
MONITORING OIL IN PRODUCED WATER DISCHARGED INTO THE SEA: A REVIEW OF CURRENT & EMERGING PRACTICES

REPORT N° 2.78/285

JANUARY, 1999

The Oil Industry International
Exploration & Production Forum
25-28 Old Burlington Street
London W1X 1LB

Telephone: +44 171 292 0600
Fax: +44 171 434 3721

http://www.epforum.org

Authors

This report has been prepared for E&P Forum by its Environmental Quality Committee through its Aqueous Discharges Task Force

E Garland	Elf, Chairman
E Forster	BHP
C Dalmazzone	IFP
SCA Bieshaar	NAM/NOGEPA
RPW Jacobs	Shell
J Campbell	E & P Forum

E&P Forum

The Oil Industry International Exploration & Production Forum is the international association of oil companies and petroleum industry organisations. It was established in 1974 to represent its members' interests at the International Maritime Organization and other specialist agencies of the United Nations, and to governmental and other international bodies concerned with regulating the exploration and production of oil and gas. While maintaining this activity, the Forum now concerns itself with all aspects of exploration and production operations, with particular emphasis on safety of personnel and protection of the environment, and seeks to establish industry positions with regard to such matters.

As of early 1999, the Forum has 60 members made up of 49 oil companies, 8 national oil industry associations and 3 international institutes, operating in more than 60 different countries.

The work of the Forum covers:

- monitoring the activities of relevant global and regional international organisations;
- developing industry positions on issues; and
- disseminating information on good practice through the development of industry guidelines, codes of practice, check lists, etc.

Executive Summary

Background

1. Ten years ago, the Paris Commission, now incorporated into the OSPAR Commission, defined a sampling and analytical procedure for the use of Contracting Parties to the Paris Convention in the measurement of oil in produced water. The introduction of a reference method was intended, at least in part, to ensure comparability in data reported to the Commission in relation to the previously adopted quality target standard of 40 milligrammes oil per litre of produced water.

1. Since then, there have been substantial developments in the technology for producing and treating oil and gas in the North Sea. Over the same period, as the reservoirs have reached maturity, the quantity of produced water has risen dramatically.

2. OSPAR has embarked on a programme to re-define its statement on Best Available Techniques and Best Environmental Practice for the management of produced water as part of its on-going programme of pollution prevention. The OSPAR review will take into account the technology advances of the past few years and may possibly recommend targets for improved produced water quality. The review will also need to reflect the move away from CFC solvents in the recommended procedure as a consequence of other regulatory developments on the protection of the ozone layer.

3. As a contribution to the discussion on a new statement on BAT/BEP, the E&P Forum has conducted a review of analytical procedures currently in use in the offshore industry for monitoring oil-in-water quality. Its aim is to demonstrate the range of techniques that are currently available and in routine use for the determination of oil in produced water. The review covers both laboratory-based and on-line methods and also makes reference to promising techniques that are in development.

Conclusions

4. There are a number of laboratory-based analytical methods, other than those relying on CFC solvents, that are capable of determining oil in water on a consistent basis and which could be suitable for a quality monitoring programme. However, there are no methods offering significantly enhanced performance.

6. There are a few on-line, automated methods that are capable of routine application to the measurement of oil in produced water. However, there are few applications in the North Sea for instance as problems associated with maintenance and calibration are not fully resolved. Moreover on-line methods are not suited to cases where batch discharges of treated produced water are made or to use on unmanned satellites where maintenance is a particular difficulty. On-line methods offer advantages in terms of intervention and avoidance of chemicals (for sample treatment). They may also, ultimately be of value in terms of process control and improvement. These latter features are of particular interest to the offshore industry.

7. In conclusion, the span of the existing or promising techniques is now clearly wide enough to provide improved monitoring of the produced water discharged into the sea. Providing flexibility in the choice of analytical approach will also require definition of a reference method, if possible similar to the existing one, and criteria of acceptance for alternative methods, so that the operator can demonstrate the necessary degree of compliance.

8. The review did not address questions relating to sampling and sample preservation, although it does recognise that these factors are at least of equal importance to the analytical method. Moreover, it did not address the requirements or scale of compliance monitoring. It is clear that the constraints attached to production water exceeding the target limit set by the regulator should be clearly defined. These must take into account the unavoidable fluctuations due to the production process, the characteristics of some unmanned installations, the quantity of oil effectively discharged to the sea, the foreseeable life time of some ageing installations in the world. The compliance regime must also address the overall environmental benefit of measures which may imply costly retrofitting of equipment.

Table of Contents

1. Introduction

1.1 Background

A key element in the control of marine pollution from human activity in the OSPAR maritime area is the development of statements of Best Available Techniques (BAT) and Best Environmental Practices (BEP). Within such statements, it is acknowledged that both BAT and BEP evolve with time and as a result, the OSPAR Commission has a rolling programme to review and, where necessary, update its recommendations.

OSPAR Recommendation 92/6 sets out a statement of Best Available Techniques for produced water management on offshore gas and oil installations. In October 1997, the Netherlands hosted a workshop that addressed a broad range of aspects covering the management of produced water discharges. The outcome of this workshop was to make recommendations for the consideration of the Sea-Based Activities Working Group as it considered the development of an updated statement on Best Available Techniques.

Although, not specifically embodied in the BAT description adopted in 1992, Contracting Parties to the OSPAR Convention were working within a framework which recommended a numerical limit for the average oil content of formation waters discharged to the maritime area of 40 mg l^{-1} (Eighth Annual Report of the Paris Commission, 1986). Furthermore, in 1988, the Paris Commission agreed a sampling and analysis procedure for implementing the target standard (Tenth Meeting of the Paris Commission, 1988). Concern over the use of chlorofluorocarbon solvents ("freon" CFC113) in the specified analytical method has resulted in the need for changing the extraction technique. Moreover, analytical advances, including the development and implementation of automated or on-line methods have let users and regulators hope that both the process control and the quality of analytical data for reporting purposes will improve.

The Netherlands workshop indicated that it was important to incorporate guidance on analytical methods in any amended statement on Best Available Techniques, without specifying individual analytical methods or techniques. To assist this work, the E & P Forum has conducted a review of the techniques usable and of the promising ones under development as well as a limited survey of the analytical techniques actually used by its members world-wide. This paper presents the results of both the review and the survey.

1.2 Previous E & P Forum Submissions on Produced Water Management

Aspects of the management of produced water discharges are regularly discussed by the E & P Forum membership. Regular reports on the topic have been prepared and these have been made available to the technical groups within the Paris and OSPAR Commissions as well as to the Netherlands-organised workshop. These have included:

- Aqueous Discharges in the North Sea: An Update from the E&P Industry (Report No. 2.76/271, January 1998; Document SEBA 98/5/NGO.2-E);
- Technologies for Handling Produced Water in the Offshore Environment (Report No. 2.71/247, September 1996; Document SEBA 98/5/NGO.1-E).
- North Sea Produced Water: Fate and Effects in the Marine Environment (Report No. 2.62/204, May 1994);

- Production Water treatment: Current and Emerging Technologies (Report No. 2.64/211, July 1994).

1.3 Current Review and Survey

The review of the techniques is based on information gathered in the literature, an analysis of the information provided by the National Associations on their R&D projects, and on the information obtained in response to a questionnaire circulated to all members of the E & P Forum. In the questionnaire members were asked for information under the following broad headings:

- Description of the technique (wet or on-line etc.);
- If on-line, manufacturer, make and model;
- Calibration against standard methods;
- Number of years in service;
- Analytical performance (precision, bias, stability);
- Sampling strategies;
- Field name and oil type for each method;
- Details of sample conditioning.

The results of this survey are summarised in the following sections.

2. What do we measure and why?

2.1 What is produced water?

Produced water is the natural aqueous fluid that is recovered from oil and gas reservoirs in association with the hydrocarbons. Typically, the produced water is separated from the hydrocarbons in separators on board the offshore facility. After treatment to remove all but trace amounts of oil, produced water is normally disposed of by discharge into the sea, in accordance with local regulations. Alternatively, produced water can be re-injected into the reservoir either to maintain reservoir pressure where this is practical or possible, or for disposal. The E & P Forum has previously published a detailed review of the composition as well as the fate and effects of produced water discharged to the North Sea.

Produced water is a complex mixture of compounds. It consists of formation water which is present naturally in the reservoir, flood water previously injected into the reservoir to maintain pressure (often this is sea water) and in the case of some gas production, condensed water. The amount of oil in production water varies considerably as does its composition. In addition to 'oil', produced water also contains other naturally occurring organic constituents and inorganic salts leached from the formation. The geology of different structures imposes an individual composition on each produced water stream. Moreover, the water chemistry varies during the life of a field. In addition, treated produced water will contain chemicals added at various stages of the production process to control scaling, corrosion, foaming, bacterial growth and emulsions, and their residues. It may also periodically contain chemicals used during drilling and completion of wells and back-flowed into the production system during clean-up operations. Thus, any analytical technique used to assess the quality of produced water is non-specific.

Recovery of oil from produced water is carried out at an installation, usually in several stages. After the primary stage, produced water still contains typically between 0.01% and 0.1% by weight of oil dispersed as fine droplets or dissolved hydrocarbons. A second or even a third stage, is often necessary to lower the oil content down to a few tens of mg per litre of water. At this stage, the droplets of oil which remain in the water are very small (their diameter does not exceed a few microns), and the composition of dissolved hydrocarbons no longer reflects the composition of the fresh crude oil. The relative concentrations of aromatic compounds and low-molecular-weight alkanes, which have a high solubility in water, are usually higher in produced water. This shift in the composition poses a considerable problem in determining the 'oil' content, in particular method of calibration. Two methods which correlate perfectly for a specific produced water may not correlate when tested on water from another source.

Monitoring the oil content of production water is routine and is carried out for two purposes. First of all, it is generally a regulatory requirement, based on environmental concern. Although produced water is a complex mixture of organic and inorganic substances a simple and effective way to monitor the quality of the produced water discharged is to monitor the content of hydrocarbons. Secondly, measurement of oil in produced water is an important component in process control, indicating the efficiency of the treatment process (ie optimising the recovery of products) and as a means of identifying process upsets that might require remedial action, including shutdown. Therefore, it is thought that more frequent measurement of produced water streams might provide a higher degree of protection for the marine environment, since the operator could respond more quickly to deterioration in quality.

For all these reasons, monitoring oil in produced water is a routine procedure and requirement in most offshore producing areas.

2.2 *Current Practices*

There is no universal technique for measuring oil in produced water. Thus regulators have tended not only to agree a target or standard concentration, but also to specify the method of measurement.

For the OSPAR maritime area the agreed target standard is 40 mg dispersed oil per litre of water. The monitoring method agreed is based on solvent-extraction of the hydrocarbon phase of the produced water, elimination of the polar phase, followed by quantification of the non-polar phase based upon infra-red absorption. At least 16 samples per month are required to demonstrate compliance with 24 to 48 hours between sampling. The issue of sampling and measurement on remote unmanned satellites, or on satellites where discharges are discontinuous, is not satisfactorily addressed by this procedure.

The principle of the analytical method used on platforms in the maritime area of OSPAR does not greatly differ from the one recommended by MARPOL 73/78 for monitoring oil in waters discharged to the sea by ships. Due to the characteristics of the waters and to the facilities on board of ships, the use of automatic devices is possible in many applications.

For the offshore waters of the United States, the US regulations specify that the oil content of the produced water is to be measured using a gravimetric method, after solvent-extraction and evaporation. The limit on oil and grease for produced water discharged is a monthly average of 29 mg l^{-1} (and a daily maximum of 42 mg l^{-1}).

It should be noted that due to differences in the analytical procedures used in the USA and OSPAR, the USEPA method is negatively biased as the 'light hydrocarbon fraction' is lost during sample evaporation. The USEPA method however, does measure more polar and soluble hydrocarbons. Therefore it is difficult to directly compare oil concentrations determined by the OSPAR and USEPA methods.

3. Manual methods of analysis

Monitoring oil in produced water by 'manual methods' ie, methods where the sample preparation is carried out manually, involve four discrete phases: sampling, sample preservation, sample preparation and quantification. This review focuses on the latter two stages of the process. It should, however, be borne in mind that sampling and sample preservation can have a substantial bearing on the accuracy of measurements and hence on the detection capability of specific procedures. It has to be taken into consideration when comparing manual and on-line methods.

The most widely used method of sample preparation for the determination of oil in water involves solvent extraction of the hydrocarbon phase with a chlorocarbon or chlorofluorocarbon solvent. Quantification is carried out by one of a range of techniques including gravimetry, infrared absorption, ultraviolet absorption, ultraviolet fluorescence, colorimetry, nephelometry and gas chromatography. The following discussion sets out the range of manual methods that are currently in use in the upstream petroleum industry or which are currently under development.

3.1 Infra-red (IR) methods

Characteristic absorption of infra-red radiation by aliphatic hydrocarbons occurs at wavelengths in the region 3040 to 2915 cm^{-1}. Quantification using this characteristic is the most widely used method and is considered to be standard in a number of regulatory regimes. All methods are based on the same measurement method, described in the ASTM D 3921-85 "Standard test method for oil and grease and petroleum hydrocarbons in water". Sample preparation requires solvent extraction with a non-interfering solvent such as carbon tetrachloride (CCl_4) or 1,2,2-trichloro,1,1,2-trifluoroethane (Freon 113).

Advantages	**Disadvantages**
• Simple and robust technique	• Use of hazardous halogenated solvents
• Reproducible	• Accuracy influenced by the composition of dispersed oil and by matrix effects at low oil in water concentrations
• Rapid and cheap	
• Lower limit of detection for the quantification stage < 1 mg l^{-1}	• Sampling and preparation induce an overall lower limit of detection > 1 *mg* l^{-1}

3.1.1 OSPAR Method

The Paris Commission recommended an analytical method based on IR quantification in 1988. This method required:

i. Manual sampling;
ii. Pre-treatment to stabilise the sample and to eliminate the lighter hydrocarbon fraction;

iii. Extraction with a halogenated solvent (CCl_4 and Freon 113 have been used) followed by florisil treatment which removes polar compounds; and

iv. Infrared quantification at 2925 cm^{-1} which corresponds to the CH_2 stretch vibration of the aliphatic component.

Quantification is performed by comparison to absorption of n-hexadecane ($C_{16}H_{34}$) at the same wavelength. The PARCOM target standard concentration is 40 $mg\ l^{-1}$. When concentrations in produced water exceed this value, further quantification at two additional wavelengths is required to assess the aromatic content of the sample.

Application: The OSPAR method is commonly used in the North Sea.

3.1.2 MARPOL 1973/1978 Method

The MARPOL 1973/1978 Method does not differ significantly from the OSPAR method. It is used to monitor waters discharged to the sea by ships. However, in that case, the oil is usually not finely dispersed, and the hydrocarbon phase contains lower concentrations of light and polar fractions. Therefore, the overall accuracy obtained is generally better than in offshore oil and gas applications. The florisil extraction is not needed, and it has been possible to automate the monitoring process in many applications.

Application: MARPOL 73/78 method is the most commonly used on ships. It is not used, as such, on platforms.

3.1.3 US Environmental Protection Agency Standard Method – EPA 413.2

In EPA 413.2 standard method, the acidified sample is extracted with Freon 113 and IR absorbance of the extract is measured at 2930 cm^{-1}. Sample absorbances are calibrated against a standard reference extract. The result is expressed as the "total oil and grease content".

Application: Marginal, as the US regulators still require the EPA 413.1 gravimetric method.

3.1.4 US Environmental Protection Agency Standard Method – EPA 418.1

This method differs from the EPA 413.2 in that the Freon 113 extract is treated with silica gel to remove polar organic components. Infra-red absorbance is measured at 2930 cm^{-1} and calibrated against a known concentration reference sample. The result is expressed as the "total petroleum hydrocarbons content".

Application: Marginal, as the US. regulators still require the EPA 413.1 gravimetric method.

3.1.5 Other IR Methods:

There have been a number of attempts to develop IR methods that do not require the use of halogenated solvents, in particular freons. Hexane has been proposed as an alternative solvent for a procedure that follows the outline of EPA 413.2. Although it shares the advantages of the earlier methods (with the additional benefit of not using a halogenated solvent), the detection limit of the technique has been substantially degraded and is of the order of 10 mg l^{-1}.

3.2 Gravimetric methods

Gravimetric methods also rely on solvent extraction as the first stage of sample preparation. The extract is evaporated and the residue weighed. Evaporation drives off both the solvent and some of the lighter fraction of the hydrocarbons. Other issues of concern are the toxicity and the flammability of the solvent.

3.2.1 US Environmental Protection Agency Standard Method – EPA 413.1

EPA Method 413.1 is a gravimetric method for the determination of oil and grease content in water. Following extraction of an acidified sample with freon, solvent is evaporated at 70°C and the residue, defined as oil and grease, is weighed.

Advantages

- Simple and robust technique
- Reproducible
- Rapid and cheap

Disadvantages

- Use of hazardous halogenated solvents
- Under estimates oil content (volatile fraction evaporated)
- Unsuitable for condensates
- Detection Limit >10 mg l^{-1}

Application: Regulatory implemented and used in all US offshore waters.

3.2.2 US Environmental Protection Agency Standard Method – EPA 1664

In 1996, the USEPA proposed Method 1664 to replace EPA 413.1. The method used hexane as an extractant (to replace Freon 113) and the determinands for the method were defined as n-Hexane Extractable Material (HEM) and Silica Gel treated n-Hexane Extractable Material (SGT-HEM). The procedure for HEM involves extraction with n-hexane, filtration through anhydrous sodium sulphate to dehydrate the extract and evaporation over steam or a water bath. The procedure of SGT HEM is similar with the additional step of treatment with silica gel to remove polar organic substances.

Advantages

- Simple
- Uses a 'friendly solvent'
- Cheap

Disadvantages

- Results not comparable with EPA 413.1
- Poor reproducibility
- Not adaptable for IR determination
- Detection Limit >10 mg l^{-1}
- Accuracy ± 10 mg l^{-1}

Application: Not used.

3.2.3 Methyltertiarybutylether (MTBE)/hexane extraction

The above solvent combination has been used in some producing areas as a replacement for freon solvents in the EPA 413.1 method. The solvent used is a 15/85 v/v mixture of its components.

Advantages	Disadvantages
• Simple	• High flammability and odorous solvent
• Uses a 'friendly solvent'	• Solvent more difficult to remove
• Rapid and cheap	• Not adaptable for IR determination
• Results comparable to EPA 413.1, in testing	• No quantification of volatiles

Application: Used in Trinidad and Tobago.

3.3 Ultraviolet (UV) absorbance

The aromatic components in crude oil absorb strongly in the UV region between 225-235, 250-270 and 315-325 nm. UV absorbance can then be used to determine the aromatic content of water samples with the total hydrocarbon content being calculated proportionally.

3.3.1 Pre-extraction methods

Acidified samples are extracted with a solvent sufficiently transparent in the UV spectral region, so that UV absorbing aromatic hydrocarbons are detected and quantified using a suitable calibration.

Advantages	Disadvantages
• Simple	• Hydrocarbon concentrations determined by proportion from the aromatic content
• Rapid and cheap	• Use of hazardous solvent

Application: No field application known.

3.3.2 Solvent-free methods

In this group of methods, an acidified sample is mixed with a UV-transparent surfactant to solubilise the oil. UV-absorbing aromatic hydrocarbons are then detected and quantified against a suitable calibration.

Advantages	Disadvantages
• Simple	• Results dependent on sample homogeneity (choice of surfactant is critical)
• Rapid and cheap	• Hydrocarbon concentrations determined by proportion from the aromatic content
• No solvent required	

Application: Automated version field tested (see § 4.2).

As an example, the SpectraScan OIW Analyser was developed by Texaco EPTD for bench-top analysis of oil in individual water samples. It operates by measuring the amount of UV/visible light absorbed by the oil in a produced water sample. It uses a fibre optic transmission probe. Two separate analyses methods have been developed: the "Solvent extraction" and the "Solvent free" methods. In the solvent extraction method, oil is extracted into a UV-transparent organic solvent (hexane, iso-octane, trichloroethane). Measurements are made by inserting the probe into the solvent extract. In the solvent-free method, a surfactant solubilises the dispersed oil and measurements are made directly on the treated, aqueous sample.

An alternative to these two latter procedures is the use of UV with a co-solvent such as isopropanol. The produced water sample is mixed with an equal volume of isopropanol and UV absorbance is measured directly.

3.4 UV fluorescence

Fluorescence occurs when a substance absorbs light of a particular wavelength and then immediately re-emits light at a longer wavelength. Aromatic compounds in crude oil fluoresce and the effect can be used as a means of quantifying oil content. Both solvent-free and extraction methods have been developed. In the latter, care has to be taken with the choice of solvent since some solvents can promote or quench fluorescence.

In solvent-free methods, either a surfactant is added to solubilise the oil or the sample is homogenised to create uniform droplet sizes.

Advantages	**Disadvantages**
Simple	Hydrocarbon concentrations determined by proportion from the aromatic content
Rapid and cheap	Results can be dependent on sample homogeneity
No solvent required	The lower detection limit varies with the fluorescence capacity of the hydrocarbon (from 0.5 to 3 mg l^{-1})

Application: Automated version field tested (see § 4.3).

3.5 Colorimetry

Colorimetric methods generally involve extraction of an acidified sample with a solvent sufficiently transparent in the visible region of the spectrum (*eg* trichloroethane). Oil concentrations are determined relative to a suitable calibration.

Advantages	Disadvantages
Simple	Requires a solvent
Rapid and cheap	The oil must be 'coloured'

Application: HACH OIW analyser on the market. No application known in offshore industry.

3.6 Nephelometry (or turbidity)

This technique consists in homogenising the sample to insure uniform droplet size so that free oil droplets are determined and quantified against a suitable calibrant.

Advantages	Disadvantages
Simple	Results depend on sample homogeneity
Rapid and cheap	Technique measures all substances causing turbidity (including particulates)
Lower limit of detection < 1 mg l^{-1}	Technique does not determine dissolved oil

Application: No application known in offshore industry.

3.7 Gas Chromatography

Chromatographic methods, including liquid or gas chromatography (LC or GC) and gas chromatography-mass spectrometry (GC-MS), usually give accurate results. The analyses are, however, time-consuming and expensive. Furthermore, a solvent extraction step is required to obtain a homogenous phase. GC-MS is certainly the best method for identification and quantification of specific hydrocarbons in complex mixtures such as crude oils, however the technique cannot be considered as a routine test method. The method has been recently "ring-tested" by 23 European laboratories, as part of the EU project SMT4-CT96-2090.

Advantages	Disadvantages
No hazardous halogenated solvent requested	Complex process.
Lower limit of detection <<1 mg l^{-1}	Needs qualified personnel
Correlates reasonably well with the IR methods	More time consuming than the IR method
	Specific equipment required

Application: Tests have been conducted in 5 offshore laboratories, under the auspices of OLF. Sampling preparation included solid phase extraction followed by iso-octane extraction of the Solid Phase Extraction disks. Extracts were sent ashore for GC-MS measurement in a specialised laboratory.

4. Automatic and On-line monitoring

For the purpose of this review, the methods described in this chapter under the general heading 'Automatic and On-line' refer to those techniques that can be installed at a production unit and operated in such a way that oil in water determinations are carried out without operator intervention. Many of the detection methods used for laboratory measurements can be applied to automatic and on-line situations. Broadly speaking, methods based on UV absorbance, UV fluorescence, turbidity and conductivity are favoured over IR methods given the need for sample pretreatment in the latter. Nonetheless some methods using IR detection have been developed.

Remarks:

1. Appraisal of the sensitivity of the methods covers sampling, treatment and measurement aspects (see introduction of chapter 3). Therefore, the information on the lower detection limit is not comparable to that given for manual methods.
2. Appraisals are given for a use on continuous and steady flows. Application for discontinuous or non-steady flows is not addressed.

4.1 Infra-red (IR) methods

Filter-based infrared analysers have been developed for use in the control of ballast and bilge water discharges from oil tankers.

Advantages	**Disadvantages**
• Proven performance under specific conditions	• Un-tested in offshore E&P activities
• Good reproducibility	• Measures only dispersed oil fraction
• Accuracy ±20%	• Lower detection limit between 5 to 10 mg l^{-1}
	• Heavy maintenance requirement (not suitable on unmanned facilities)

Application: No application known on offshore installation, but over 200 instruments have been installed on oil tankers (OILI Analyser)

4.2 UV absorbance or UV/visible light absorbance

The principle of these techniques is essentially the same as described in chapter 3.3.2.

6675
al + ar.
11

Advantages	**Disadvantages**
• Rapid	• Measures only dispersed oil fraction: Hydrocarbon concentration is calculated from the aromatic content
• No solvent required	• Results dependent on sample homogeneity
• Reduced maintenance for systems equipped with non-fouling, non-contact flow cells	• Specific calibration curve requested for each application
• Results comparable to extractive IR and EPA 413.1 methods, once a specific	

calibration curve have been established

Application: The SpectraScan OIW Monitor has been already field tested on several installations, in the North Sea, with satisfactory results.

4.3 UV fluorescence

The principle of these techniques is essentially the same as described in chapter 3.4. Differences of detail come from the sampling and sample preparation procedures. Samples for analysis are generally tapped from the main produced water line. The sample stream may then be homogenised with the addition of a surfactant or by a high shear pump. In some non-contact systems, flow cell maintenance is minimal.

Advantages	Disadvantages
• Rapid	• Results dependent on sample homogeneity
• No solvent required	• Measures only dispersed oil fraction: Hydrocarbon concentration is calculated from the aromatic content
• Reduced maintenance for systems equipped with non-fouling, non-contact flow cells	• The lower detection limit varies with the fluorescence capacity of the hydrocarbon (up to 3 mg l^{-1})
• Results comparable to extractive IR and EPA 413.1 methods, under specific circumstances	• Calibration requires competent personnel

Application: Several monitors are marketed.

- EOA on-line monitor has been field tested on several installations, worldwide (USA, Saudi Arabia). Its accuracy is estimated between 5 to 10 % of the reading.
- Steptech OIW 2233 has been field tested on a few installations, in the North Sea. Some operators have obtained good results, some others faced problems (appropriate location to be found, daily flushing requested). Method is accepted by some regulators in North Sea.
- Sigrist UV and Houston Photonics UV monitors currently under test, in the North Sea.
- No known application of the TD-4100 from Turner Designs.

4.4 Nephelometry

Oil in water measurements using turbidimetry are still at the development stage. Recent studies in optical scattering, in conjunction with neural network processors have demonstrated the capability to oils in suspension over a wide concentration range.

Advantages	Disadvantages
	• Still in development

Application: No application, so far.

4.5 Chromatography

On-line Gas Chromatographic (GC) techniques require two stages, extraction to concentrate the determinand and detection/quantification principally using flame ionisation detection (FID). Extraction using air stripping has been tested by a number of groups as the basis of a solvent-free analysis of oil in produced water and drainage water. in the offshore industry. Results have been compared with standard methods employed in Norway. Commercial systems are now available that give linear detection in the range 1-1000 mg l^{-1} (based on tests in the off-line mode).

Advantages	Disadvantages
• Long linear range	• Heavy equipment and maintenance
• Low detection limit	• Competent personnel required
• Results comparable to extractive IR method (± 10 %)	

Application: ABB Wista GC System under evaluation, on a Norwegian field.

An alternative approach uses supercritical fluid extraction after adsorption of oil from produced water onto a stationary phase. A number of adsorbents have been tried and there appear to be a variety of problems ranging from adsorption on to glass surfaces and bleeding from the stationary phase during elution by supercritical CO_2.

Advantages	Disadvantages
• Solvent-free method	• Not yet proven
	• Interference from extraction phase
	• Adsorption to glass apparatus

Application: No application known, so far.

4.6 Other techniques

Pulsed laser photoacoustic methods, using laser diode sources are being developed for the detection of oil contamination in water. The methods have achieved measurements on crude oil emulsions and hydrocarbon mixture solution in the range 0-900 mg l^{-1}. At the lower end of the range (0-60 mg l^{-1}), measurement accuracy of ±10 mg l^{-1} has been reported. The analytical development work has shown that dispersed and dissolved hydrocarbon components give an additive response. The first application of this sensor technology is in the continuous monitoring of hydrocarbons in return process water from oil production installations. A prototype measuring head has been constructed which uses fibre optic delivery of diode laser sources and optimised acoustic detection to allow the legislative limit for oil concentration of 40 ppm to be monitored. The relatively simple design of the sensor head allows on-line operations, with low maintenance requirements.

[illegible] Analytical Capability, Standards and Compliance

It has been established that the instrumental techniques outlined in the previous sections each has the instrumental capability to detect and quantify dispersed oil in production water at concentrations somewhat less than current regulatory requirements (*eg* 40 mg dispersed oil per litre in the OSPAR maritime area). It is far less clear what the overall uncertainty associated with the different analytical methods is and how this in turn bears on compliance regimes.

There are many sources of error in analytical methods and it is likely that the instrumental quantification (*eg* by IR or fluorescence) is the part of a procedure which is most easy to control and hence where best precision and bias performance can be achieved. On the other hand, the nature of the sample, in terms of its mixture composition and physical factors, sampling and preservation techniques are likely to play a major role in determining the precision (*ie* reproducibility) and bias (*ie* how close to the actual concentration in the sample) of the final analytical result.

Reference has already been made to the wide variation in composition of produced water streams within and between reservoirs as well as with age of field. As measurement of oil in water is neither an absolute method nor a single determinand procedure, standardisation represents a considerable challenge. Similar considerations must be taken into account in relation to physical interference with analytical procedures. For example, optical methods using scattered light will be unable to distinguish between an oil droplet and a grain of sand. If a reservoir starts to produce sand, this will introduce bias to the measurements.

Sampling and sample preservation are frequently key contributors to analytical errors. Given the conditions under which samples are often required to be taken and the distance to a laboratory and time elapsed before measurement, analytical performance is likely to be substantially degraded. This factor militates for the development and implementation of automated, on-line procedures both for operational and compliance monitoring. Furthermore, if the data are to be used as an overall indicator of industry performance in a geographical area, questions of standardisation/normalisation of analytical data need to be addressed.

Therefore, the realistic accuracy of oil in water measurement will be considerably less than that indicated by instrumental performance. This has clear implications for the scale of analytical effort required for compliance purposes. The formal and statistical requirements of a compliance regime will dictate the number and frequency of samples and it has to be pointed out that substantial increases bring with them increased risk to workers offshore and increases in cost. These factors need to be carefully considered alongside the environmental aims and benefits of a compliance regime.

6. Conclusions

1. Currently, for the purposes of OSPAR, oil-in-water is measured in accordance with a single protocol. It has been demonstrated that this protocol does not give accurate results under all circumstances. The analytical procedure requires the use of solvents that are environmentally damaging and that are being phased out. The single, agreed procedure is not suitable for application to unmanned installations, not is it amenable to automation.

2. There are a number of laboratory-based analytical methods, other than those relying on CFC solvents, that are capable of determining oil in water on a consistent basis and which could be suitable for a quality monitoring programme. However, there are no methods offering significantly enhanced performance. Moreover, there are promising on-line, automatic methods that offer improved operational control and monitoring performance.

3. While there is no single technique that is broadly applicable with uniformly good performance characteristics, flexibility is required for the operators to optimise their monitoring. However, for compliance purposes, it may be necessary to establish a reference method to ensure comparability across the spectrum of methods that may be used.

4. Where concentrations of oil in water do exceed a regulatory limit (currently 40 mg l^{-1}), subsequent reporting requirements need to be carefully defined. These conditions need to take into account the unavoidable fluctuations due to the production process, the characteristics of some unmanned installations, the quantity of oil discharged to the sea, the foreseeable lifetime of the installations in the question. The costs of retrofitting in relation to the environmental benefit that would accrue also need to be borne in mind. Such an approach might reduce the requirement for exemptions on which agreement would be contentious.

5. Finally, it must be kept in mind that the review did not address questions relating to sampling and sample preservation, although it does recognise that these factors are at least of equal importance to the analytical method. It also did not address the requirements or scale of compliance monitoring.

References

Norms and standards:

ASTM D.3921-85

OSPAR:
- Eighth annual report of the Paris Commission, 1986.
- Summary record of the tenth annual meeting of the Paris Commission, 1988.

MARPOL 73/78:
- IMO Resolution A.393(X), amended by MEPC .24(22)
- IMO Resolution A.586(14), amended by MEPC .24(22)
- IMO Resolution A.445(XI)
- IMO Resolution A.543(13)
- MEPC.4(XIII)
- MEPC.10(18)
- MEPC.15(21)
- MEPC.24(22)

USEPA 413.1; 413.2; 418.1; 1664.

Literature:

Bastow T; Durnie W H; Jefferson A; Pang J: Ultraviolet spectroscopy for the analysis of oil-in-water effluent using isopropanol as co-solvent, in Appl. Spectrosc., 51(3) 318-322 (1997).

Brost D F: The SpectraScan Oil-in-Water Monitoring System, Environmental technology Water Treatment Conference, July 22-23, 1996.

Caudle D D; Raia J; Doyle A B : Comparison of EPA methods 1664 and 413.1 for oil and grease in produced water Prepared for API, February 1998.

Coursin K: Effluent monitoring for oil in water, in Pollut. Eng. V20 N.11 100-2 (Nov. 1988) .

Frost M; Huber E E: Continuous oil in water measurement (Sigrist Photometer) SPE Offshore Europe Conference, Aberdeen, 1995 (SPE paper n°30435).

Green D A; Naimimohasses R; Barnett D M; Smith P R: An optimised nephelometer and nonlinear processor for oil-in-water monitoring, Proceedings. SPIE-Int. Soc. Opt. Eng., (Pub. 1995) 2503 35-43 (1995).

Jenssen L; Kvernheim A L; Berg B E: Supercritical fluid extraction method for oil-in-water analysis. Testing and selection of solid-phase adsorbents (Norwegian State Pollution Control Agency SFT Norway) SINTEF Rep., STF66 A96507 (1996) 15p.

Kvernheim A L; Landmark K E; Oren H M; Caspari I: Air stripping combined with FID (Flame Ionisation Detection) detection for oil-in-water analysis, in Produced Water 2, Proceedings of the Produced Water International Seminar, Trondheim, 1995, Plenum Press, 1996, pp. 415-423;

Maharaj U S; Roodalsingh R: Oil-in-water testing: The controversy and its effect on produced water monitoring in Trinidad, in Proceedings of the 4th SPE Latin American & Caribbean Petroleum Engineering Conference, Port of Spain, 1996, pp. 757-768, 1996 (SPE paper n° 36159).

Means C M; Uhrich M D: Direct, Continuous Measurement of Oil in Produced Water Supports Discharge and Reinjection Applications, in the Proceedings of the 6th Annu. Amer. Filtration Soc. Prod. Water Seminar (League City, TX, 1/18-19/96).

Niemela P O: On-line Measurement of Oil Contaminants in Water by Filter-Based Infrared Analysers, (Oulu Univ) Diss. Abstr. Int., Sect. C, 57(1) 287-C (1996).

Paus J: OLF - OIW project reports 95R.BE5 and 97Q.DN8.

Raia J C: A Review of Methods for Oil in Water Measurement, 7th Annu. Amer. Filtration Soc. Prod. Water Seminar (League City, TX, 1/16-17/97).

Sevin B; Saujon R: Enhanced Produced Water Management with Oil-in-Water Monitoring Systems, 7th Annu. Amer. Filtration Soc. Prod. Water Seminar (League City, TX, 1/16-17/97).

Teledyne Analytical Instruments: On-line monitoring of parts per million oil in water, in The Chemical Engineer N.480 25 (8/23/90).

Wilks P A: A Simplified Procedure for Oil-in-Water Analysis Based on Hexane Extraction and Infrared Absorption, 7th Annu. Amer. Filtration Soc. Prod. Water Seminar (League City, TX, 1/16-17/97).

Non-published documents:

UKOOA report on Produced Water monitoring - Operator experience (draft report, December 1998).

OLF report on Produced Water monitoring (private communication).

Appendix 1

Table of Company Experience (routine or development)

COMPANY	METHOD	MANUAL / ONLINE	ROUTINE / DEVELOPMENT
A	US - EPA 413.1 UK - PARCOM method using TCE Australia - Automated fluorescence method Spectrophotometric	Manual Manual *On-line* Manual	Routine Routine Routine
B	USA - PARCOM method API RP45 US EPA Oil and Grease 413.1 UK - Photoacoustic spectroscopy	Manual Manual	Routine Routine Routine Development
C	PARCOM Method	Manual	Routine
D	Gravimetric method IR spectrophotometric - total oil and grease IR spectrophotometric - total petroleum hydrocarbons	Manual Manual Manual	Routine Routine Routine
E	PARCOM Method	Manual	Routine
F	PARCOM Method	Manual	Routine
G	PARCOM Method	Manual	Routine
H	Steptech OIW 2233, 'No-cell' Fluorescence	*On-line*	Routine
I	PARCOM Method US EPA Oil & Grease Method	Manual	Routine

Other methods in development:

ISSWD 9377-3: Water quality-determination of hydrocarbon oil index-Part 3; Gravimetric determination for high concentrations.
ISO/CD 9377-4; Water quality-determination of hydrocarbon oil index-Part 4; Method using solvent extraction and gas chromatography

What is the E&P Forum?

The Oil Industry International Exploration and Production Forum is the worldwide association of oil and gas producers. Our members include private and state-owned oil companies, national associations and petroleum institutes.

What do we do?

Our purpose is to:

- provide information to interested bodies on the oil and gas exploration and production industry;
- represent our members' interests at global and regional regulatory bodies; and
- develop operating guidelines.

What are our aims?

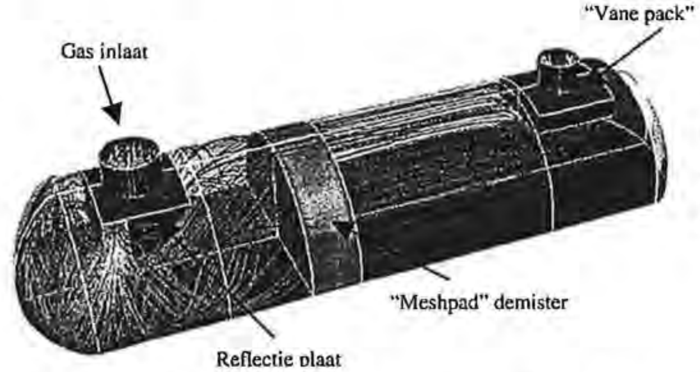
We aim to:

- increase understanding of the industry;
- work with international regulators to develop workable proposals which take full account of industry views;
- contribute to continuous improvements in industry operating standards;
- be a visible and approachable organisation to which governments and others refer on matters relating to the industry;
- maintain a large, diverse and active membership; and
- communicate issues affecting members to international bodies and the public.

Optimalisatie scheidingsvaten

Om de werking van de separatoren goed te kunnen inschatten is een uitgebreide studie uitgevoerd naar de scheidingsefficiëntie, stromingspatronen en de geometrie van de vaten. Met behulp van computer zijn de vaten gemodelleerd en getest. Uitgegaan is van het in het verleden veel toegepaste ontwerp, waarmee op andere Clyde installaties goede resultaten zijn behaald.

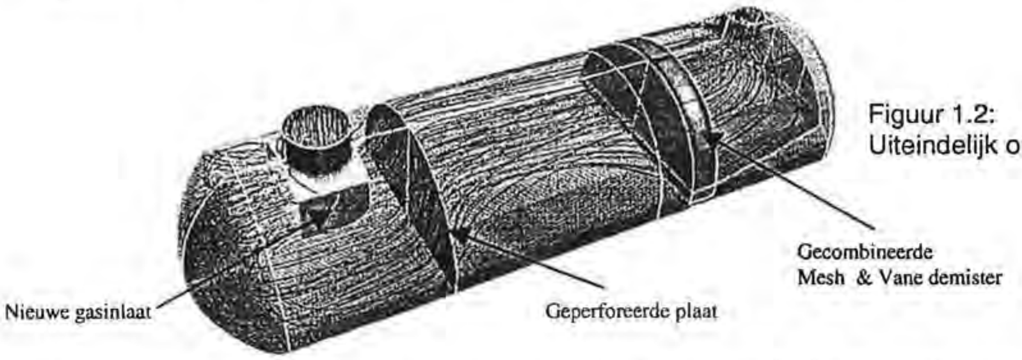
Gas/Vloeistof separator V-101



Figuur 1.1: Uitgangspositie voor gas/vloeistof separator.

In het bovenstaande ontwerp is het vat uitgerust met een afgeschuinde reflectieplaat, een "meshpad" demister en een "vane pack".
De reflectieplaat in de inlaat is om het gas op een gecontroleerde manier in het vat te laten intreden en het voorkómen van weer in de gasstroom intreden van druppels uit de vloeistoffase. Het "vane pack" is geinstalleerd om de grote druppels uit de gasstroom te verwijderen en als laatste is er nog een demister bij de uitlaat van het gas geplaatst om de fijne mistvormige deeltjes uit de gasstroom te verwijderen.

Onderwerp van de uitgevoerde studie was een verdere optimalisiatie van het gekozen scheidingssysteem. Uit de berekeingen volgt dat de druppelgrootte van de intredende druppels gemiddeld 150 μm is. Door de aanvankelijke toegepaste inlaat configuratie bleken de druppels opgedeeld te worden tot een gemiddelde van 40 μm. Het voorkómen van het opbreken van de druppels zal de efficiëntie van het vat verbeteren.



Figuur 1.2: Uiteindelijk ontwerp.

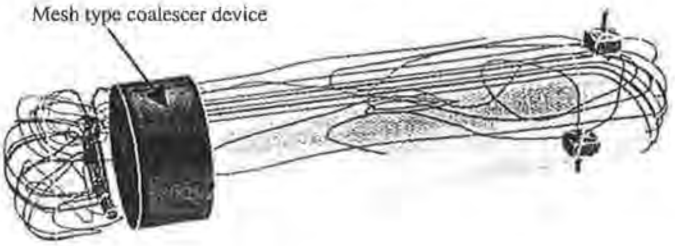
Met de toepassing van een nieuwe gasinlaat wordt voorkomen dat de druppels opbreken. Naast de vergroting van de druppelgrootte bij intreden is het tweede behaalde voordeel dat de gassnelheden in het vat gemiddeld lager worden door een betere verdeling van de intredende gasstroom. Locaal kunnen echter ook in het verbeterde ontwerp de gassnelheden zo groot worden dat er vloeistofdruppels kunnen herintreden in de gasstroom. Om een nog betere

verdeling te krijgen wordt er een geperforeerde plaat in het vat geplaatst waardoor de snelheid in het vat bijna uniform wordt.De overgang van vloeistof druppels naar de gasfase treedt in deze situatie niet meer op. Als laatste is het "vane pack" vervangen door een gecombineerde "mesh" en "vane demister". Hierdoor wordt bereikt dat de resterende druppels efficiënter verwijderd worden.
Met de bovengenoemde verbetering is de efficiëntie verhoogd van 94.8% tot 99.7%.

Door de verbeteringen aan gaszijde van de gas/vloeistof separator zullen er ook verbeteringen optreden aan de vloeistof zijde. Door het niet opbreken van de binnenkomende druppels in de separator is de grootte van oliedruppels in de vloeistoffase gemiddeld toegenomen van 40 μm tot 150 μm. Door deze verhoging van de gemiddelde druppelgrootte zal het scheidingsproces in het volgende procesvat, de vloeistof/vloeistof separator, beter en sneller verlopen.

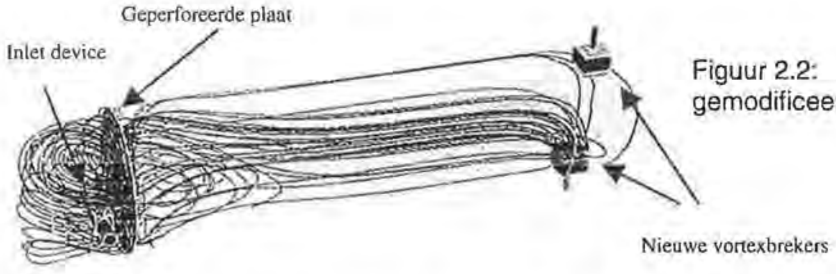
Vloeistof/Vloeistof separator V-C100

Met dezelfde methode van werken als voor de gas/vloeistof separator is ook de vloeistof/vloeistof separator geoptimaliseerd. Het basis ontwerp is gemodelleerd en met dit als uitgangspositie zijn wijzigingen in het model gemaakt.



Figuur 2.1:
Basis model vloeistof/vloeistof separator

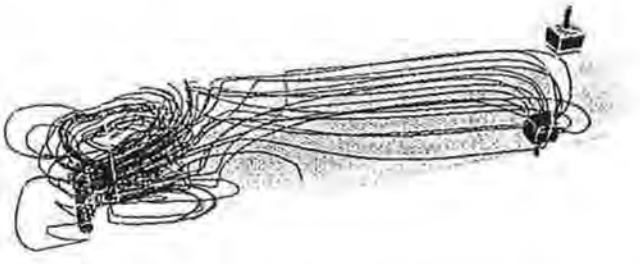
In het basisontwerp is uitgegaan van een horizontaal vat met een "mesh type coalescer device". Uit de eerste berekeningen is naar voren gekomen dat de vloeistofsnelheden in het vat zeer laag zijn. Door deze lage stroomsnelheden en het gegeven dat de gemiddelde druppelgrootte 150 μm is kan er in het vat op basis van zwaartekracht een zeer goede olie/water scheiding plaatsvinden. Uit de simulatie blijkt dat het "mesh type coalescer device" geen enkele bijdrage levert aan de scheiding.



Figuur 2.2:
gemodificeerd ontwerp

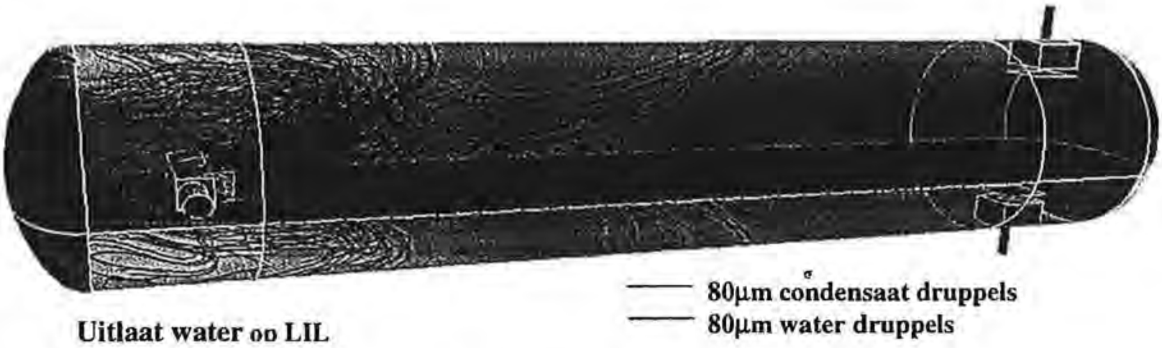
Het tweede model dat opgesteld is, bevat geen "mesh type coaleser device" meer. In plaats van dit pakket is er gekeken naar de invloed van een geperforeerde plaat op het stromingsgedrag van de condensaat en waterdruppels. Naast de geperforeerde plaat is er aan het model een inlaat

device toegevoegd om een betere verdeling van de inkomende vloeistoffen te verkrijgen en zijn er op de olie- en wateruitlaten verbeterde vortexbrekers geplaatst.
Uit de simulaties blijkt dat het inlet device geen verbetering laat zien in de efficientie van de scheiding. De verklaring hiervoor is dat de stroomsnelheden zeer laag zijn. De geperforeerde plaat in het vat heeft verrassenderwijs een negatieve invloed op het scheidingsproces. Door de drukval over de plaat worden de binnenkomende druppels verdeeld over de water en condensaat laag.
Door de modificaties van de vortexbrekers is de verstoring van de olie- en waterscheidingszone minder in het vertikale vlak. Hierdoor is de kans kleiner dat er olie druppels die nog niet volledig afgescheiden zijn van de waterlaag mee de wateruitlaat ingezogen worden.



Figuur 2.3:
2de gemodificeerde ontwerp

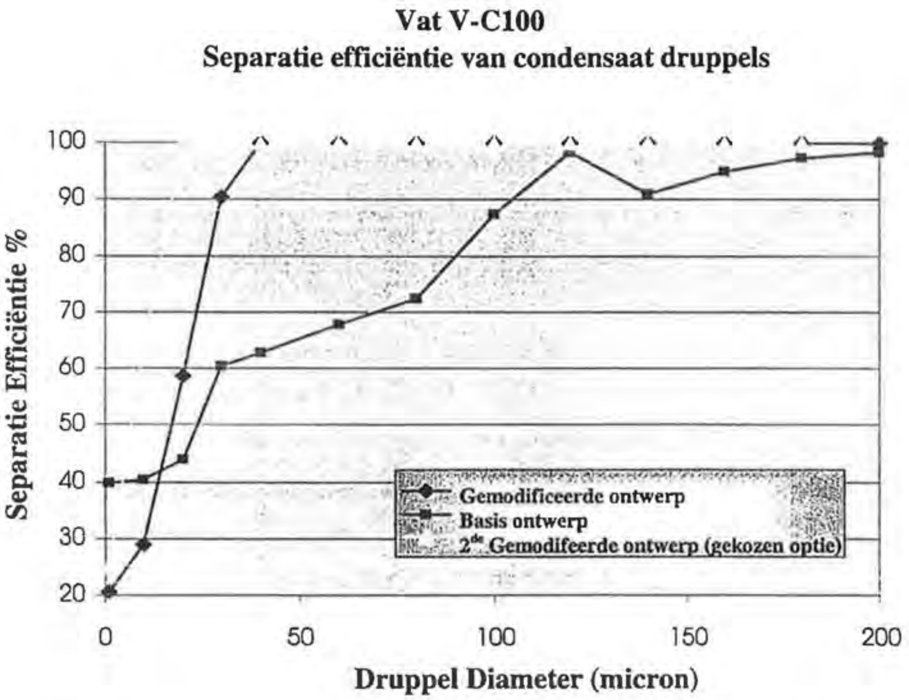
Met het resultaat van de berekeningen van het basisontwerp en de 2 gemodificeerde ontwerpen is gekozen voor het toepassen van het 2de gemodificeerde ontwerp, de condensaat/water scheider zonder het "mesh type coalescer device" en geperforeerde plaat, doch met de vernieuwde vortexbrekers op de uitlaten en een inlet device.



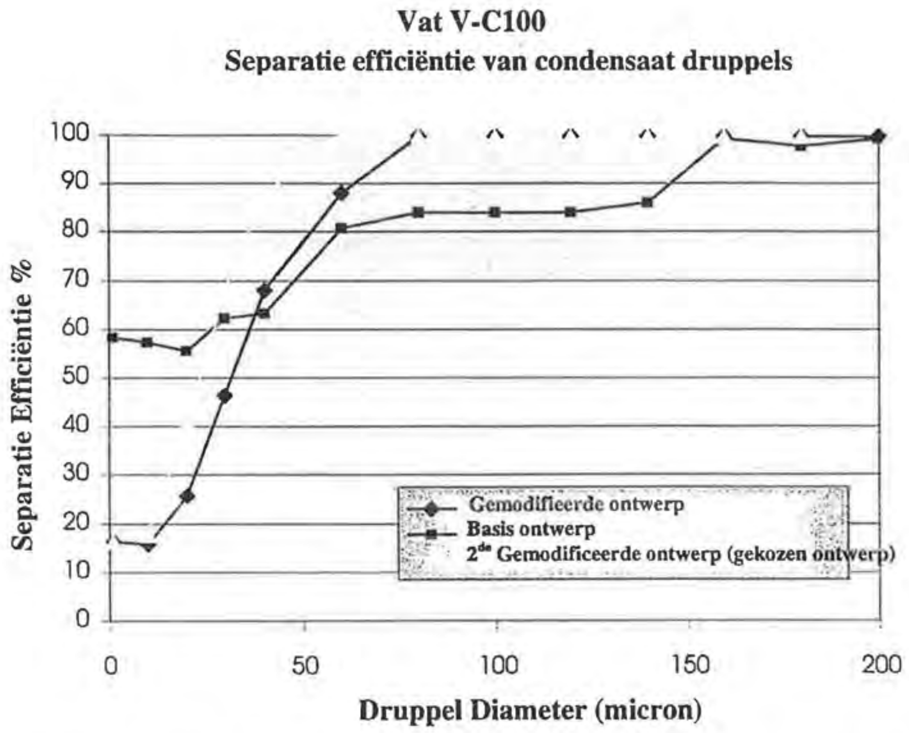
Figuur 2.4: Water/condensaat scheiding in V-C100

De voordelen van het nieuwe ontwerp zijn, naast een hogere scheidingsefficiëntie ook nog van operationele aard.
Door het ontbreken van pakking in de separator is de kans op verstopping/vervuiling van het vat geminimaliseerd. Hierdoor is de kans dat het olie/waterscheidingsproces verstoord wordt door vervuiling zeer gering.

Om een vergelijking te kunnen maken van de efficiënties zijn deze in onderstaande grafieken de efficienties van de 3 besproken gevallen in een grafiek weergegeven.



Figuur 2.5: Separatie efficiëntie van olie druppels bij hoog interface niveau (HIL) tijdens waterdump



Figuur 2.5: Separatie efficiëntie van olie druppels bij laag interface niveau (LIL) tijdens waterdump