampling point, like the one shown in Fig. 2.8, should be avoided. For a two phase flow like oil in produced water, oil has a different density than water, and due to inertia it can become difficult to change the particle direction by 90° as side wall sampling demands.

For the same reason, it is important that one considers iso-kinetic sampling. Iso-kinetic sampling means that samples are taken such that the velocity of fluid in the sampling pipe is the same as that in the main flow pipe. In general, the flow rate inside the main produced water flow line is measured, and therefore with a known pipe diameter, one can easily calculate the velocity of fluids. To check if sampling conforms to iso-kinetic conditions, one needs to work out the velocity of the fluid in the sampling pipe. This can be done by using a container with known volume and a

**Fig. 2.7** A good example of an oil-in-water sampling approach (IMO Resolution MEPC.107(49) 2003):  $A < 400$  mm,  $B$  high enough for sample bottles,  $C < 60$  mm,  $D \leq 2$  mm,  $E$  chisel-edged chamfer ( $30^\circ$ )



**Fig. 2.8** Schematic of side wall sampling point



stopwatch to obtain the flow rate, and knowing the sampling pipe entrance diameter, the fluid velocity can be calculated.

When a sample is procured from a sampling line that is not left to flow continuously, it is important that one allows the sample line to flow for at least 1 min before the sample is taken.

Sample bottles are also important. They must be extremely clean with no oil/hydrocarbon contamination. To achieve this, the sample bottles are often washed with soapy water, rinsed with clean water, then left to dry. The dried bottles are then washed with solvent and dried before use. In general, with oil concentrations in the range of a few ppm to several hundred ppm, 500 mL glass bottles are adequate for taking produced water samples. Plastic bottles should not be used as hydrocarbons may diffuse through these. Similarly for the glass bottles, the caps should be Teflon lined to prevent possible contact of hydrocarbon with plastic.

## 6.2 Sample Handling

Once a representative sample is obtained, the sample must be properly handled. Sample handling will depend on when, where and how the sample is to be

analysed and also on whether the samples are for regulatory compliance or process optimisation. In general, sample handling may include the following aspects:

- Acidification;
- Cooling;
- Transportation;
- Storage.

Acidification serves two purposes: (a) to preserve the samples by killing bacteria which can degrade oil; (b) to dissolve precipitates such as iron oxide and calcium carbonate, which can stabilise an emulsion and therefore prevent a complete separation between solvent extract and water after the extraction process.

For a 500 mL sample, 2.5 mL of diluted HCl is generally sufficient for lowering the pH of the sample to less than 2. Acid can be added to the sample bottle either before or after sample procurement. As a best practice, in particular from a safety point of view, adding acid after filling the sample bottle is probably better.

Produced water can be hot with a temperature as high as 90°C. Before an extraction is carried out, the sample should be left to cool. For the OSPAR GC-FID method, it is actually specified that it should be cooled to 10°C before extraction to prevent the loss of volatile hydrocarbons during the extraction process.

If a produced water sample is to be transported (e.g. sending a sample to an onshore laboratory), in addition to sample preservation by adding acid, the sample should be stored and transported in a suitable sealed container to prevent the ingress of light. Exposure to light may degrade hydrocarbons in the water sample.

Similarly if samples are to be stored for whatever reason, according to ISO5667-3 (2003), in an ideal situation, they should be stored in a refrigerator with a temperature kept between 1°C and 5°C. The ISO standard also states that the maximum recommended preservation time before analysis for an oily water is one month.

## 7 Calibration

Calibration is a set of operations that establish, under specific conditions, the relationship between the output of a measurement system (i.e. the response of an instrument) and the accepted values of the calibration standards (i.e. the amount of analyte present) (Barwick 2005). For general calibration issues, such as the number of calibration standards, number of replicate samples, plotting the results and performing regression, etc., a best practice guidance entitled “Preparation of calibration curves – a guide to best practice” (Barwick 2005) is available, which is a very good and useful reference. The following discussion will however focus specifically on calibration that is related to oil in produced water measurement.



## 7.1 Calibration for Lab Methods

Two issues are specifically discussed here.

- Calibration oil
- Method for preparing calibration standards

For a reference method, usually calibration oil is defined. For example, in the ISO9377-2 and OSPAR GC-FID methods, this calibration oil is a 50:50 (in weight) mix of two types of mineral oils, Type A and Type B, both containing no additives. An example of Type A is a diesel fuel; an example of Type B is a lubricant.

Before the OSPAR GC-FID method came into force in the North Sea in January 2007, a reference method based on using a single wavelength infrared was used (OSPAR Agreement 1997). Despite the specification in the method for using a stabilised crude oil from the individual installations as a calibration standard, not everyone used crude oil as a calibration standard. The use of different calibration oils can have a marked effect on the final oil in water results. This is because instruments can respond differently to the different calibration oils.

To demonstrate this effect, Fig. 2.9 shows two calibration curves (not real data) – one is prepared using a synthetic oil (a 50:50 mixture of isooctane and cetane) and one by using crude oil – taking the single wavelength method NS 9803 IR (Norsk Standard NS 9803 1993) as an example. For the calibration standards prepared using synthetic oil, as the oil contains all aliphatic with no aromatic hydrocarbons, they can give higher IR absorbance (in comparison to those prepared using crude oil, which contains aromatic hydrocarbons). As a result, when an oily water sample is collected and analysed, the calibration curve prepared using the synthetic oil would give lower concentrations compared to that from using crude oil as the calibration standard. A Norwegian study carried out in 2000 showed that using synthetic

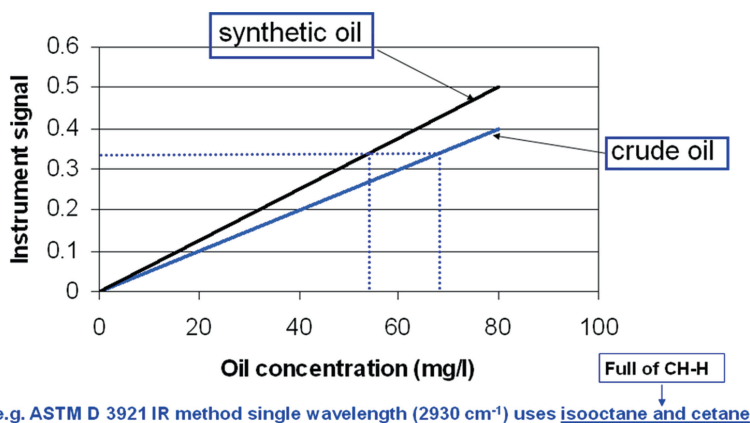


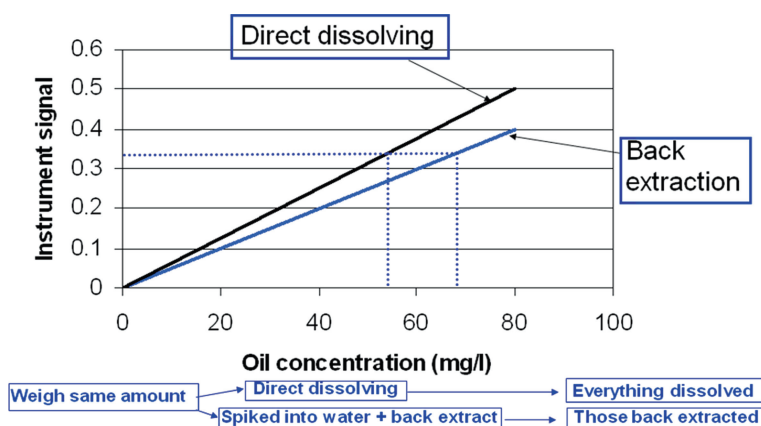
Fig. 2.9 A schematic showing the effect of calibration oil on results (Yang 2009)

oil resulted in an average reduction of 19% as opposed to using crude oil (Paus et al. 2001).

The second issue is related to how standard solutions are prepared. There are two methods that have been used. The first one (*direct dissolving method*) is by weighing a certain amount of the calibration oil and dissolving it directly into a solvent to make up a stock solution, and from this stock solution, subsequent standard solutions are prepared by dilution. A second method (*back-extraction method*) is by weighing a certain amount of calibration oil, spiking it into a salt water solution, and then back extracting the oil to form a stock solution. Subsequent standards are then prepared from the stock solution by dilution. The first one is easy to do, but the sample matrix, i.e. water solution, is not taken into consideration. The second method will have more steps involved (procedure-wise) and will be more time consuming, but it takes the sample matrix into consideration.

Using the same analogy in demonstrating the calibration oil effect, it is not difficult to see that when a calibration curve is generated by using standards that are prepared by directly dissolving oil into a solvent, it will lead to lower concentrations of oil in water compared to the cases where a calibration curve is obtained by using the back-extraction method. The reason is that only the oil that is back extracted will respond to the infrared absorption, and therefore will produce lower absorbance as is shown in the Fig. 2.10.

The foregoing discussion has clearly demonstrates the importance of calibration. By choosing a different calibration oil or a different method for preparing the calibration standard solutions, different oil in water results can be produced. The discussion also shows that if one wants to generate an artificially low oil in water result, one can do so by establishing the calibration curve using synthetic oil, and by preparing the standard solutions using the *direct dissolving method*.



**Fig. 2.10** A schematic showing the effect of calibration standard preparation on the results for oil in water (Yang 2009)

## 7.2 Calibration for Online Monitoring

Calibration for online oil in produced water monitoring is extremely difficult. This is because each produced water stream is different and also the fact that produced water is notoriously difficult to simulate in a laboratory environment, which means that it is very difficult to calibrate online monitors offsite. In the author's view, calibration of online monitoring can only be realistically achieved in the field.

## 8 Non-reference Method Acceptance

Reference methods cannot always be directly applied in the field. For example, on an FPSO movement of the vessel can prevent the accurate weighing that is required for the gravimetric method. Also there are situations where operators may not feel comfortable with the use of certain instruments for reasons such as the purchase of a new and costly instrument, safety, shortage of skilled personnel, etc. There is often a need to be able to use a non-reference method in the field, but a requirement for use of the results in reporting. This is the crux of non-reference method acceptance.

To be able to accept a non-reference method for the purpose of reporting, one has to demonstrate that the results obtained from the non-reference method are statistically equivalent to those that are produced by the reference method. Two possible ways to overcome this problem that are briefly discussed here are:

- (i) Statistical significance tests ( $F$ -test and Student's  $t$ -test);
- (ii) Establishing a valid correlation between a non-reference method and a reference method.

Statistical significance tests allow someone to compare two sets of results (in this case one from the reference method and one from the non-reference method) in an objective and unbiased way. The  $F$ -test compares the spread of results from the two methods to check if they can be reasonably considered to have come from the same parent distribution. The Student's  $t$ -test is a statistical procedure used to compare the mean values of the two data sets (Burke 1997). By carrying out such tests, one is able to state if the results from one method are statistically equivalent to those from the other method.

Unfortunately, statistical significance tests are limited to comparing two methods with a single concentration or a narrow range of concentrations (same order of magnitude). For oil in produced water, measurement methods often need to cover a concentration range from 0 to 100 mg/L (at least two orders of magnitude). Hence, establishing a correlation between a non-reference method and a reference method is thought to be more appropriate for accepting the non-reference method (Yang and McEwan 2005). The key here is to establish a valid correlation between the two methods and then continue to validate the correlation over time.

To establish this correlation and continue to validate it, two approaches have been suggested by OSPAR. Details can be found in the OSPAR Guidance document (2006).

## 9 Summary

The measurement of oil in produced water is essential for regulatory compliance monitoring, oil and gas production process control, and optimisation. The measurement is method-dependent. Using a different method will almost certainly result in different values.

There have been many reference methods for the analysis of oil in produced water, which are mainly based on three principles – infrared absorption, gravimetry and gas chromatography. Infrared-based methods have been dominant and popular until recent years, but due to issues associated with the use and availability of the chlorofluorocarbons, they are becoming obsolete. The gravimetric method is particularly popular in the USA where it is used for compliance monitoring. GC-FID is becoming increasingly popular, in particular in the OSPAR nations around the North Sea where it has recently become the reference method for compliance monitoring of produced water discharge.

Reference methods are important, since without them the comparison of results is impossible, and the regulatory framework for compliance monitoring cannot be constructed. Yet reference methods are not always user-friendly and practical in the field. As a result, alternative methods that may be inexpensive, easy to use, and can produce results quickly, are needed in particular for routine measurements. There are many techniques and instruments now available for both laboratory bench-top and online monitoring. For laboratory bench-top types, UV fluorescence and HATR instruments are probably most widely used for oil in produced water measurements. Recently, however, a solventless approach based on membrane filtration and infrared has been developed. Also, a new infrared method that uses a non-traditional wavelength has been made available. For online monitoring, light scattering and UV fluorescence instruments were popular. However with recent the development of Laser Induced Fluorescence, UV fluorescence is now becoming the main technology for online analysis of oil in produced water.

Sampling can lead to a significant amount of uncertainty in the final results. One has to remember that measurement can only provide results as good as the samples can give.

Instrument calibration is an integral part of a measurement method (both reference and non-reference). Calibration procedures are often well defined in a reference method and therefore errors associated with the procedures are often included in the precision data (i.e. repeatability and reproducibility). However experience in the North Sea has shown that the exact calibration procedures are not always adopted and followed. When different calibration procedures are used, results can be significantly different. These have been clearly demonstrated by using different calibration oils and different methodologies in preparing the calibration standards.

To accept an alternative (non-reference) method for the purpose of reporting, two possible approaches are discussed – one based on using statistical significance testing and the other based on establishing a valid correlation. For the determination of oil in produced water, establishing a valid correlation between an alternative method and a reference method is thought to be more appropriate. This is now used in North Sea countries.

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