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A REVIEW OF TECHNOLOGIES TO MEASURE THE OIL AND GREASE CONTENT OF PRODUCED WATER FROM OFFSHORE OIL AND GAS PRODUCTION OPERATIONS

REGULATORY AND SCIENTIFIC AFFAIRS
PUBLICATION NUMBER 4698
NOVEMBER 1999

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A Review of Technologies to Measure the Oil and Grease Content of Produced Water From Offshore Oil and Gas Production Operations

Regulatory and Scientific Affairs

API PUBLICATION NUMBER 4698

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NOVEMBER 1999

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ACKNOWLEDGMENTS

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT:

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ABSTRACT

The traditional monitoring methods for monitoring oil and grease, EPA Methods 413.1 and 413.2, rely on Freon 113® extraction of oil and grease. Owing to the phase-out of Freon 113® use mandated by the Montreal Protocol and 1990 Clean Air Act Amendments, these methods can no longer be considered viable and hence a new method must be sought. This study identified and evaluated practical alternative methods for routine offshore monitoring of oil and grease in produced waters. Three methods were addressed in this study: 1) an infrared absorption method in which transmitted infrared radiation is measured and correlated to the oil and grease content; 2) an infrared absorption method in which reflected infrared radiation is measured and correlated to the oil and grease content; and 3) an ultraviolet fluorescence (UV) method in which the fluorescent radiation from the sample or sample extract is measured at a specific wavelength and correlated to the oil and grease content. The two infrared absorption methods employed two different configurations of a particular analytical instrument, and the ultraviolet fluorescence method was conducted using two different analytical instruments. All instruments and methods were found capable of measuring oil and grease in produced water. They demonstrated acceptable performance in terms of linear response, analytical sensitivity, sensitivity to changes in crude oil composition, interferences, flexibility, ease of use, and correlation of results to the EPA hexane extraction method, EPA Method 1664.

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EXECUTIVE SUMMARY

The objective of this study is to identify practical alternative methods for routine monitoring of oil and grease in produced waters. The traditional monitoring methods, EPA Methods 413.1 and 413.2, rely on Freon 113® extraction of oil and grease. Owing to the phase-out of Freon 113® use mandated by the Montreal Protocol and 1990 Clean Air Act Amendments, these methods can no longer be considered viable and hence a new method must be sought.

The United States Environmental Protection Agency (EPA) is soon to promulgate a new method for oil and grease, EPA Method 1664. This method entails hexane extraction of the sample, followed by separation of the oil and grease from the hexane by evaporation, and weighing of the oil and grease remaining behind. Although this method will be required for compliance monitoring, it is generally unsuitable for routine monitoring on offshore platforms. The method is not simple to conduct, requires access to fume hoods and other equipment, and requires a quiescent and physically stable environment for weighing the samples.

Since Method 1664 is considered impractical for routine offshore monitoring of produced water oil and grease, an alternative method must be sought for routine monitoring and verification of compliance. Offshore operators charged with this important compliance verification task must have an analytical method that is reliable and relatively easy to conduct, while at the same time consistently provides analytical results that can be accurately correlated to EPA's compliance method, Method 1664.

The American Petroleum Institute's (API's) Produced Water Oil and Grease Workgroup (Workgroup) initiated this study to identify and evaluate promising practical alternatives. The study was conducted in three phases. In the first phase of this study, EPA Methods 413.1 and 1664 were compared using five sets of replicate produced water samples from production operations in Louisiana and California. The results by the two methods appeared to be weakly related; however, because of high variability between replicates, a statistically defensible relationship between the results of the two methods could not be established.

In the second phase of the study, field-proven alternative methods and instruments that might be successfully used for routine offshore produced water monitoring were identified. Viable methods and associated instruments must:

- Give a significant response to oil and grease;
- Give a linear response to oil and grease over the concentration range of interest;
- Measure oil and grease with acceptable precision;
- Provide analytical results which can be correlated to results by the official EPA method using hexane extraction, EPA Method 1664;
- Be easy to calibrate and operate on offshore platforms;
- Provide consistent performance; and
- Be rugged, durable, and require infrequent repair and adjustment.

In consideration of these criteria, three methods were recommended:

- **Infrared absorption (IR-ABS)** method in which the sample extract is deposited on a sapphire window, infrared radiation is passed through the sample, and transmitted radiation is measured and correlated to the oil and grease content.

- **Infrared absorption (IR-HATR)** method in which the sample extract is deposited on a sapphire plate or zinc sulfide surface, infrared radiation is passed through the sample, and reflected radiation is measured and correlated to the oil and grease content.

- **Ultraviolet fluorescence (UV)** method in which ultraviolet radiation from the sample or sample extract is measured and correlated to the oil and grease content.

In the third phase of the study, the performance of these methods was evaluated in the laboratory, using two UV fluorescence instruments and two modifications of a single IR instrument. All instruments and methods were found capable of measuring oil and grease in produced water. In evaluating the performance of these methods and instruments, the following observations were made:

- **Linear Response** – All instruments provided a linear response to oil and grease concentration over the desired working range (15 mg/L – 100 mg/L).

- **Analytical Sensitivity** - The UV method demonstrated higher sensitivity and lower detection limits than the IR methods.

- **Sensitivity to Changes in Crude Oil Composition** – The UV method was shown to have a greater sensitivity to changes in crude oil composition than the IR methods. Crude oils may differ significantly in fluorescence intensities from one production operation to another. If a parent crude oil is used to calibrate an UV instrument and a significant change occurs in the production feed stream, the instrument calibration could be affected.

- **Precision** – All three methods exhibited acceptable precision, well within the precision limits of the sampling and extraction steps.

- **Interferences** – n-Hexane may be used as a solvent in both IR methods. Hexane absorbs IR radiation, however, and so may become a significant analytical interference. Verification of complete solvent evaporation is essential when using n-hexane as a solvent in the IR methods. Dissolved ferric ion proved to be a significant negative interference on UV in the direct reading (no extraction) mode. Ferric ion is not extracted by hexane and therefore has no effect on the method when sample extraction is used.

- **Correlation to the Official EPA Method** – None of the methods measures oil and grease directly, but rather measures component properties that can be correlated to oil and grease as defined by EPA Method 1664. All three methods provide results that can be correlated to oil and grease as defined by Method 1664.

- **Flexibility and Ease of Use** – The UV method offered greater flexibility and ease of use. The UV method could analyze produced water without extraction or solvent evaporation steps. The evaporation step in the IR methods was required when extracting the sample with hexane, because hexane absorbs IR radiation and would thus provide false positive readings.

Beyond these considerations, vendor information, advice, support, and service should be considered carefully in selecting an appropriate method or instrument for a particular field application. The optimal instrument and method for monitoring oil and grease will ultimately depend on the above considerations, as well as the discharge point to be monitored, the capabilities of the operator(s), and the services provided by the vendors of the analytical technologies.

Section 1
INTRODUCTION

The objective of this study is to identify practical alternative methods for routine monitoring of oil and grease in produced waters. The traditional monitoring methods, EPA Methods 413.1 and 413.2, rely on Freon 113® extraction of oil and grease. Owing to the phase-out of Freon 113® use mandated by the Montreal Protocol and 1990 Clean Air Act Amendments, these methods can no longer be considered viable and hence a new method must be sought.

The United States Environmental Protection Agency (EPA) is soon to promulgate a new method for oil and grease, EPA Method 1664. This method entails hexane extraction of the sample, followed by separation of the oil and grease from the hexane by evaporation, and weighing of the oil and grease remaining behind. Although this method will be required for compliance monitoring, it is generally unsuitable for routine compliance monitoring on offshore platforms. The method is not simple to conduct, it requires access to fume hoods and other equipment, and it requires a quiescent and physically stable environment for weighing the samples.

Since Method 1664 is considered impractical, the American Petroleum Institute's (API's) Produced Water Oil and Grease Workgroup (Workgroup) initiated this study to identify and evaluate promising practical alternatives for routine offshore monitoring of produced water oil and grease. In seeking alternative analytical methods, the Workgroup held that viable methods and associated instruments must:

- Give a significant response to oil and grease;
- Give a linear response to oil and grease over the concentration range of interest;
- Measure oil and grease with acceptable precision;
- Provide analytical results which can be correlated to results by the official EPA method using hexane extraction, EPA Method 1664;
- Be easy to calibrate and operate on offshore platforms;
- Provide consistent performance; and
- Be rugged, durable, and require infrequent repair and adjustment.

In order to systematically identify candidate analytical methods and instruments, then select the promising ones meeting the above criteria, the study was subdivided into three phases:

- **Phase I** – A comparison of the performance of the Freon 113® extraction/gravimetric method, EPA Method 413.1, with the EPA's new hexane extraction/gravimetric method, EPA Method 1664, in the determination of oil and grease in produced water from Gulf of Mexico platforms;
- **Phase II** - A survey of commercially available methods and recommended protocols for preliminary performance testing on field samples, followed by selection of the most promising methods and instruments for performance testing; and
- **Phase III** – Laboratory testing and performance evaluation of selected methods and field instruments.

Crude oil samples, for preparation of simulated produced water, as well as actual produced water samples, were collected for use in Phase I and Phase III of this study. These samples were collected from five platforms, representing the range of offshore operations and crude oil characteristics. The five platforms were classified as follows:

- One light gravity crude oil platform;
- Two medium gravity crude oil platorms;
- One heavy gravity crude oil platform; and
- One gas condensate platform.

The three phases of this study are discussed in detail in the following three sections of this report, and in Appendices A and B.

Section 2
PHASE I – COMPARISON OF EPA METHODS 413.1 AND 1664

Oil and grease analysis is fundamentally an extraction process, in that the oil and grease is extracted from a water sample by the use of an appropriate solvent. The properties of the solvent determine the amount and chemical nature of the oil and grease extracted by it. Since the solvent used in the analytical procedure defines the quantity and composition of the extracted oil and grease, the switch from EPA Method 413.1, using Freon 113®, to EPA Method 1664, using hexane, is likely to alter the composition and reported concentration of oil and grease for a given produced water sample.

The objective of the Phase I study was to compare produced water oil and grease concentrations determined by EPA Method 413.1 with those determined by EPA Method 1664. A consistent and significant disparity between results by the two methods might suggest that a platform's oil and grease compliance status might be affected, or that an alteration of oil and grease discharge limits might be forthcoming. At the same time, inasmuch as routine monitoring of produced water oil and grease is currently by a method similar to Method 413.1, Method 413.2 (Freon 113® extraction coupled with infrared detection), a significant disparity between Methods 413.1 and 1664 would underscore the need to identify alternative methods for routine monitoring of produced water oil and grease.

A summary of the Phase I findings is presented here. For more complete details, the reader is referred to Appendix A, where is presented the complete Phase I study report.

In Phase I, replicate produced water samples were taken at five platforms - four in the Gulf of Mexico and one in California. In the laboratory, twelve replicates were randomly selected and six of them were analyzed by EPA 413.1 and EPA 1664. The results are shown in Table 2-1.

Table 2-1. Produced Water Oil and Grease Data from Five Offshore Platforms (mg/L)

Platform – Produced Water Source	**4**	**2**	**5**	**3**	**1**
	Medium Gravity Crude Oil	Medium Gravity Crude Oil, WSO in Produced Water	Gas Condensate, WSO in Produced Water	Heavy Gravity Crude Oil	Light Gravity Crude Oil
Hexane	6.07	20.40	26.20	12.50	48.60
	3.92	23.90	15.20	18.10	51.80
	7.47	20.20	19.50	7,72	41.30
	5.69	26.30	31.10	15.50	66.30
	6.46	24.30	29.50	12.00	71.30
	8.57	17.30	41.70	15.50	68.90
Freon	15.70	29.60	26.70	18.70	33.10
	15.10	26.30	23.40	10.00	31.20
	7.48	29.10	41.50	13.20	46.70
	20.60	35.20	47.70	12.20	78.40
	22.60	34.70	23.80	16.10	44.90
	32.80	35.40	27.30	17.90	47.90
Hexane Blank	2.24	3.57	2.62	3.57	4.22
Hexane Seawater Blank	3.00	2.34	3.61	3.88	0.84
Freon Blank	1.23	2.12	2.94	1.79	2.30
Freon Seawater Blank	3.53	2.09	3.66	2.57	5.61
Hexane Mean	6.36	22.07	27.20	13.55	58.03
Hexane Std Dev	1.59	3.32	9.33	3.63	12.41
Hexane RSD	24.96	15.06	34.29	26.77	21.39
Freon Mean	19.05	31.72	31.73	14.68	43.70
Freon Std Dev	8.54	3.88	10.27	3.43	10.13
Freon RSD	44.84	12.23	32.37	23.35	23.17

Table 2-2 provides summary statistics, including mean and confidence interval data, for the data set provided in Table 2-1.

Table 2-2. Summary Statistics for the Phase I Produced Water Data

Platform – Produced Water Source	4	2	5	3	1
	Medium Gravity Crude Oil	Medium Gravity Crude Oil, WSO in Produced Water	Gas Condensate, WSO in Produced Water	Heavy Gravity Crude Oil	Light Gravity Crude Oil
Hexane Mean	6.36	22.07	27.20	13.55	58.03
Freon Mean	19.05	31.72	31.73	14.68	43.70
Hexane/Freon Ratio	0.33	0.70	0.86	0.92	1.33
Hexane-Freon Difference	-12.68	-9.65	-4.53	-1.13	14.33
Upper 95% CI	-4.77	-5.00	8.10	3.41	28.92
Lower 95% CI	-20.59	-14.30	-17.17	-5.87	-0.25

For all data sets, EPA Method 413.1 gave higher results than the hexane method, EPA Method 1664. At the 95% confidence interval, however, no statistical difference could be established by analysis of variance, because the variance within the individual data sets was so great that the relationship could not be quantified.

Although the results do not indicate a statistically defensible difference between Method 413.1 and Method 1664, it is clear that changing the extraction solvent does alter individual analytical results. The variable results observed, both within each analytical method and for each platform tested, indicate that the composition and amount of extracted oil and grease depend on many factors, including the extraction solvent, the sample matrix, and the analytes present.

Section 3

PHASE II – SURVEY OF CANDIDATE METHODS

Given that the EPA's new hexane extraction method, Method 1664, is impractical for routine monitoring in an offshore platform environment, and that Freon 113® extraction methods are being phased out, an alternative analytical method for routine produced water oil and grease monitoring must be sought. In Phase II of this study, the objective was to identify and evaluate candidate alternative methods.

A summary of the Phase II findings is provided here. For additional details on how the survey was conducted, and on the selection process for identifying the most promising instruments, the reader is referred to Appendix B, wherein is presented the complete and detailed Phase II report.

As stated previously, the candidate methods must meet the following criteria:

- Give a significant response to oil and grease;
- Give a linear response to oil and grease over the concentration range of interest;
- Measure oil and grease with acceptable precision;
- Provide analytical results which can be correlated to results by the official EPA method using hexane extraction, EPA Method 1664;
- Be easy to calibrate and operate on offshore platforms;
- Provide consistent performance; and
- Be rugged, durable, and require infrequent repair and adjustment.

The survey of candidate methods was limited to proven methods - that is, methods and instruments with demonstrated performance in an industrial monitoring application. New and undemonstrated emerging technologies were not considered.

To classify candidate methods and instruments, the first task in Phase II was to identify measurement technologies meeting the above criteria. A "measurement technology" is a means for quantifying a particular oil and grease property that can be correlated to concentration. The selected measurement technologies were:

- Infrared absorption;
- Ultraviolet absorption; and
- Ultraviolet fluorescence.

Next, commercially available instruments and methods making use of these measurement technologies were identified. For most measurement technologies, there are several suppliers providing instruments and methods making use of that technology. In the Gulf of Mexico, the measurement technology used over the last 20-25 years has been infrared absorption. Although one instrument has a dominant share of the market, more than one manufacturer supplies proven instruments making use of infrared absorption technology.

Table 3-1 presents a comparison of the features and performance specifications of five representative instruments employing these measurement technologies:

Table 3-1. Analytical Instruments for Oil and Grease Measurement

Instrument	Instrument 1	Instrument 2	Instrument 3	Instrument 4	Instrument 5
Technology	IR Absorption	UV Absorption	UV Absorption	UV Fluorescence	UV Fluorescence
Target Material Measured	Aliphatic C-H bonds	Aromatic compounds	Aromatic compounds	Aromatic compounds	Aromatic compounds
Method	Hexane extraction; Evaporation on plate or card; IR unit	Extraction or surfactant addition; fiber optic UV probe	Extraction or surfactant addition; UV cell	Extraction or surfactant addition; UV cell	Extraction or surfactant addition; UV cell
Calibration: Instrument Correlation	Produced oil or standard oil; 1664 or other	Produced oil or standard oil; 1664 or other	Produced oil or standard oil; 1664 or other	Proprietary compound; Produced oil or standard oil; 1664 or other	Produced oil or standard oil; 1664 or other
Nominal Detection Limit	10 mg/L*	1 mg/L	1 mg/L	1 mg/L	1 mg/L
Footprint **Weight**	6x6x4 in. < 5 lb.	4x13x15 in. 5 lb.	16.5x11x6 in. 20 lb.	9x11x8 in. 13 lb.	15x10.5x5.5 5 lb.
Tech Support	good tech o.k. field	? tech good field	good tech. ? field	Good tech. o.k. field	? tech. ? field

* Dependent on the extraction ratio used and the mass loading of the extract to the sample volume. May be as low as 5 mg/L.

Based on available literature data on method performance, instrument characteristics and limitations, compatibility with produced water analysis, and operability and repair information, the most promising technologies, instruments and methods were selected for performance testing in Phase III of the study. Selected for further study were three analytical methods making use of IR absorption and UV fluorescence technologies:

- **Infrared absorption (IR-ABS)** method in which the sample extract is deposited on a sapphire window, infrared radiation is passed through the sample, and transmitted radiation is measured and correlated to the oil and grease content.

- **Infrared absorption (IR-HATR)** method in which the sample extract is deposited on a sapphire plate or zinc sulfide surface, infrared radiation is passed through the sample, and reflected radiation is measured and correlated to the oil and grease content.

- **Ultraviolet fluorescence (UV)** method in which ultraviolet radiation from the sample or sample extract is measured and correlated to the oil and grease content.

Performance testing of the two infrared absorption methods was carried out using two different configurations of a particular analytical instrument. Performance testing of the UV method was carried out using two different ultraviolet fluorescence instruments.

The technology review also identified several properties of produced water that should be considered in an evaluation of these oil and grease methods:

- The water soluble organic portion of the oil and grease in produced water;
- The level of fluorescence (background and parameter) in the individual produced waters; and
- The iron content of produced water.

The effects of these properties on oil and grease measurements by the three analytical methods were evaluated during Phase III performance testing. In the next section of this report, performance testing of the analytical methods and instruments is discussed.

Section 4
PHASE III – LABORATORY PERFORMANCE TESTING

LABORATORY PERFORMANCE TESTING

For this study, it is assumed that oil and grease is defined by EPA Method 1664 - that is, oil and grease is defined as the material that is extracted from a water sample by hexane at pH 2, and remains behind after evaporating the hexane. EPA 1664 provides a direct measurement of oil and grease, in that the extracted oil and grease is weighed directly. Ultraviolet and infrared field methods, on the other hand, measure oil and grease only indirectly, through an instrument response that measures two properties of oil and grease – specifically, emission of ultraviolet fluorescent radiation and absorption of infrared radiation, respectively. Not every molecule of oil and grease as determined by EPA 1664 will fluoresce in the ultraviolet region, and not every chemical bond within every molecule will absorb infrared radiation to the same degree. Consequently, to provide accurate and useful measurements of oil and grease, these instrument responses must be correlated to the oil and grease concentration as measured by EPA 1664, and this correlation must hold over the course of repeated measurements. The principal objective of laboratory performance testing was to establish these correlations and to test their validity over a range of conditions.

Laboratory performance testing of ultraviolet and infrared methods and instruments was conducted on both simulated and actual produced water samples. Recovery data from the analysis of simulated produced waters of known composition provided information about the effects of instrument calibration. Both instrument precision and the sensitivities of the various measurement technologies to the calibration material were determined.

Using crude oil from a variety of sources, synthetic samples were prepared and analyzed by the instruments and methods selected in Phase II. The instruments were calibrated several ways, and the results were used to examine the effect of the sample matrix (produced water composition) on instrument response.

To examine the effect of water-soluble organics (WSOs) on the measurement of oil and grease by the selected instruments and methods, an array of synthetic samples containing a combination of dispersed crude oil and WSOs, including aliphatic and aromatic carboxylic acids, was prepared and analyzed. This array is shown in Table 5-1 of Appendix B.

In addition, actual produced water samples were analyzed using the selected instruments calibrated with several different calibration materials. These analyses showed the effect of calibration material on instrument response, and also were used to test the correlation between instrument response and EPA 1664 concentration.

INSTRUMENT CALIBRATION

To properly calibrate an instrument for oil and grease measurement, the following relationships must be established:

1) A linear relationship between the instrument response and the known concentration of the calibration material must be established, and this relationship must not change with time or repeated measurement.

2) A linear relationship between the known concentration of the calibration material and the true oil and grease concentration as measured by EPA 1664 must be established by correlating instrument response with oil and grease concentration determined by EPA 1664.

Instruments can be calibrated with a number of different materials, depending on the measurement technology used. For example, instruments using infrared absorption could potentially be calibrated with:

- Crude oil (either from the site for which produced water is being monitored or some other site);
- A standard oil such as 3-in-1 machine oil;
- A pure organic compound such as octane or octanoic acid; or
- The oil and grease concentrations measured by EPA 1664.

For instruments using UV fluorescence, potential calibration materials may include:

- Crude oil (either from the site for which produced water is being monitored or some other site);
- A pure organic compound that fluoresces; or
- The oil and grease concentration measured by EPA Method 1664.

An acceptable calibration material is dependent on the user's requirements for instrument sensitivity and working range, within specified limits of precision and accuracy. Often the instrument manufacturers will recommend calibration procedures, and many instruments are delivered "factory calibrated" and require no further calibration. Manufacturer's calibration procedures (and recommended calibration procedures) are usually performed under well-defined and perhaps unnatural working conditions. The factors for testing instrument response to calibration are:

- Instrument configuration;
- Sample matrix;
- Sample preparation (direct analysis or extraction); and
- Calibration material.

UV Fluorescence Instruments

Three calibration studies were conducted to determine the response of the selected UV fluorescence instruments to oil and grease in produced water. In the first calibration study, the instrument calibration and sample analysis proceeded as follows:

- A crude oil, designated Crude #2, was spiked into a synthetic seawater matrix to make up the calibration solutions.
- The calibration solutions were adjusted to pH 2, then extracted with hexane. The two UV instruments were calibrated on these extracts.
- Crude #2 and a second crude oil, Crude #1, were added to a synthetic seawater matrix in varying amounts, to make up a sequence of simulated produced water samples with defined concentrations of 15-60 mg/L.
- The calibrated instruments were used to analyze for oil and grease in these simulated produced water samples directly, without extraction.

The results are shown in Table 4-1.

Table 4-1 indicates the response of the UV instruments to oil and grease concentration, and Figure 4-1 shows this response to be linear. The linear response indicates that Crude #2 can be used to calibrate the UV instruments within the concentration range of interest (15 – 100 mg/L).

Table 4-1. UV Analysis of Simulated Produced Water Samples Using Instruments Calibrated with Crude #2 Simulated Produced Water

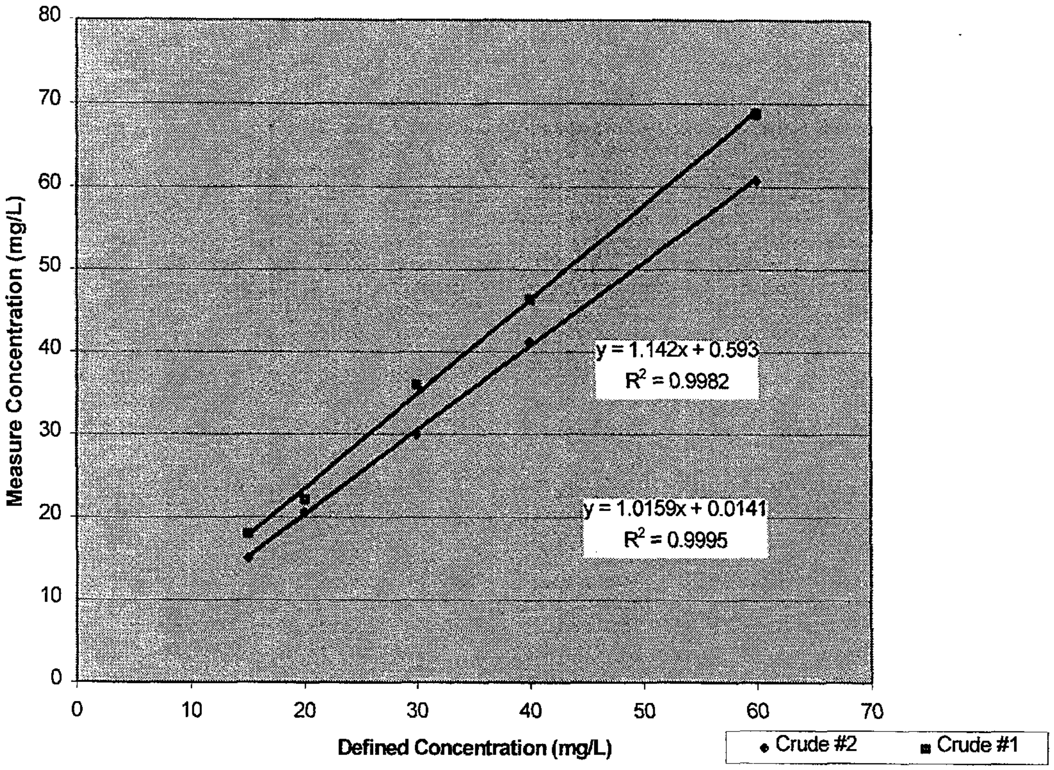
Defined	Measured Oil and Grease Concentration in Crude #2 Simulated Produced Water (mg/L)		Measured Oil and Grease Concentration in Crude #1 Simulated Produced Water (mg/L)	
Concentration (mg/L)	Instrument A	Instrument B	Instrument A	Instrument B
15	15.1	15.4	18.3	18.0
20	20.6	20.2	24.3	22.2
30	30.0	30.3	42.3	36.0
40	41.2	40.6	50.4	46.4
60	60.8	61.2	75.5	68.8

Since different concentrations were obtained for the two different types of simulated produced water samples, resulting in two different calibration lines, it is apparent that Crude #1 and Crude #2 have different fluorescence intensities. If the substance being measured is from the same source as the crude oil used to calibrate the instrument, the instrument will return the same concentrations used to calibrate the instruments. In this case, the instruments were calibrated using Crude #2, so measurements on synthetic waters made from Crude #2 give back the same concentrations as were used to make the calibration. Since Crude #1 has more fluorescence per unit of oil than Crude #2, a higher measured concentration will result.

The actual concentration is correlated to analytical results by EPA Method 1664; so any concentration difference due to calibration material is unimportant, provided a reliable correlation with Method 1664 results has been established. Therefore, despite appearances, neither of these data sets is more “correct” than the other, and either crude oil could be used to calibrate the UV instruments for measuring produced water on either platform. It is important to recognize, however, that the calibration curves are not interchangeable. The data show that the oil and grease matrix can strongly affect instrument calibration. If the composition of the oil and grease or the produced water changes on a given platform, the instrument may have to be recalibrated.

The two UV instruments give very similar responses. They are made by different manufacturers and are physically dissimilar but use the same measurement technology.

Figure 4-1.
Measured vs. Defined Concentration:
UV Instrument B, Calibrated with Crude #2 Simulated Produced Water, Measuring Oil and Grease in Crude #1 and Crude #2 Simulated Produced Water



In the second calibration study, the UV instruments were calibrated using simulated produced water samples containing Crude #1 and Crude #2. Replicate produced water samples were collected from the platforms that were the source of Crude #1 and Crude #2. Three replicate sets of samples from platform SPW, and two sets of replicate samples from platform CPW, were directly analyzed (without extraction) by each of the calibrated instruments, and by EPA 1664.

The results are shown in Table 4-2.

Table 4-2. Oil and Grease in Produced Water Samples from Platforms SPW and CPW

Sample	EPA 1664 Concentration (mg/L)	Measured Oil and Grease Concentration, Calibration with Crude #1 Simulated Produced Water (mg/L)		Measured Oil and Grease Concentration, Calibration with Crude #2 Simulated Produced Water (mg/L)	
		Instrument A	Instrument B	Instrument A	Instrument B
SPW1	18.0	28.1	27.0	35.2	32.3
SPW2	20.3	24.5	24.1	38.5	33.8
SPW3	22.2	25.0	24.7	39.4	34.0
CPW1	14.5	17.0	18.0	17.4	16.8
CPW2	15.6	18.6	18.1	18.0	18.8

The data provided in Tables 4-1 and 4-2, taken together, show that the UV instruments can be calibrated to give a linear response, and that this linear response can be correlated with oil and grease concentration as determined by EPA 1664. Again, however, Table 4-2 shows that the instrument response is dependent on the calibration material and on the composition of the oil and grease being measured.

The data in Table 4-2 also provide information on the precision and repeatability of the UV instruments and EPA 1664. Table 4-3 provides averages and standard deviations for each method:

Table 4-3. Averages and Standard Deviations for Replicate Samples

	EPA 1664 Concentration (mg/L)	Measured Oil and Grease Concentration, Calibration with Crude #1 Simulated Produced Water (mg/L)		Measured Oil and Grease Concentration, Calibration with Crude #2 Simulated Produced Water (mg/L)	
		Instrument A	Instrument B	Instrument A	Instrument B
SPW Average	20.2	25.9	25.3	37.8	33.4
SPW Std. Dev.	2.10	1.95	1.53	2.10	.93
CPW Average	15.1	17.8	18.1	17.7	17.8
CPW Std. Dev.	.78	1.13	.07	.42	1.41

The third calibration study was designed to verify instrument calibration over an extended working range. Instrument A was calibrated using simulated oil and grease extracts, prepared by dissolving a crude oil, designated Crude #4, in hexane at five different concentrations. Once calibrated, the instrument was used to analyze oil and grease in simulated extracts, prepared by dissolving two crude oils, Crude #3 and Crude #4, in hexane at concentrations varying from 100-800 mg/L.

The results are shown in Table 4-4.

Table 4-4. Oil and Grease Concentrations Determined by UV Instrument A Calibrated with Crude #4 Simulated Extracts

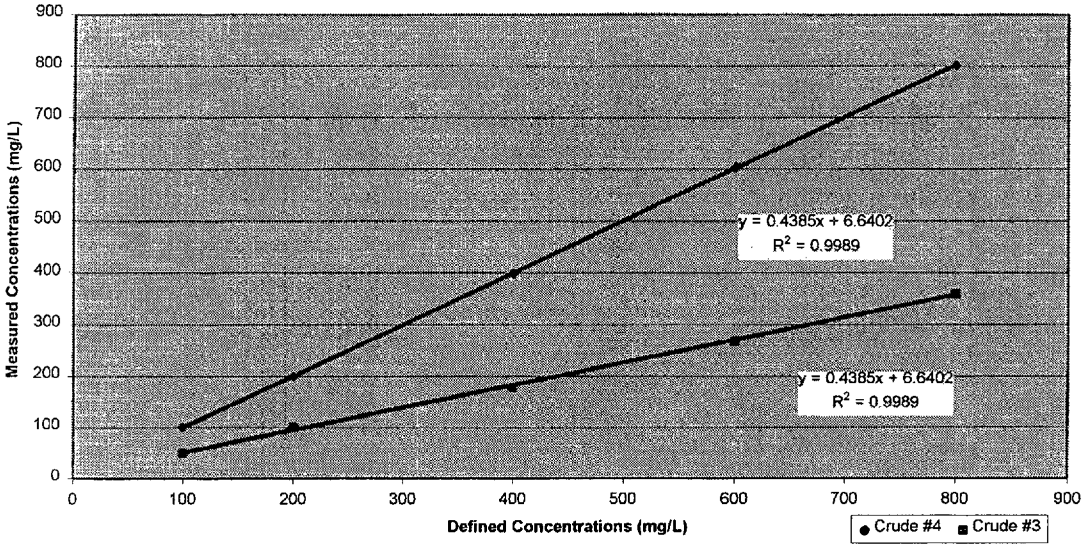
Defined Concentration (mg/L)	Measured Oil and Grease Concentration in Crude #4 Simulated Extract (mg/L)	Measured Oil and Grease Concentration in Crude #3 Simulated Extract (mg/L)
100	100	49
200	199	100
400	399	177
600	602	268
800	801	360

Figure 4-2 provides a plot of these data, and demonstrates the linear relationship between the defined concentration and measured instrument response for both sets of simulated extracts. The linear plots verify that the instrument can be calibrated over an extended concentration range of 0-800 mg/L for these oils.

Although the calibration relationship is linear, simulated Crude #3 extract concentrations measured by Instrument A were a little less than one-half of the defined concentrations. Oil and grease from Crude #3 fluoresces less than oil and grease from Crude #4. This again demonstrates the sensitivity of the instrument to the oil and grease composition.

Another method of calibrating a UV fluorescence instrument is to set its operating range with a standard fluorescent dye, then record the response of the instrument in raw

Figure 4-2.
UV Instrument A Calibrated with Crude #4 Simulated Extracts: Measured Oil and Grease Concentrations in Crude #3 and #4 Simulated Extracts



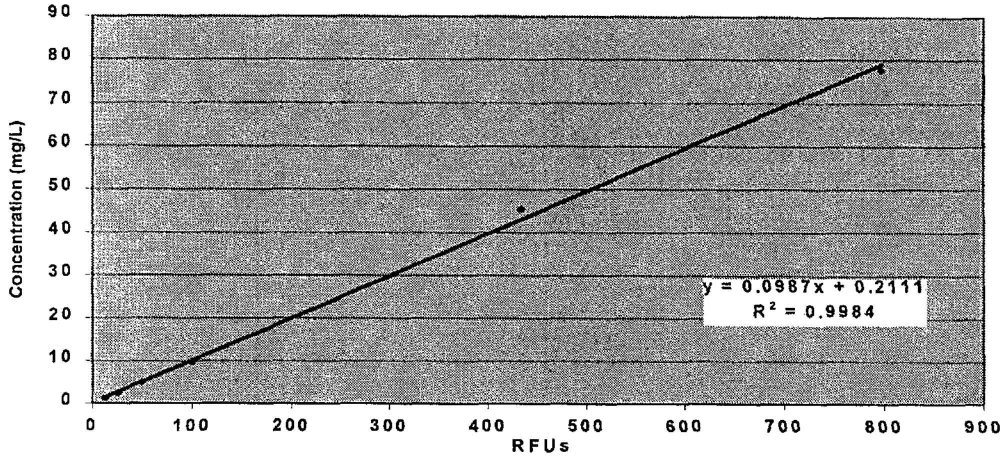
fluorescent units (RFUs) for a series of known oil and grease concentrations. A correlation can then be developed between RFUs and the oil and grease concentrations. Table 4-5 provides data from the calibration of Instrument A with a stock dye solution supplied by the instrument manufacturer. The RFU readings on instrument A were recorded for pre-defined volumetric dye concentrations, and were used to establish a calibration plot. Then the instrument response in RFUs was determined for defined concentrations of Crude #1 in hexane. Using a standard curve based on the instrument response to the dye, equivalent concentrations of Crude #1 were recorded.

Table 4-5. Correlation of Fluorescence Units and Crude #1 Concentrations With Dye Concentrations Used to Calibrate Instrument A

Dye Concentration (mL/100mL)	Fluorescence Unit (RFU) Readings	Crude #1 Concentrations (mg/L)
0.025	12.8	1.2
0.050	25.5	2.4
0.100	49.8	5.0
0.200	100	9.6
1.000	434	45.5
2.000	798	77.7

Figure 4-3 shows that fluorescence units correlate strongly with the Crude #1 concentrations, indicating that the fluorescence instruments can be calibrated with dye, and that results can be correlated with oil and grease concentrations.

Figure 4-3.
Crude #1 Concentration vs. RFUs



After it was established that Instrument A could be calibrated with the dye supplied by the manufacturer, a series of analyses were done on several dilutions of a natural produced water. These analyses included:

- EPA Method 1664;
- Hexane extraction and analysis by Instrument A calibrated with dye;
- Direct measurement of the raw sample using Instrument A;
- Direct measurement of the sample acidified to pH 2 using Instrument A; and
- Direct reading of the sample acidified to pH 2 with added surfactant using Instrument A.

The results of these analyses are shown in Table 4-6.

The first column of Table 4-6 simply provides the reciprocal of the dilution factor. The data for each analysis were correlated against both the dilution factor and the relative concentration. Further, the results were correlated against the EPA Method 1664 results. The goodness of fit (R^2) for each correlation is shown in Table 4-7. Since a goodness-of-fit (R^2) test above 0.90 shows a high degree of correlation, the data show that 1)

Instrument A can be calibrated with the dye supplied by the manufacturer, and 2) the results can be correlated with crude oil concentration and with EPA Method 1664 results.

Table 4-6. Analyses of a Natural Produced Water Using Instrument A With a Dye Calibration and Various Analytical Factors

	EPA 1664	Instrument A Results			
Sample Dilution	(mg/L)	Extracted Sample (FU)	As Received Sample (FU)	pH Adjusted (FU)	PH Adjusted & Added Surfactant (FU)
SPWA-1	10.8	102	151	156	156
1.3 x	9.0	74	122	140	145
2.0 x	6.1	50	95	99	104
4.0 x	3.5	25	52	65	69

Table 4-7. Goodness of Fit for Fluorescence Analyses of a Natural Water

	EPA Method 1664 Sample	Extracted Sample	As Received Sample	pH Adjusted Sample	pH Adjusted & Added Surfactant Sample
Dilution Factor	-.94501	-.91923	-.96155	-.95274	-.9602
Relative Conc.	.997938	.998158	.993816	.990914	.983098
EPA Method 1664	1.0	.992305	.993497	.997482	.992822

Defined concentrations of crude oil in water and natural produced water containing oil and grease as defined by EPA Method 1664 have been shown to correlate with Instrument A readings when the instrument is calibrated with a fluorescent dye.

An examination of the data indicates that adjusting the pH and adding surfactant both increase the instrument response slightly on these lab analyses. Since all of the results correlate very well, this means that the sensitivity is increasing, but not the accuracy. Consistency of procedure is important, and the analyses should be performed in a standard manner every time. Analyses done in the field may be more strongly affected by these variables and this should be tested when field evaluations are done.

Table 4-8 provides a comparison of fluorescence units measured for the hexane extract, the extracted water, and through direct sample analysis:

Table 4-8. Comparison of Fluorescence Analyses on a Natural Water Sample Analyzed Directly and by Extraction

	Fluorescence Units			
Sample I.D.	**Hexane Extract**	**Extracted Water**	**Sum of Extract & Water**	**Direct Analyses**
SPWA-1	102	75	177	151
1.3x	74	101	175	122
2x	50	92	142	95
4x	25	48	73	52

It should not be expected that all the fluorescing species are extracted by hexane with the same efficiency, and so it is surprising that the total fluorescence in the extract and the extracted water is larger than the fluorescence measured by direct analysis of the whole sample. A possible explanation is that the natural water contained iron, and iron is expected to suppress fluorescence. This phenomenon needs further study in field testing.

Another set of analyses was done to show the effect of matrix on the calibration of a UV fluorescence instrument. In this set of determinations, defined crude oil concentrations in hexane for Crude #1 and Crude #2 were prepared and analyzed using EPA Method 1664, then Instrument A was calibrated using the dye furnished by the manufacturer and the fluorescence readings were made on each of the prepared samples. The results are shown in Table 4-9.

Except for the 15 mg/L defined concentration of Crude #2, the ratios of EPA Method 1664 results to the defined concentrations are in the range of 0.55 to 0.80. This finding indicates that the percentage of crude oil measured as oil and grease is similar for both crudes. The measured concentration of 18 mg/L for the Crude #2 defined concentration of 15 mg/L is in error, since the amount found cannot be more than the amount added.

Table 4-9. Comparison of EPA Method 1664 Results to UV Fluorescence Results on Defined Concentrations of Crude Oil in Hexane

	Crude #1		Crude #2	
Defined Concentration (mg/L)	**Fluorescence Units**	**EPA 1664 Results (mg/L)**	**Fluorescence Units**	**EPA 1664 Results (mg/L)**
15	140	10	54	18
30	266	23	108	24
60	501	36	210	35
80	665	44	294	53

Another important observation is that Crude #1 has much more fluorescence per unit mass than Crude #2. EPA Method 1664 results can be correlated with fluorescence units for both crude oils, but the correlation is different for each oil. Therefore, the produced water matrix makes a significant difference when correlating an instrument that measures fluorescence. Based on these results, it is obvious that the matrix strongly affects calibration and must be accounted for in using fluorescence instruments. Field testing is needed to determine the impact of this feature in actual applications.

Infrared (IR) Absorption Instrument

Performance evaluations were conducted on two infrared absorption methods, employing modifications of a single instrument:

- **Infrared absorption (IR-ABS)** method in which the sample extract is deposited on a sapphire window, infrared radiation is passed through the sample, and transmitted radiation is measured and correlated to the oil and grease content.

- **Infrared absorption (IR-HATR)** method in which the sample extract is deposited on a sapphire plate or zinc sulfide surface, infrared radiation is passed through the sample, and reflected radiation is measured and correlated to the oil and grease content. In IR-ABS, the sapphire window is placed in an IR energy beam and the oil absorbs the IR energy. In IR-HATR, an IR energy beam is reflected along the horizontal surface, with the source on one end and the detector on the other. IR-HATR provides a greater path length, increasing instrument sensitivity.

Since water absorbs infrared radiation, and this absorption would interfere with oil and grease analysis, all analyses based on infrared adsorption must be done on sample extracts. The infrared absorption methods chosen for performance evaluation use hexane as an extraction solvent. As with the oxygen-hydrogen bonds of the water molecule, the carbon-hydrogen bonds of the hexane molecule also absorb infrared radiation and thus interfere with the analysis. Consequently, the hexane solvent must be evaporated from the extracted oil and grease prior to analysis.

The IR instrument can be calibrated with any material containing carbon-hydrogen (C-H) bonds. A common calibrant is the crude oil produced at the source of the produced water discharge, however any hydrocarbon material will suffice (see Appendix A). In this study crude oils were used.

Using the instrument in the ABS mode, a calibration was made using Crude #1 solutions in hexane. Then simulated extracts of Crude #1 and Crude #2 in hexane were prepared and analyzed three times each. The results are shown in Table 4-10:

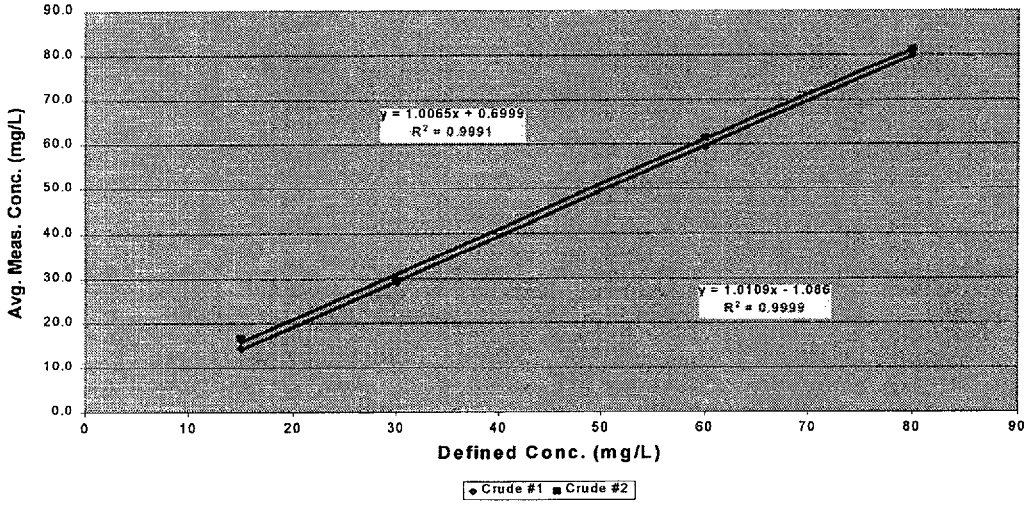
Table 4-10. Oil and Grease Concentrations Determined by IR-ABS, Calibrated with Crude #1 in Hexane

Defined Conc. (mg/L)	Oil and Grease Concentration from Simulated Extracts of Crude #1 in Hexane* (mg/L)			Oil and Grease Concentration from Simulated Extracts of Crude #2 in Hexane* (mg/L)		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
15	13	16	14	15	17	18
30	30	28	29	27	30	32
60	60	60	58	63	61	60
80	80	80	80	80	82	82
R^2	0.999726	0.999078	0.999647	0.997313	0.999499	0.999306

*Original sample concentration, assuming sample:solvent volume ratio of 10:1.

Since these simulated samples represent extractions at an extract volume of 10% of the sample volume, the measured concentrations in hexane were ten times the nominal amount shown in the table. Figure 4-4 plots the average measured concentration versus the defined concentration for both data sets. Although these measured values were obtained using a calibration with Crude #1, measured values for both oils are very close to the defined values. There may be minor differences in the results for each oil, but they are well within the limits of the method. The very high R^2 values indicate that there is an excellent correlation between the defined values and measured values for both oils. Therefore, at least for Crude #1 and Crude #2, oil and grease composition does not seem to be a strong factor in the calibration of this instrument.

Figure 4-4.
Average Measured Oil and Grease Concentration
from Simulated Extracts,
Determined by IR-ABS, vs. Defined Concentration



Actual produced water samples from the platforms that produce Crude #1 and Crude #2 were also analyzed by IR-HATR and compared to UV readings from UV Instrument A. Calibration of the IR-HATR instrument was by simulated extracts of Crude #1 and Crude #2 in hexane. The actual produced water samples were extracted with hexane and were analyzed with both instruments, using both calibrations. The results are shown in Table 4-11.

These data show that calibration of IR-HATR with either oil gives similar results. The calibration material makes a significant difference, however, in the results obtained by UV Instrument A. Both methods can give accurate results, but calibration of the UV instrument must take into account the site-specific oil and grease composition, and must be recalibrated at each site, or whenever the oil and grease composition changes significantly.

Table 4-11. Comparison of UV Instrument A vs. IR-HATR in the Analyses of Oil and Grease in Actual Produced Water Samples

Sample ID	EPA 1664 Conc. (mg/L)	Calibration with Crude #1 Simulated Extracts		Calibration with Crude #2 Simulated Extracts	
		HATR-IR (mg/L)	UV (mg/L)	HATR-IR (mg/L)	UV (mg/L)
SPW-1	18	29	28.0	27	35.2
SPW-2	20	24	24.5	22	38.5
SPW-3	22	28	25.0	24	39.4
CPW-1	14	18	17.4	21	17.0
CPW-2	16	19	18.0	20	18.6

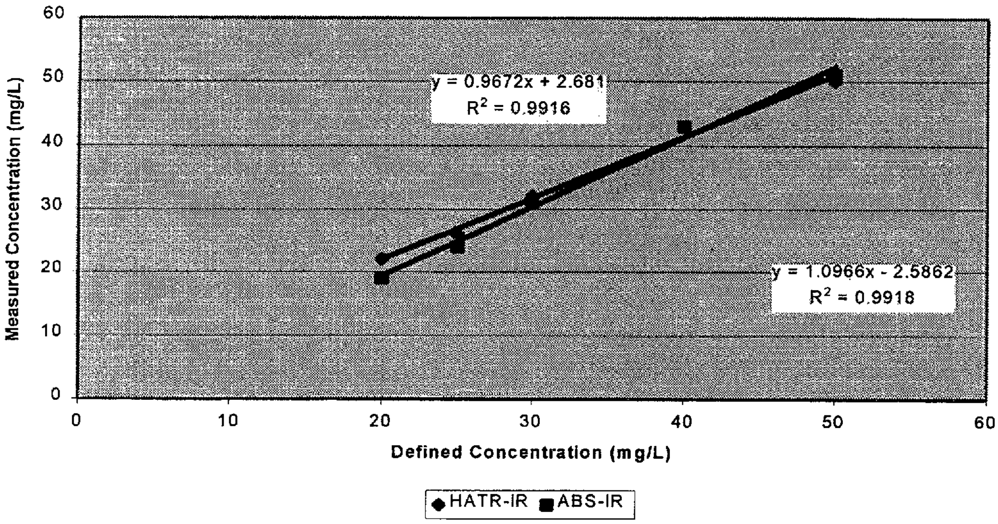
A comparison was made of IR-HATR and the IR-ABS methods in analyzing oil and grease in simulated produced water samples containing Crude #2, at defined concentrations of 20-50 mg/L. Oil and grease was extracted with hexane before analysis. For both methods, the insturment was calibrated using simulated Crude #1 extracts. The results are shown in Table 4-12.

Table 4-12. Comparison of IR-HATR and IR-ABS Methods in Analyzing Oil and Grease in Simulated Produced Water Samples Containing Crude #2

Defined Conc. (mg/L)	Measured Oil and Grease Concentration (mg/L)	
	IR-HATR	IR-ABS
20	22	19
25	26	24
30	32	31
40	43	43
50	50	51

These results show that both methods produce linear results over the range tested, and the two methods give comparable results. Figure 4-5 shows that the relationships between the defined concentration and the measured concentrations are linear. The slope of each curve is close to one and the intercepts are within measurement error of zero. The R^2 values indicate that the correlation is near perfect. These results show that both instruments can be calibrated with crude oil and give similar results to each other.

Figure 4-5.
Comparison of IR-HATR and IR-ABS Oil and Grease Concentrations Measured in Simulated Produced Water Samples Containing Crude #2



WORKING RANGE

It was assumed for the purpose of this study that a normal working range expected of a field instrument would fall within 15-100 mg/L oil and grease in produced water. The above discussion, and associated data tables and figures, on instrument calibration indicate that both the UV fluorescence instruments and infrared absorption instruments considered in this study are capable of measuring over this concentration range.

PRECISION

UV Fluorescence (Technology)

Instrument A was evaluated for instrument precision by calibrating it using Crude #3 in hexane at three concentrations - 15, 30 and 60 mg/L - then analyzing simulated extracts of Crude #3 in hexane at two produced water concentration levels, 15 mg/L and 60 mg/L. After instrument calibration, the test solutions were alternately read on the instrument ten times each. A second check was made using simulated produced water samples, prepared by spiking synthetic seawater solutions with Crude #3 to a concentration of 10 mg/L. One sample was read directly (without extraction) ten times, and one was extracted into hexane and the extract read ten times. The resulting data are shown in Table 4-13.

Table 4-13. **Precision Study of UV Instrument A**

	Simulated Extracts		Simulated Produced Waters	
	15 mg/L	**60 mg/L**	**Direct Reading**	**Extract Reading**
	15.17	59.98	9.8	10.5
	15.20	60.03	10.2	10.2
	15.21	59.98	10.1	9.9
	15.16	59.97	10.3	9.8
	15.12	59.95	10.2	10.0
	15.15	59.82	9.9	10.3
	15.14	59.66	10.1	9.8
	15.15	59.65	10.1	10.0
	15.13	59.70	10.0	10.1
	15.14	59.69	10.1	10.0
Std. Dev.	0.029078	0.154636	0.147573	0.222111
Rel. Std. Dev.	0.19%	0.26%	1.46%	2.21%
Avg. Dev.	0.0224	0.139	0.108	0.172
Mean	15.157	59.843	10.08	10.06
Median	15.17	59.885	10.1	10.0

The data show the UV fluorescence instrument to be very precise. The precision, as measured by relative standard deviation, for the simulated extracts is excellent. The precision is somewhat poorer for the simulated produced waters, but is still quite acceptable.

ABS-IR and HATR-IR

The infrared instruments were tested using simulated extracts of Crude #3 in hexane at 20 mg/L and 40 mg/L. The same solutions were used to test both instruments. Each concentration was measured on both instruments 15 times each. The results are shown in Table 4-14.

The data in Table 4-14 show the IR instruments to be very precise. For both methods, the precision, as measured by relative standard deviation, at the lower concentration was poorer, though still acceptable.

Table 4-14. Precision Study of IR-ABS and IR-HATR

	IR-ABS		IR-HATR	
	20 mg/L	**40 mg/L**	**20 mg/L**	**40 mg/L**
	22	39	20	40
	21	41	20	40
	21	41	18	40
	22	42	20	40
	23	39	21	41
	21	39	22	40
	20	40	21	42
	22	41	20	41
	19	40	23	42
	22	41	20	40
	20	40	21	41
	20	41	19	40
	21	41	20	42
	22	40	22	41
	21	41	19	41
Std. Dev.	1.060099	0.910259	1.298351	0.798809
Rel. Std. Dev.	5.02%	2.25%	6.36%	1.96%
Avg. Dev.	0.826667	0.773333	1.013333	0.684444
Mean	21.13333	40.4	20.4	40.73333
Median	21	41	20	42

EFFECT OF WATER SOLUBLE ORGANICS

The effect of water soluble organics (WSOs) on the performance of the instruments was investigated by preparing and analyzing simulated produced water samples containing both dispersed crude oil and a mixture of carboxylic acids. These samples formed a matrix as shown in Table 4-15.

Table 4-15. Sample Matrix for WSO Studies

Crude Oil Conc. (mg/L)	**Concentration of WSO (mg/L)**			
0	0	15	30	60
15	0	15	30	60
30	0	15	30	60
60	0	15	30	60

The WSO mixture was an 80%/20% mixture of hexanoic acid and 1-naphthalene acetic acid. These samples were analyzed by each instrument considered in this study. None of the instruments gave any discernable response to the WSO content of these synthetic samples. The reason for this lack of WSO detection by either UV fluorescence or IR absorption is not known.

EFFECT OF IRON ON DIRECT READING UV ANALYSES

Ferric ions (Fe(III)) are known to affect UV measurements. To investigate this effect, several aliquots of an actual produced water from the platform producing Crude #1 were collected, adjusted to pH 2, and spiked with ferric ion concentrations of 5, 10, 30 and 50 mg/L. The concentrations of UV fluorescent material were then read on UV Instrument A in the direct mode, and reported as raw fluorescence units. These data are shown in Table 4-16.

Table 4-16. Effect of Ferric Ion on Direct Reading UV Determinations by Instrument A, Recorded as Raw Fluorescent Units

Ferric Conc. (mg/L)	0	5	10	30	50
Fluorescence Reading (RFU)	134	96	66	50	28

A second set of aliquots of actual produced water from the platform producing Crude #3 was also spiked with ferric ion at various concentrations. These samples were read directly by Instrument A, calibrated with Crude #3. The results of these tests are shown in Table 4-17.

Table 4-17. Effect of Ferric Ion on Direct Reading UV Determinations by Instrument A, Recorded as Oil and Grease Concentration

Ferric Conc. (mg/L)	0	5	10	50
Measured Oil & Grease Conc. (mg/L)	23.6	22.5	18.3	9.8

Finally a set of simulated produced water samples was prepared and spiked with ferric ion at pH 2. These samples were analyzed using Instrument A in the direct reading mode. The results are shown in Table 4-18.

Table 4-18. Ferric Ion Effect on UV Instrument A Determinations of Oil and Grease in Simulated Produced Water Samples

Ferric Ion Conc. (mg/L)	Measured Concentrations of Oil and Grease (mg/L)	
	Defined Conc. = 20 mg/L	Defined Conc. = 30 mg/L
0	20.8	31
5	18.3	29.6
10	17.0	26.4
30	13.6	21.8
50	11.5	14.6

It is obvious that ferric ion does affect the UV instrument response. Ferric ion appears to affect raw fluorescence more than the measured values obtained by calibrating the instrument with crude oil. To provide some measure of the magnitude of the impact of ferric ion, the ratio of the measured oil and grease concentration to the defined oil and grease concentration (or zero-iron oil and grease concentration) was calculated for each of the Fe(III) concentrations considered. These data are shown in Table 4-19.

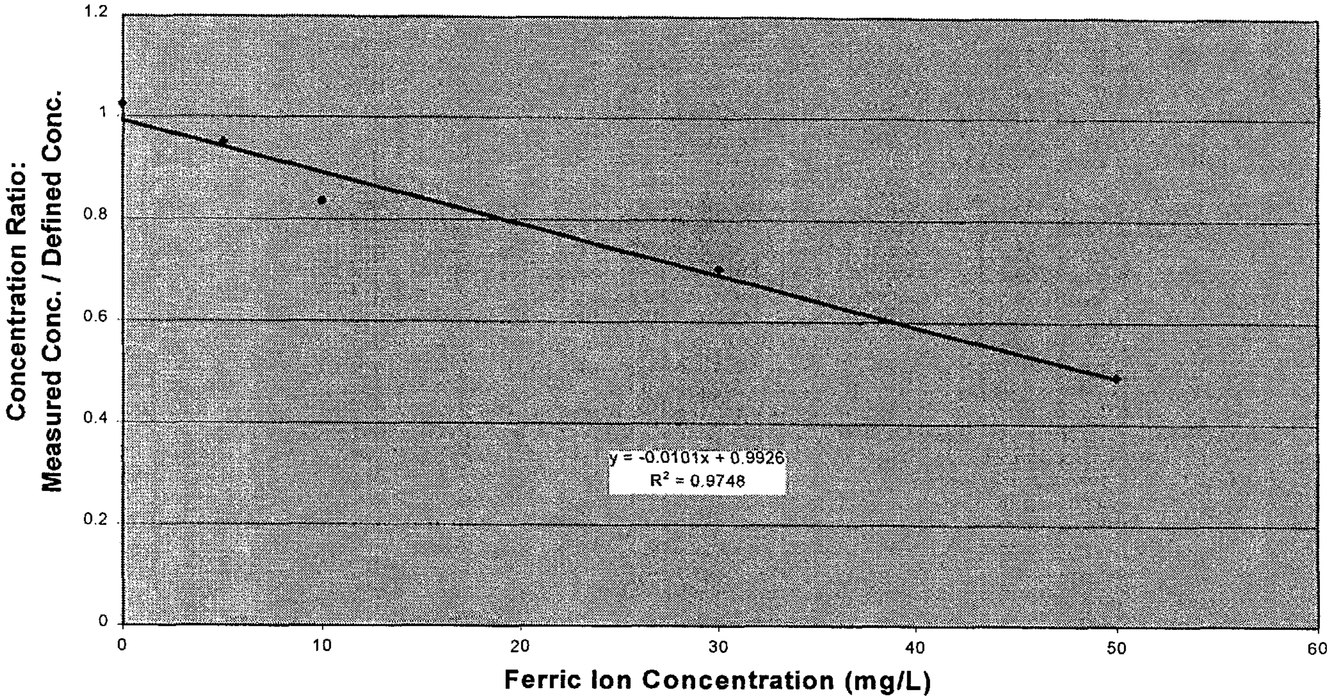
Table 4-19. Ratio of Measured to Defined Oil and Grease Concentration at Various Ferric Ion Concentrations

Oil & Grease Conc. (mg/L)	20	30	23.6	
Ferric Ion Conc. (mg/L)	**Concentration Ratio**			**Average**
0	1.040	1.033	1.000	1.024
5	0.915	0.987	0.953	0.952
10	0.860	0.880	0.775	0.835
30	0.680	0.727		0.703
50	0.575	0.487	0.415	0.492

A plot of the concentration ratio (measured concentration / defined concentration) vs. ferric ion concentration is shown in Figure 4-6.

The y intercept of the regressed line shown in Figure 4-5 is near unity, indicating no effect on measured oil and grease concentrations as the Fe(III) concentration approaches zero. The slope of the curve indicates, approximately, a 1% drop in instrument response for each ppm of ferric ion present.

Figure 4-6.
Concentration Ratio vs. Ferric Ion Concentration



This ferric ion interference with UV measurement is small enough that it should not deter use of the method or instrument for routine monitoring, unless the iron content of the produced water is high or very variable. If the ferric ion concentration remains fairly constant, its effect on UV instrument response will be accounted for in correlating that response with EPA 1664 results.

Section 5
CONCLUSIONS

In the first phase of this study, EPA Methods 413.1 and 1664 were compared using five sets of replicate produced water samples from production operations in Louisiana and California. The comparison demonstrated that the two methods gave results that were weakly related. Because of the variability between replicates, a statistically defensible relationship between the results of the two methods could not be established.

In the second phase of the study, field-proven alternative methods and instruments that might be successfully used for routine monitoring for produced water oil and grease on offshore platforms were identified. Viable methods and associated instruments must:

- Give a significant response to oil and grease;
- Give a linear response to oil and grease over the concentration range of interest;
- Measure oil and grease with acceptable precision;
- Provide analytical results which can be correlated to results by the official EPA method using hexane extraction, EPA Method 1664;
- Be easy to calibrate and operate on offshore platforms;
- Provide consistent performance; and
- Be rugged, durable, and require infrequent repair and adjustment.

In consideration of these criteria, three methods were recommended:

- **Infrared absorption (IR-ABS)** method in which the sample extract is deposited on a sapphire window, infrared radiation is passed through the sample, and transmitted radiation is measured and correlated to the oil and grease content.
- **Infrared absorption (IR-HATR)** method in which the sample extract is deposited on a sapphire plate or zinc sulfide surface, infrared radiation is passed through the sample, and reflected radiation is measured and correlated to the oil and grease content.
- **Ultraviolet fluorescence (UV)** method in which ultraviolet radiation from the sample or sample extract is measured and correlated to the oil and grease content.

In the third phase of the study, the performance of these methods was evaluated in the laboratory, using two UV fluorescence instruments and two modifications of a single IR instrument. All instruments and methods were found capable of measuring oil and grease in produced water. The following specific conclusions support this finding:

- The instruments gave a linear response to oil and grease over the desired concentration range of 0-100 mg/L oil and grease in water.
- The response of both instruments could be correlated to the results of the defining method, EPA 1664.
- Both instruments exhibited a high degree of precision on replicate measurements, well within the precision of the sampling and extraction steps of the analytical procedure.
- The UV instruments demonstrated greater sensitivity and had lower detection limits than the IR instruments.
- The UV method offers the option of analyzing for oil and grease without a solvent extraction step. However, this option is only viable if all of the oil is dissolved.
- The UV instruments were shown to be sensitive to ferric ion interference when used in the direct reading mode. If the ferric ion concentration is fairly constant, however, calibration and correlation can account for this interference. There appears to be no ferric ion interference when solvent extraction is employed.
- n-Hexane may be used as a solvent in both IR methods. Hexane absorbs IR radiation, however, and so may become a significant analytical interference. Verification of complete solvent evaporation is essential when using n-hexane as a solvent in the IR methods.
- Because of the solvent extraction and evaporation steps, the IR methods require greater operator skill than the UV method.
- The instruments do not measure oil and grease directly. Each measures a particular property of oil and grease that can be correlated to oil and grease concentrations as defined by EPA 1664.

Beyond these considerations, vendor information, advice, support, and service should be considered carefully in selecting an appropriate method or instrument for a particular field application. The optimal instrument and method for monitoring oil and grease will ultimately depend on the above considerations, as well as the discharge point to be monitored, the capabilities of the operator(s), and the services provided by the vendors of the analytical technologies.

APPENDIX A

A COMPARISON OF EPA METHOD 413.1 AND EPA METHOD 1664 FOR THE DETERMINATION OF OIL AND GREASE IN PRODUCED WATER FROM OFFSHORE PRODUCTION OPERATIONS

PREPARED FOR

Water Technology International Corporation
Burlington, Ontario, Canada

ABSTRACT

The generation of produced water is an integral part of oil production activities. In most offshore operations, produced water is discharged overboard in accordance with the regulatory limits of 29 mg/L monthly average and 42 mg/L daily maximum concentration of oil and grease in the disposal water. Until recently, the analytical method for the regulatory monitoring of the oil and grease content of these streams was EPA 413.1. This method involves freon extraction followed by gravimetric quantitation of the extract. As an extension to this method, freon extraction followed by infrared detection is routinely used by operators of offshore production facilities for monitoring their oil - water separation process units to ensure efficiency and compliance with regulatory limitations.

The regulated use of freon under the Montreal Protocol has produced the requirement for an alternate (replacement of EPA 413.1 and process monitoring methods using freon) method for monitoring platform production discharges. Oil and grease is a parameter that is defined by the solvent (and method) used for its determination. Changing the solvent therefore could have a significant impact on the extraction efficiency (analyte definition), the quantification step and thus the concentration obtained. This interim (phase 1) report provides a statistical comparison of the former EPA freon extractable method for the determination of oil and grease (EPA 413.1) with the present EPA sanctioned replacement hexane extractable method (EPA 1664).

One of the objectives of this work is to evaluate the similarities and differences of the two analytical methods (EPA 413.1 and EPA 1664) on oil and grease determinations. Produced water samples from a variety of production operations (ranging from gas condensate to heavy oil production) were studied to determine the effect of the varying amounts and/or types of both the dispersed and the soluble oil on the concentrations measured and reported as oil and grease. In some cases, there were observable differences between samples that were representative of a given sample point.

The analytical results also reflected these disparities and as a result the values of extractables found for some of the samples within a single sample matrix varied as significantly as those found between extraction protocols. In summary, there appears to be similar performance for both freon and n-hexane for determining the oil and grease content of the matrices studied.

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INTRODUCTION

The USEPA working within the mandate of the Montreal Protocol, replaced the use of freon (EPA method 413.1) as the solvent of choice for the extraction of oil and grease. In the replacement method (EPA method 1664), n-Hexane is used as the solvent for establishing oil and grease values. In phase 1 of this project, the relative extraction efficiencies of the two solvents and thus the concentration values of oil and grease in flows being discharged to the receiving environment are the primary focus. In this phase of the study, the API is requesting a statistical evaluation of how the two methods compare when applied to the analysis of oil and grease from offshore platform discharges. Water Technology International Corporation in Burlington, Ontario was contracted to provide this service.

In this first phase activity, the emphasis was placed on comparing the performance of n-hexane versus freon for the routine monitoring of oil and grease discharges to the environment. It is clearly recognized by analysts that the values obtained in the analysis of oil/water mixtures by these methods are greatly defined by the solvent used for extraction. Changing from freon to hexane for regulatory monitoring purposes could therefore result in different limits for oil and grease discharge concentrations being targeted by platform operators. Also, relative to this, the need for a method that could provide oil and grease as a rapid measure of continual production efficiency is needed. In consideration of using oil and grease as a measure of optimal production practices, the use of freon extraction followed by IR, quantitative detection, was routinely performed by platform operators. Now that freon-113® is being phased out under the guidelines of the Montreal Protocol and the Clean Air Amendments Act of 1990, the challenge will be to find an alternate solvent with appropriate extraction characteristics that is transparent to IR or an alternate method that does not require either extraction or gravimetric detection, but remains defined as simple, robust and rapid. These challenges will be the primary focus of phase 2 of this project.

A COMPARISON OF EPA METHOD 413.1 vs. EPA METHOD 1664 FOR THE DETERMINATION OF OIL & GREASE IN PRODUCED WATER FROM OFFSHORE PRODUCTION OPERATIONS

As per API's Request for Proposal to examine analytical methods for Oil and Grease from Effluent Samples taken from Offshore Oil Platforms, WTI has completed phase 1 of the study. This activity focused on a performance comparison of EPA method 413.1 (freon extraction) relative to EPA 1664 (Hexane Extraction). This study forms Phase I of a program to evaluate alternate analytical methods for Oil and Grease for use on offshore oil platforms.

SAMPLING

Wide mouth, one litre glass bottles were pre-charged with 5.0 mL 1+1 Hydrochloric acid and shipped to five offshore platforms. The operators of the platforms were asked to fill 24 bottles with effluent being discharged from the platform. They were asked to ensure that, as much as possible, the effluent samples be homogeneous and representative of steady state operation. Samples were not to be taken within three days of the use of biocides, corrosion inhibitors or other down-hole chemicals as this would not represent normal steady state operation. Sampling of four gulf coast and one west coast offshore production platforms was completed. The platforms are identified in this report as platform #1 through #5.

The samples were shipped by non-refrigerated surface transportation to WTI between February and March of 1996. Upon receipt (7 - 10 days after shipping), they were stored at 4°C until analysis commenced within 3 days of arrival at WTI. The question of sample integrity with respect to aging and transportation was not addressed.

SAMPLE ANALYSIS

Observation of the samples indicated that they were not as homogeneous as anticipated. The samples of Platform #4 showed a range of colours from pale green to colourless and there were deposits of varying amounts of a white, crystalline material on the container bottom. The Platform #5 samples had varying degrees of free oil deposited on the sides of the bottles above the waterline and varying quantities of white crystals precipitated on the bottom. The Platform #2 samples similarly exhibited variations in the amount of salt and free oil separated on the walls of the container.

Analysis was carried out on six randomly selected sample replicates from each platform by USEPA 413.1 and EPA 1664 modified with respect to solvent recovery. The actual analytical protocol used is described in Appendix B. After the extracted sample had been rotovapped, the final weighing was done in a round bottom flask. A synthetic seawater blank and a distilled water blank were carried out for each group of six replicates and for each method applied.

RESULTS AND DATA REVIEW

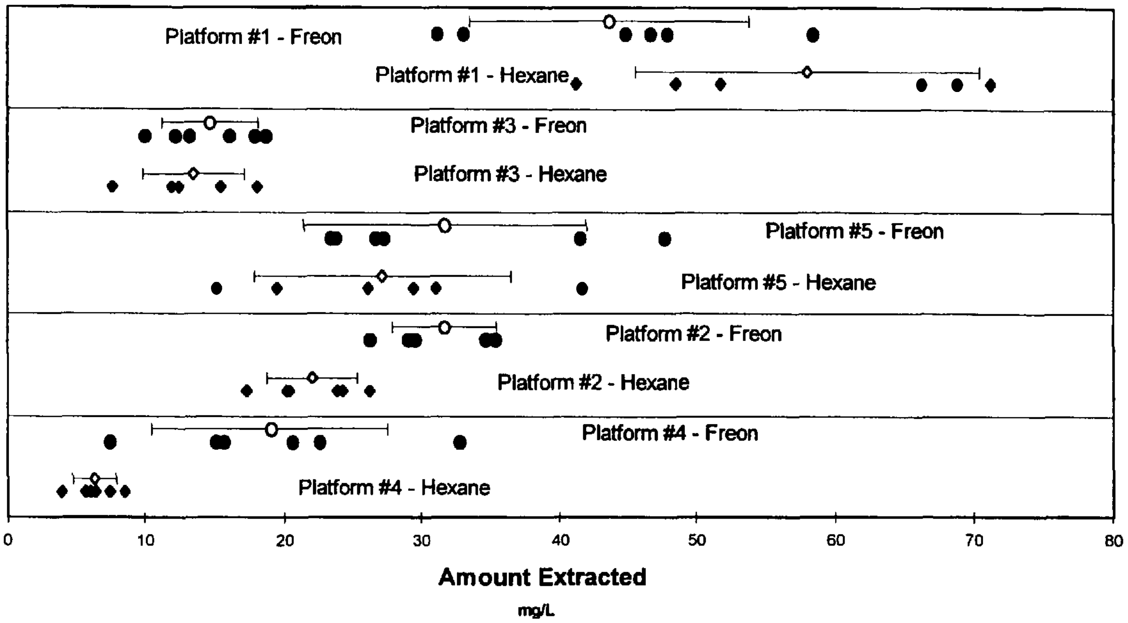
Measured values are shown in Table 1 along with the mean, standard deviation, and relative standard deviation (RSD) of the six replicates. The supporting QA/QC blank data are also included in this table. These data are subsequently presented as a scatter plot in Figure 1. There is considerable variability in the data due in part to the observed lack of sample homogeneity. The values generated in all but one of the sample sets were higher for freon extractables. All replicate values reported in Table 1 are blank corrected.

Both from the data table and the scatter plot, there is an observable loose relationship between the two methods. The trend from lower to higher concentrations of extractable material within the five matrices analysed are paralleled by the two solvents.

Table 1. Oil and Grease Data from 5 Offshore Platforms (mg/L)

	#4	#2	#5	#3	#1
Hexane	6.07	20.40	26.20	12.50	48.60
	3.92	23.90	15.20	18.10	51.80
	7.47	20.20	19.50	7.72	41.30
	5.69	26.30	31.10	15.50	66.30
	6.46	24.30	29.50	12.00	71.30
	8.57	17.30	41.70	15.50	68.90
Freon	15.70	29.60	26.70	18.70	33.10
	15.10	26.30	23.40	10.00	31.20
	7.48	29.10	41.50	13.20	46.70
	20.60	35.20	47.70	12.20	58.40
	22.60	34.70	23.80	16.10	44.90
	32.80	35.40	27.30	17.90	47.90
Hexane Blank	2.24	3.57	2.62	3.57	4.22
Hexane Seawater Blank	3.00	2.34	3.61	3.88	0.84
Freon Blank	1.23	2.12	2.94	1.79	2.30
Freon Seawater Blank	3.53	2.09	3.66	2.57	5.61
Hexane Mean	6.36	22.07	27.20	13.55	58.03
Hexane Std Dev	1.59	3.32	9.33	3.63	12.41
Hexane RSD	24.96	15.06	34.29	26.77	21.39
Freon Mean	19.05	31.72	31.73	14.68	43.70
Freon Std Dev	8.54	3.88	10.27	3.43	10.13
Freon RSD	44.84	12.23	32.37	23.35	23.17

Figure 1. Scatter Plot of Raw Data



Platform #3 (Heavy Crude) effluent shows the least spread of data for the pair of methods with an RSD of 27% for hexane and 23% for freon. Both methods agree that this effluent has a relatively low oil and grease value of 14 and 15 mg/L. Platform #4 discharge (Medium Crude) provided the least agreement between the two solvents. The Platform #5 (Gas Condensate) sample exhibited relatively high scatter in the data, even so, the average results of 27 mg/L with hexane and 32 mg/L with freon are in reasonable agreement. Platform #1 (Light Crude) effluent sample also showed considerable scatter in the data, though it is significantly less for freon as compared to hexane. The Platform #2 (Medium Crude) sample results were fairly reproducible at 22 and 32 mg/L even though the samples were visually different. There is not enough information to explain the differences in oil and grease results on produced water samples from different platforms. The gathering of these data was beyond the scope of the present project.

In four of five cases the average hexane result was lower than the average freon result. Only in the case of the Platform #1 sample did hexane produce a numerically greater average result. The ratio of the average results is shown in Table 2 and graphically in

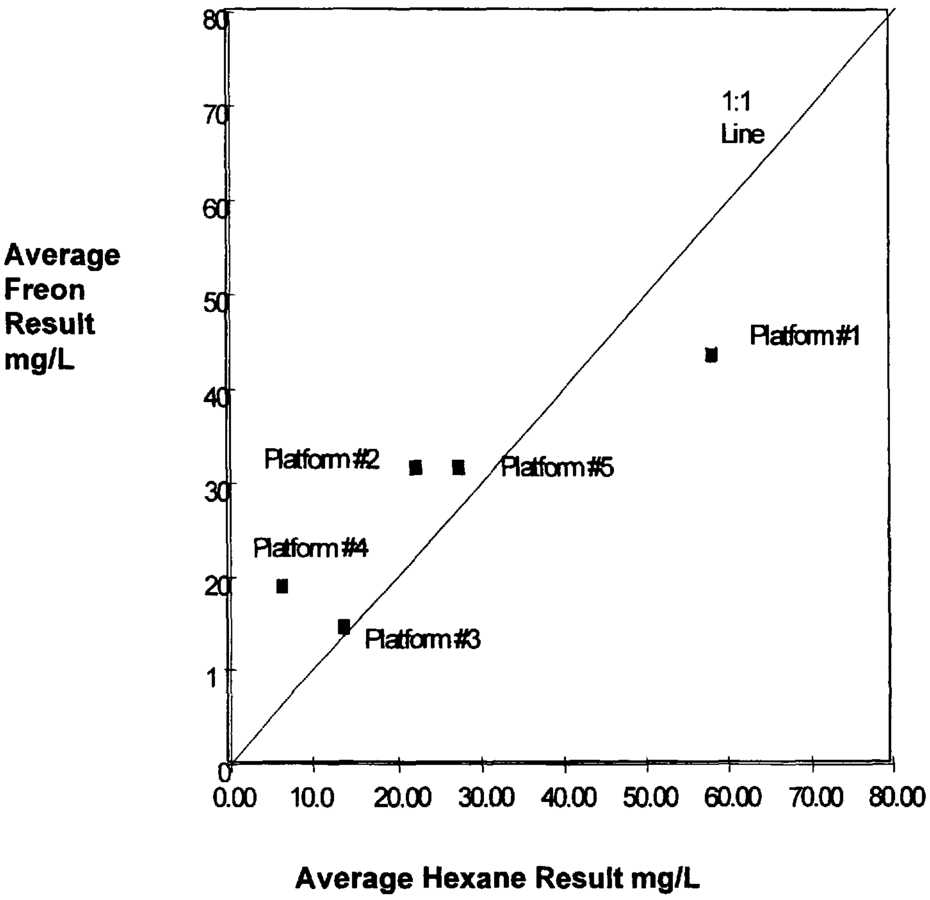
Figure 2. The average of the ratios is 0.83 meaning that on average hexane gives a result 83% of the result obtained using freon. The ratio can be quite different for different sample matrices.

Table 2. Average, Ratio and 95% Confidence Limits on Hexane and Freon Extractions From Produced Water of:

	#4 Crude	#2 Medium with WSO	#5 Soluble Organics	#3 Heavy Crude	#1 Light Crude
Hexane Mean	6.36	22.07	27.20	13.55	58.03
Freon Mean	19.05	31.72	31.73	14.68	43.70
Hexane/Freon Ratio	0.33	0.70	0.86	0.92	1.33
Hexane Mean – Freon Mean	-12.68	-9.65	-4.53	-1.13	14.33
Upper 95% CI	-4.77	-5.00	8.10	3.41	28.92
Lower 95% CI	-20.59	-14.30	-17.17	-5.67	-0.25

Also shown in Table 2 is the difference between the average hexane result and the average freon result and the 95% confidence interval for this difference. If the 95% confidence interval includes zero, then there is no difference between methods. For Columns 1, 3 and 5 there is no difference, although for Column 1 the lower 95% limit just exceeded zero. For Columns 2 and 4 the hexane result was significantly lower.

Figure 2. Freon Hexane Comparison on 5 Offshore Platforms



STATISTICAL ANALYSIS OF SAMPLE DATA

A two factor Analysis of Variance (ANOVA) was carried out on the entire dataset. The ANOVA result is in Table 3. Using this data analysis approach, experimental variables can be isolated from the random background and measured. Within this experiment, sample non-homogeneity can be compared to the differences in results obtained using the two solvents, and to the matrix differences associated with the five respective sample points. The F-ratios obtained can be compared with the critical F-ratios gathered from statistical tables at 95% confidence to determine whether the differences seen are significant.

Table 3. Two Factor Analysis of Variance (ANOVA)

SUMMARY	**Platform #4**	**Platform #2**	**Platform #5**	**Platform #3**	**Platform #1**	**Total**
Hexane						
Count	6	6	6	6	6	30
Sum	38.18	132.40	163.20	81.32	348.20	763.30
Average	6.36	22.07	27.20	13.55	58.03	127.22
Variance	2.52	11.05	87.01	13.16	154.05	267.80
Freon						
Count	6	6	6	6	6	30
Sum	114.28	190.30	190.40	88.10	262.20	845.28
Average	19.05	31.72	31.73	14.68	43.70	140.88
Variance	72.95	15.05	105.54	11.76	102.56	307.86
Total						
Count	12	12	12	12	12	
Sum	152.46	322.70	353.60	169.42	610.40	
Average	25.41	53.78	58.93	28.24	101.73	
Variance	75.47	26.10	192.55	24.92	256.61	

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Solvent	112.01	1	112.01	1.95	0.17	4.03
Sample	11349.81	4	2837.45	49.29	0.00	2.56
Interaction	1331.77	4	332.94	5.78	0.00	2.56
Within	2878.27	50	57.57			
Total	15671.86	59				

Comparison of the F Ratio for the Sources of Variation with the Critical F Ratio at the 95% confidence level shows that there is a significant difference between the 5 sample types tested and that this accounts for the largest difference in the data recorded. The F Ratio for sample types is 49.29 compared to a critical F Ratio of 2.56 demonstrating the difference. Interestingly, there is no effective significant difference between solvent performance, since an F ratio of 1.95 (for solvent variation) is less than the Critical F ratio of 2.56. The interaction term, however, is significant at the 95% level. The interaction term implies that although freon and hexane give an overall similar result, there are significant differences in respective performance for some of the samples representing the same matrix. Considering all the sample results, some are higher, some are lower and some show little difference, but there is no overall difference between solvents. Note that this result is obtained with samples that exhibit a high degree of non-homogeneity. Significant differences may be revealed with more homogeneous samples that result in a smaller Mean Square variance within the replicates.

SUMMARY

A performance comparison between EPA method 413.1 (freon extractables) and EPA method 1664 (hexane extractables) for oil and grease analysis of offshore platform discharges was carried out. The assessment was based on the analysis of six replicates, by the two methods, on five different matrices. There appears to be little overall difference in performance between the two solvents, though this is based on relatively non-homogenous samples.

Section 1

Sample Information Sheets

SAMPLE DESCRIPTION :

Please provide the following information.

SAMPLE DATE	SAMPLE TIME	SAMPLE LOCATION	PLATFORM NAME
2/8/96	15:50	WEMCO DISCHARGE	GC-65-A

Type of Production (Check One):

GAS; -------------- OIL; -------------- OIL AND GAS; ✓

(GAS - Only gas producing wells are on the platform. OIL - Platform has only oil producing wells. OIL AND GAS - platform has both the gas and oil producing wells.).

High soluble Organics: Yes ✓ No ---------

API Gravity of the Crude 28.7

Chemical Treatment

Type	Chemical Supplier	Product name	Dosage/ Frequency	Injection Location
Demulsifier	Nalco/Exxon	EC 2231	10ppm	FWKO Inlet
Corrosion Inhibitor		None		
Scale Inhibitor		None		
Reverse Emulsion Breaker or Water Clarifier	Nalco/Exxon	EC 6047	30ppm	Wemco Inlet
Biocide		None		
Other Chemicals Defoamer	Nalco/Exxon	EC 9017	15ppm	H.P., I.P., & Test System

Water Treatment Equipment Used (Circle One)

[✓ Flotation cells] Hydrocyclones Centrifuges Other

Produced Water

Discharge Rate (Barrels/day) 11,500 B/D

Total Dissolved Solids (mg/l)

Custody Transfer

Oo

Name of Person Sampling (please print):

FRED T. MAYER

Date and Time that Notification For Samples Pick up was made:

2/14/96 16:45

Date and Time Samples Left at Shorebase for Pick up:

Please provide any other information (if applicable) that would add definition to the sampling procedure (foaming in the sample container, color change after sampling, phase separation within the sample container etc.).

SAMPLE DESCRIPTION :

Please provide the following information.

SAMPLE DATE 1-25-96 SAMPLE TIME 0815 SAMPLE LOCATION Wemco IN PLATFORM NAME COSD Hermosa

Type of Production (Check One):

GAS; ______ OIL; ______ OIL AND GAS; ✓

(GAS - Only gas producing wells are on the platform. OIL - Platform has only oil producing wells. OIL AND GAS - platform has both the gas and oil producing wells.).

High soluble Organics: Yes ______, No X

API Gravity of the Crude [redacted] 19.6°

Chemical Treatment

Type	Chemical Supplier	Product name	Dosage/ Frequency	Injection Location
Demulsifier				
Corrosion Inhibitor				
Scale Inhibitor	CHAMPION TECH.	GYPTRON T-155	38.5 qts/day	UPSTREAM OF SEPARATORS
Reverse Emulsion Breaker or Water Clarifier	CHAMPION TECH.	EMULSOTRON XZ1064	252 qts/day	"
Biocide				"
Other Chemicals	CHAMPION TECH.	DEFOAMER V 136	14 qts/day	

Water Treatment Equipment Used (Circle One)

[✓ Flotation cells] Hydrocyclones Centrifuges [✓ Other CPI Separators]

Produced Water

Discharge Rate (Barrels/day) 15,105

Total Dissolved Solids (mg/l) N/A

Custody Transfer 00

Name of Person Sampling (please print):

GARY PERLMUTTER, LTS

Date and Time that Notification For Samples Pick up was made:

1-27-96

Date and Time Samples Left at Shorebase for Pick up: 1-30-96

Please provide any other information (if applicable) that would add definition to the sampling procedure (foaming in the sample container, color change after sampling, phase separation within the sample container etc.).

SOME ACID WAS LOST DURING INITIAL SHIPMENT TO CHEVRON USA. AFTER SAMPLING EACH SAMPLE WAS pH TESTED TO FIND 5 SAMPLES ABOVE pH 4. TO THESE SAMPLES ADDITIONAL HCl WAS ADDED TO BRING THE pH BELOW 2.

Section 2

Applied Analytical Procedures

TOTAL OIL AND GREASE OF LIQUID SAMPLES BY FREON EXTRACTION AND GRAVIMETRIC QUANTIFICATION

(adapted from EPA method 413.1)

Scope and Application

1. This method includes the measurement of Freon-113® extractable matter from surface and saline waters, industrial and domestic wastes. It is applicable to the determination of relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related matter.

2. The method is not applicable to measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels from gasoline through #2 fuel oils are completely or partially lost in the solvent removal operation.

3. Some crude oils and heavy fuels contain a significant percentage of residue-type materials that are not soluble in Freon-113®. Accordingly, recoveries of these materials will be low.

4. The method covers the range from 5 to 1000 mg/L of extractable material.

Summary of Method

The sample is acidified to a low pH (<2) and serially extracted with Freon-113® in a separatory funnel. The solvent is evaporated from the extract and the residue weighed.

Definitions

The definition of oil and grease is based on the procedure used. The nature of the oil and/or grease, and the presence of extractable non-oily matter will influence the material measured and interpretation of results.

Sampling and Storage

1. A representative sample of 1 litre volume should be collected in a glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by the addition of 5 mL of HCl at the time of collection and refrigerated at 4°C.

2. Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.

The suggested maximum storage time is 28 days, though studies carried out internally on steel industry waste streams have shown no significant change over 40 days when acidified and stored at 4°C.

Apparatus

1. Separatory funnel, 2000-mL with Teflon® stopcock.
2. Rotovap unit
3. Flask, boiling, 125-mL (Corning No. 4100 or equivalent).
4. Distilling head, Claisen or equivalent.
5. Filter paper, Whatman No. 40, 11-cm diameter.
6. Aspirator or vacuum pump

Reagents

1. Hydrochloric or sulphuric acid, 1:1 ACS grade. Mix equal volumes of conc. acid and distilled water.
2. Freon-113® (1,1,2-trichloro-1,2,2-trifluoroethane), b.p. 48°C.
3. Sodium sulphate, anhydrous crystal.

Procedure

1. Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 mL of hydrochloric acid to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

2. Transfer the entire sample into a separatory funnel.

3. Tare a boiling flak (pre-dried in an oven at 103°C and stored in desiccator).

4. Add 30 mL of Freon-113® to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate, and filter the solvent layer into the flask through a funnel containing solvent-moistened filter paper. Note: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate into the filter paper cone and slowly draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.

5. Repeat step 4 twice more, with additional portions of fresh solvent, combining all solvent in the boiling flask.

6. Rinse the tip of the separatory funnel, the filter paper, and then the funnel with a total of 10-20 mL of solvent and collect the rinsings in the flask.

7. Connect the boiling flask to the tap water cooled condenser, on the Rotovap unit. Immerse the flask ~ 50% into the water bath at 35°C. and adjust it's rotation to approximately 60 RPM. Apply approximately 0.5 atmosphere of vacuum and collect the solvent for reuse. A solvent blank should accompany each set of samples.

8. When the solvent condensing activity is visually complete and the sample appears dry, release the vacuum and remove the flask from the condenser. Wipe the flask dry with a lint free lense cloth or paper and place it in a dessicator.

9. Cool the boiling flask in the desiccator for ~ 30 minutes and weigh; return the flask to the dessicator for a further 5 minutes and re-weigh. Repeat this activity until a constant weight is attained.

Calculations

$$\text{total freon extractables (mg/L)} = \frac{R - B}{V} \times 1000$$

where:

R = residue, gross weight of extraction flask minus the tare weight, in milligrams
B = method blank determination - the residue retained from applying the exact procedure to a matrix matching that of the sample (devoid of extractables), or distilled water, in milligrams.
V = volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary, in litres.

Quality Control

- Method blanks must be run at a minimum one per five samples analysed (20%).
- Any changes in the reagents used must be accompanied by a blank check.
- Duplicates are encouraged on a one per ten sample analysis basis, (10%);
- Sample volume may not permit duplicate analyses.
- Spikes, where appropriate should be run on a 10% sample analysis basis. It should be noted that unless the spike material matches that of the targetted species, liitle value may be gained from incorporating spikes.

Precision and Accuracy

The manual, *EPA Methods for Chemical Analysis of Water and Wastes* (EPA, 1979), documents single-laboratory (EMSL) tests of Method 413.1 on sewage. This method determined the oil and grease level in the sewage to be 12.6 mg/L.

When 1 litre portions of the sewage were dosed with 14.0 mg of mixture of #2 fuel oil and Wesson® oil, the recovery was 93% with a standard deviation of 0.9 mg/L

The rotovap modified version used in this study demonstrated a correlation of between 0.9 and 1.0 when compared to the registered method. The comparison was determined on synthetic EPA check solutions and on an industrial discharge stream from the steel industry.

Bibliography

1. *Standard Methods for the Examination of Water and Wastewater.* 14th Edition. 1975. p. 515 Method 502A.

2. United States Environmental Protection Agency. 1979. *EPA Methods for Chemical Analysis of Water and Wastes.*

TOTAL OIL AND GREASE OF LIQUID SAMPLES BY n-HEXANE EXTRACTION AND GRAVIMETRIC QUANTIFICATION
(adapted from EPA method 1664)

Scope and Application

1 This method may be used for the determination of n-hexane extractable material (HEM) in surface waters, ground waters, domestic aqueous wastes and industria wastewaters.

2 Extractable materials that may be determined by this method include vegetable oils, animal fats, waxes, soaps, greases some surfactants and hydrocarbons that volatilize at temperatures of greater than 85°C. Petroleum fuels from gasoline through #2 fuel oil may be partially lost during analysis whereas heavy fuel oils and some crude oils contain constituents that are not hexane extractable.

3 This method is capable of measuring hexane extractable materials in the 5 to 1000 mg/L range.

Summary of Method

The sample is acidified to a pH <2.0 and serially extracted with n-hexane in a separatory funnel. The solvent is recovered from the extract and the residue is weighed.

Definition

The definition of oil and grease is dependent upon the solvent used for extraction. The results obtained by applying this method is therefore dependent upon the nature of the material being extracted.

Sampling and Storage

1 A representative sample of a minimum 1 litre volume, collected in a glass wide mouth bottle is preferrable. The sample should be preserved by the addition of HCL or H_2SO_4 to a pH <2 and refrigerated at 4°C.

2 The collection of a composite sample is not recommended due to potential losses of oil on the sampling equipment. Individual samples taken at discreet time intervals and analysed separately to obtain an average concentration over time is most appropriate.

The suggested maximum storage time is 28 days, though studies internally on steel industry waste streams have shown no significant change over 40 days when acidified and stored at 4°C.

Apparatus

1. Separatory funnels, 2 Litre, with Teflon® stopcock.
2. Filter paper, Whatman No. 40, 11-cm diameter.
3. Analytical balance capable of weighing to the nearest 0.1 mg.
4. Rotovap unit.
5. 125 mL boiling flask.
6. Distilling head.
7. Vacuum source - aspirator or vacuum pump.
8. Desiccator.

Reagents

1. Hydrochloric acid or sulphuric acid 1:1 ACS grade. Mix equal volumes of concentrated acid and deionized water. (acid to water)
2. n-Hexane - ($CH_3(CH_2)_4CH_3$, Hexanes, mixture of isomers), b.p. 68°C., 85% purity, 99% min. saturated C_6 isomers, residue <1 mg/L
3. Sodium sulfate, anhydrous crystals.

Procedure

1. Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 mL of 1:1 hydrochloric acid to the sample bottle. After mixing the sample, check the pH by touching pH paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

2. Pour the sample into a clean separatory funnel.

3. Add 30 mL of n-hexane to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate. The solvent layer will separate and appear as the top layer in the funnel.

4. Drain the water layer into the original sample container and filter the solvent layer through a layer of sodium sulfate into a previously weighed 125mL evaporation flask. Repeat step 3 and the extract recovery operation twice more, combining all solvent filtrates in the evaporation flask.

5. Empty the sample bottle, and determine the volume of sample by adding tap water into sample bottle to the mark previously made. Pour water into a graduated cylinder and record the volume.

6. Rinse the tip of the separatory funnel, filter paper/sodium sulfate, and the funnel with a total of 5 - 10 mL of solvent and collect the rinsings in the evaporation flask.

7. Connect the boiling flask to the water cooled condenser on the Rotovap unit. Immerse the flask ~ 50% into the water bath at 37°C. and adjust it's rotation to approximately 60 RPM. Apply ~ atmosphere of vacuum and collect the solvent for reuse. A solvent blank should accompany each set (up to 10) samples or if solvent batch changes.

8. When the solvent condensing activity is virtually complete and the sample appears dry, release the vacuum and remove the flask from the condenser. Wipe the flask dry with a lint free lense cloth or paper and place it in a dessicator.

9. Cool the residue containing flask in the dessicator for ~30 minutes or to a constant weight.

10. Determine the concentration of oil and grease in the extract based on the net weight gain and the starting sample volume.

Calculations

$$\text{total HEM (mg/L)} = \frac{R - B}{V} \times 1000$$

where:

R = Final weight in grams of residue - gross weight of flask + residue minus tare weight of flask.
B = method blank determination - residue retained from applying the exact procedure to a matrix matching (as closely as possible) that of the sample (devoid of extractables), or distilled water, in grams.
V = Volume of sample, determined by refilling the sample container to original sample volume and correcting for acid addition if necessary, in litres.

Quality Control

- Method blanks must be run at a minimum of one per five samples analysed (20%).
- Any change in the reagents must be accompanied by a blank check.
- Duplicates are encouraged on a one per ten sample analysis basis (10%).
- Though duplicate analysis on a 10% basis is encouraged, sample volume may not permit this.
- Spikes, where appropriate should be run on a 10% basis. It should be noted that unless the spike material matches that of the targetted species, little value may be gained from incorporating spikes.

Safety

1. Standard laboratory safety precautions should be adhered to at all times. This assumes that all samples are hazardous. The use of hoods, safety glasses or goggles, and lab coats is mandatory. Material safety data sheets are available for all chemicals used in this procedure and should be referred to by all analysts.

Bibliography

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APPENDIX B

A REVIEW OF TECHNOLOGIES TO MEASURE THE OIL AND GREASE CONTENT OF PRODUCED WATER FROM OFFSHORE OIL AND GAS PRODUCTION OPERATIONS

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ABSTRACT

This report presents a review of analytical technologies and instrumentation for the measurement of oil and grease in produced water. Alternatives are needed to replace the infrared method with Freon-113® extraction used in the past. Operators need such methods to monitor treatment process performance and evaluate equipment. The goals of this work included: evaluation of produced water composition and properties and their impact on oil and grease analytical technologies, evaluation of instruments using these technologies, and recommendations for laboratory and field testing. Three currently available technologies were identified: infrared absorption, ultraviolet absorption, and ultraviolet fluorescence. Two of these technologies are recommended for experimental evaluation: infrared absorption and ultraviolet fluorescence. Several instruments were identified that use each of these technologies, two of which are recommended for further evaluation: an infrared absorbance instrument and an ultra violet fluorescence instrument. The recommended instruments are not necessarily the best instruments, but do afford a broad evaluation of the impact of produced water properties and production practices affecting oil and grease analysis. A laboratory testing protocol and field testing protocol for evaluating the technology and instruments are presented in the report. Implementation of these test protocols, using the recommended instruments, will provide a strong direction for any future evaluation of oil and grease analytical methods. It was concluded that there is probably no single best method for field analysis of oil and grease. Among the potentially viable technologies and instruments that have been identified, the best choice for a particular operator will be determined by factors such as operability, technical and field support from the vendor, personal preference, and the purpose for the analysis.

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Section 1
INTRODUCTION

In the past, the Environmental Protection Agency (EPA) required that oil and grease in water discharged to the sea be monitored using EPA Method 413.1 (EPA, 1983). This method requires extraction of the water with Freon-113®, the subsequent boiling off the Freon, and weighing the resulting oil and grease. Operators also monitored the operation of their water treatment processes with on-site field methods, which typically use Freon-113® extraction of the water and infrared (IR) spectrophotometric measurement. However, Freon-113® is a chlorofluorocarbon and the use of such substances is being phased out under the Montreal Protocol and the Clean Air Act Amendments of 1990. In 1996, the EPA proposed Method 1664 for oil and grease and total petroleum hydrocarbon measurements (EPA, 1995; Federal Register, 1991 and Federal Register, 1996). This method uses n-hexane as the extraction solvent instead of Freon-113®. Oil production operations depend on oil and grease analysis for process control of separation processes, monitoring equipment performance, and evaluating equipment. Consequently, field methods that do not use Freon are needed to replace the previously used field IR methods.

This study is done to aid operators in finding a suitable field method for measuring oil and grease in produced water. The field method chosen is not intended as an EPA-required method for reporting NPDES compliance monitoring, but rather as a tool to measure oil content of produced water streams to ensure effective process treatment operations. The field method should correlate with EPA Method 1664, which defines oil and grease. However, because of chemical differences in produced waters, it would not be likely that a single correlation factor universally applicable to all produced waters would be established.

Two factors make it difficult to identify a single new method suitable for produced water applications. First, the properties of produced water and the operational limits in the offshore environment strongly affect the choice of a suitable analytical method. Second, a large number of analytical instruments would have to be investigated. Such extensive research was not practical within the constraints of this project. A procedure was needed to effectively screen the many methods and instruments available and focus on those that are most applicable to produced water.

This technology review was commissioned to identify technologies and applications (instruments) that are compatible with the composition and properties of produced water and that can be used in the offshore environment for measuring oil and grease in produced water. Only proven technologies were investigated. That is, only technologies using measuring principles that have already been successfully applied for measuring oil in water were examined. All of the technologies examined involved measurements of some type of electromagnetic spectra. This included technology employing colorimetric measurements and spectra on either side of the visible spectra range. Technologies involving such things as radio frequencies, microwave frequencies and refractive index were not considered because there is no well-established body of experience using these measurement principles. Various applications of those chosen technologies were considered and a representative of each of them is recommended for actual study in the laboratory and in the field.

Originally, it was intended that only one or two optimal instruments would be recommended. However, it quickly became apparent that there are a large number of analytical instruments sold that are all operable, and for some applications each of them might be the best instrument for that particular job. Therefore, it was decided to choose two instruments each of which would represent a class of instruments. The evaluation of these would then illustrate the procedure for evaluating other instruments sharing the same measurement principle. The instruments recommended for this study were chosen on the basis that they:

- are representative of a technology,
- represent different measurement principles,
- can contrast direct analysis versus extraction followed by measurement,
- have different types of interferences, and
- have good technical and field applications support from their manufacturer.

These factors allow the study of their impact on the different technologies and will illustrate the extension of the evaluations done of the selected instruments to similar instruments that the operator may be interested in using. Unproven instruments and unsuitable methods of analysis were identified and eliminated without field or laboratory testing. This process not only focuses the scope of necessary testing, but also specifically addresses the limitations imposed by the chemistry of produced water and current operating practices. Therefore, analytical testing time and associated costs, which would otherwise be expended in the overall project, were eliminated.

This study was developed using the following approach:

1. The properties of produced water were considered. Their potential impact on oil and grease is explained in Section 2.
2. An evaluation of the various technologies for measuring oil in water was conducted. The produced water properties, as explained in Section 2, were also incorporated. This evaluation is presented in Section 3.
3. Analytical instruments that used the recommended technologies were considered. The two that were chosen for study are discussed in Section 4.
4. A laboratory testing program that uses synthetic produced waters was recommended. This testing program will allow for the evaluation of the produced water property variables to be tested outside the complicated matrix found in real produced waters. The testing program will enable the researchers to become familiar with the instruments before using them in field tests. The testing program is presented in Section 5.
5. The criteria used for selecting the sites for field testing are presented in Section 6. These criteria were chosen to allow testing of the instruments on a variety of produced waters and over changing production conditions. The platforms and operations were chosen to show any limitations of the instruments.
6. Because it was not feasible to study all of the technologies and instruments, Section 6 develops guidelines for those operators who want to do their own evaluation of instruments not covered in the study.

If the program recommended in this study is followed, then the data collected can be used to predict the behavior of a large number of instruments that use similar technologies and are subject to the limitations of those technologies because of the properties of produced water.

Section 2

PRODUCED WATER PROPERTIES AND PRODUCTION PRACTICES THAT AFFECT OIL AND GREASE ANALYSES

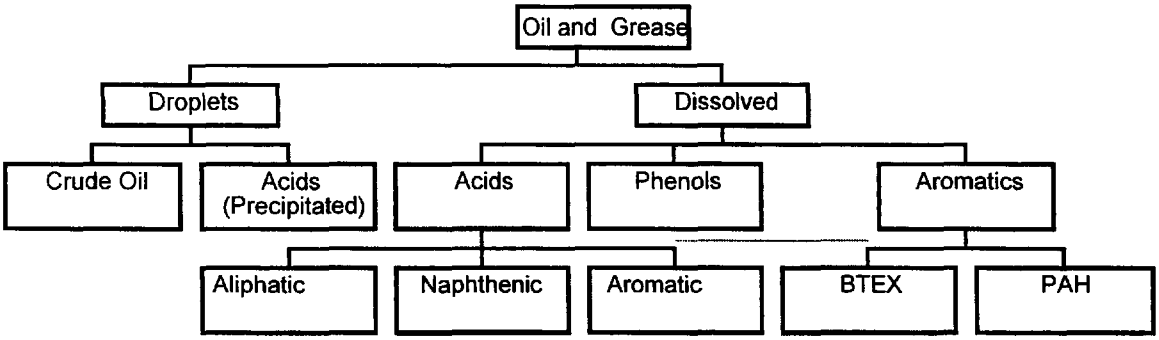
PRODUCED WATER PROPERTIES

A typical produced water averages about 2000 mg/l of organic constituents. These include the following materials in the approximate order of decreasing concentration in which they are present:

- carboxylic acids (including aliphatic acids, naphthenic acids, and perhaps aromatic acids),
- droplets of the crude oil being produced,
- BTEX (benzene, toluene, ethylbenzene, and xylenes),
- phenols (phenol and substituted phenols),
- naphthalene, substituted naphthalenes and other aromatic hydrocarbons with limited solubility in water.

The majority of these materials are dissolved in the water, but some of them are in the form of dispersed droplets. Oil and grease forms only a small subset of the total organic content of produced water. This subset is defined by the method used to measure it. The definition of oil and grease used in this document is found in EPA Method 1664 (1995). That is, oil and grease is that fraction of the organic content of produced water that is extractable in n-hexane at pH 2 or below and remains after the hexane is evaporated. Any field method chosen should correlate with this official method. Figure 2-1 shows a diagram of possible oil and grease constituents.

Figure 2.1. Composition of Oil and Grease



Oil and grease in produced water includes constituents dispersed in the water by mechanical forces due to flow during the production operations and droplets of carboxylic acids precipitated from solution. The dissolved constituents of oil and grease are acids, phenols, and aromatic hydrocarbons. However, only a small portion of the carboxylic acids in produced water are included in oil and grease. The very low molecular weight acids such as acetic, propionic, etc. are too water soluble to extract into hexane. Likewise, the lighter BTEX compounds are not constituents of oil and grease since they are too volatile to remain after evaporation, even though they may be soluble in hexane or Freon-113®. Therefore, the constituents of oil and grease in produced water are a mixture of hydrocarbons (both aliphatic and aromatic), and oxygenate of hydrocarbons (carboxylic acids and phenols). They are limited in molecular weight by their volatility and their distribution coefficients between oil and water. Compounds meeting the limits imposed by the defining method are included in oil and grease.

Any instrumental method intended to correlate with the defining method (EPA Method 1664) must consider these things. For example, IR absorbance correlations are affected by the ratio of the number of carbon hydrogen bonds (C-H bonds) to the molecular weight of the oil and grease constituents. Oil and grease that has a higher proportion of oxygen in its constituents will have a different calibration factor than oil and grease that has a lower proportion of oxygen in its constituents. However, all constituents of oil and grease will produce an instrument response. Ultraviolet (UV) methods measure materials that absorb UV energy or fluoresce as a consequence of such absorption. Such materials usually contain an aromatic ring and multiple ring compounds, such as naphthalene, and give a higher response. UV methods depend on maintaining a constant ratio between total oil and grease and the materials that absorb UV or fluoresce in the UV range. Since produced water from a given discharge point may come from several different wells in different locations, this ratio may vary on some platforms as wells are turned on and off, presenting problems in maintaining proper calibration of the analytical method. Research results have shown that this is not always or even frequently a problem, but is a factor that must be taken into account.

In addition to the organic materials in produced water that could contribute to oil and grease measurements, there are materials in produced water that might interfere with some analytical methods. For example, all produced water contains some small quantity of iron ions or compounds. Until the produced water is contacted by air, the iron will likely be in the form of iron (II) ions (Fe^{+2}). If it has been in contact with air, the iron will be in the form of iron (III) oxide (Fe_2O_3), a solid dispersed in the water. Iron (III) oxide occurs in water as a highly hydrated compound with varying numbers of waters of hydration ($Fe_2O_3 \bullet nH_2O$). Hydrated iron oxide is non-stoichiometric and n can be a quite large number. In addition to adding turbidity, these hydrates absorb particulate oil and grease and concentrate it in large particles that can interfere with extraction and fluorescence.

Crude oil and condensate can vary widely in color, from absolutely clear and colorless, to very dark black. If color is used as a detector for oil, the sensitivity will depend on the darkness of the oil. For many medium grade crude oils, the color is not dark enough to permit accurate oil and grease determinations at the concentrations of interest. This includes most oils produced in the Gulf of Mexico. Although operators in areas where very dark oils are produced, such as parts of California, Canada and Venezuela use colorimetric methods, these methods work only on dark oils and they were excluded from this study.

The oil in produced water is a mixture of dispersed and dissolved materials. Therefore, an analytical method such as nephelometry that depends on detecting a separate phase, such as particles or droplets is not a good choice for measuring total oil and grease. Although, there may be applications where only the particles are of interest, turbidity and nephelometry were excluded from this study.

PRODUCTION PRACTICES AFFECTING OIL AND GREASE ANALYSIS

The produced water stream is subjected to a series of pressure drops (or a continuous pressure drop) as it moves from the formation through the perforations into the well casing. Flow up the production tubing causes further pressure drops. Flow through sub-surface safety valves and production chokes in the Christmas tree result in further pressure drops. Finally, the actual discharge to the environment also causes a pressure drop on the water. These pressure drops result in changes in the produced water composition. Gases such as carbon dioxide, hydrogen sulfide, and the BTEX compounds constantly re-distribute themselves between the liquid and gaseous phases as pressure drops occur. This results in a constantly changing composition of the water and changes in such parameters as pH. Errors may occur if an analytical method assumes that concentrations of oil and grease indicators, and their proportional relationship to the oil and grease content remain constant. For example, the produced water may have a sizable BTEX content measured by UV fluorescence as an indicator of oil and grease. BTEX concentrations may be highly variable, however, because of gas phase partitioning and such variability will not, in general, coincide with variability in oil and grease content. Since it is unclear which aromatic molecules contribute strongly to UV measurements of oil and grease, the importance of this effect is not known.

Another composition variable that might affect oil and grease analyses is the ratio of carboxylic acids to total oil and grease. The Ten Platform Study (EPA, 1981) shows that the concentration of polar (soluble) materials in treated streams ranged from 17.7% to 89.5%, and the average for the ten platforms was 59.4%. Oil removal processes tend to remove a higher proportion of the dispersed or insoluble materials because they are usually present in larger droplets. Therefore, the untreated water must have contained much lower ratios of polar materials to oil and grease. The impact of this situation on an oil and grease analysis is that there may be a different calibration factor for untreated water than there is for treated water for methods using IR absorbance. The fact that this has not been reported could mean that the difference is not significant, or perhaps has just not been examined previously.

Production treatment systems can vary widely. Some are contained on a single platform, treating the production from a relatively few wells. Others are very large treatment systems at a central facility, treating the production from a number of platforms and, perhaps, hundreds of wells. The character of produced water tends to vary from one formation to another. There is an easily observable difference in the character of water from gas platforms and oil platforms, as the Ten Platform Study demonstrated. If a platform includes a small number of wells that produced both oil and gas, then the daily nature of the water discharged from that platform can change significantly, depending on the number and type of wells producing at any given time. Large, central facilities produce from so many wells that variation due to turning wells on and off are smoothed out. Therefore, short-term variations in composition are not an important factor in determining the accuracy of an oil and grease monitoring method for large facilities. However, for smaller systems, one should ensure that the oil and grease analytical method chosen is not affected by the type of changes in composition that the platform is likely to experience.

Since some of the oil and grease components are in dispersed droplets, sampling procedures are especially important. After sampling, oil droplets tend to absorb onto the surface of the sampling container. Therefore, if an extractive method is used, the container must be extracted as well as the water in it and samples must never be subdivided. If a method is used that analyzes oil and grease in-situ, without extraction, this consideration may not be as important if a dispersant is added before subdividing. If a dispersant is not used, samples for measurement without an extraction step should be analyzed soon after sampling.

Section 3

ANALYTICAL TECHNOLOGIES FOR OIL AND GREASE MEASUREMENT

There are a number of properties of the constituents of oil and grease that can be measured to determine oil and grease concentrations. These include:

- absorbance of visible light,
- absorbance of infra red energy,
- absorbance of ultra violet energy,
- ultra violet fluorescence,
- absorbance of radio frequencies,
- absorbance of microwaves,
- scattering of energy beams including visible light, infra red, radio frequencies and microwaves,
- refractive index, and
- weight.

Contrary to popular belief, there is no standard field method currently in use. Popular opinion holds that "the IR method" is presently used in the field. However, observation at a number of field sites reveals that no single method is practiced. What is practiced is some variation of:

- acidification of the water sample with hydrochloric acid to a pH near 1,
- extraction with Freon 113®, and
- measurement of infra red absorbance using instruments such as Wilks Miran, Horiba, or similar infra red spectrophotometers rugged and simple enough to use offshore. This measurement is done using a cuvette filled with extractant that is inserted into the machine.

These instruments are usually calibrated with produced hydrocarbons (crude oil or condensate from the platform where discharge takes place). The concentrations determined with the field instrument are correlated with EPA 413.1 to determine oil and grease.

These field applications do not form a single method for oil and grease because they differ in a number of ways from location to location. These differences include:

- the ratio of extraction solvent volume to sample volume,
- the volume of the water sample, and
- the amount of mixing used in extracting the oil.

There is no standard procedure recognized by a significant number of users for this general way of determining oil and grease in produced water. The problem with these traditional procedures is that they depend on the use of a solvent that does not contain carbon-hydrogen (C-H) bonds. Since the infra red instruments measure the number of C-H bonds present, a solvent containing such bonds would make it impossible to distinguish oil and grease from extraction solvent. Replacing these traditional procedures then means that one of three approaches must be used:

- finding an acceptable solvent to replace Freon 113® that does not contain C-H bonds,
- removing the solvent from the extractant before making infra red measurements, or
- finding another measurement principle on which to base oil and grease determinations.

The first of these options is not technically different from the present method using Freon 113®. In Europe, methods using perchloroethylene are already being used. Some operators may not want to use this option because of other considerations besides analytical technology. For example, it is possible that perchloroethylene will be banned in the future, or disposing of used solvent offshore may be a problem. Since such considerations are outside the scope of this study and the technology for applying perchloroethylene to oil and grease analysis is already well developed, it will not be considered further in this study. The other two options are discussed below.

It was decided to limit this study to technologies that had already been successfully applied to oil and grease measurement by more than one manufacturer. That is, the objective is to find existing technology for measuring oil and grease. Studying new technologies or experimental technologies would take more resources than are available for this work. Weight measurement is the basis for the present EPA methods for oil and grease (Method 413.1 and Method 1664). Obviously the EPA methods are unsuitable as field methods and are used in this study only as a standard against which to compare the field methods being studied.

No manufacturers of instruments using measurements of radio frequencies or microwaves were found and therefore these energy sources were discounted as being suitable for inclusion in this study. One instrument was identified which used a refractive index measurement but it had no competitors and was not widely applied when this study started. Therefore, it was not included in further considerations in the search for suitable methods to test.

Separate phase particulate matter dispersed in a liquid will scatter energy beams (light, infra red, microwave, and radio frequency). This particulate matter can be solid particles or liquid (oil) droplets. The amount of energy scattered is a function of the concentration of the particulate matter and the particle sizes. The amount of energy scattered can be determined by measuring the reduction in energy transmission (turbidity) or by measuring the amount of energy diverted away from the original beam direction (nephelometry). Although several technologies make use of such measurements, they were not included in this study. A significant portion of the oil and grease in produced water can be dissolved and therefore would not be measured by technologies using energy beam scattering measurements. Therefore, all energy beam scattering measurement methods are excluded from this study because they do not measure all the components of oil and grease.

Absorbance of visible light (colorimetry) has been used to measure oil and grease for many years. Operators in areas with heavy oil production such as western Canada, California, and eastern Venezuela routinely use colorimetry to measure oil in produced water. A major supplier of field test kits widely used in the oil and gas industry by both operating companies and oilfield chemical suppliers furnishes an instrument that makes use of this measurement method. A well-known supplier of laboratory instruments markets a spectrophotometer that is used in Venezuela to measure oil and grease in produced water. These instruments have been sold for over 30 years. The problem with colorimetry is that the oil must be dark enough to yield an acceptable instrument response. Very heavy crude oils such as those in the places listed above are black in color and strongly absorb light. Most light crude oils are not dark enough to measure with colorimetry. If a typical Gulf of Mexico produced water was extracted with hexane at a ratio of 1 volume of hexane to 10 volumes of produced water, a concentration of oil in the produced water of 25 to 50 parts per million would be required to get an instrument response statistically different from zero. Over 100 parts per million of condensate from gas production would be required to yield a statistically significant response. Clearly, such responses are not sufficient for measuring oil and grease in the range needed in production operations.

One instrument was identified that uses a refractive index measurement for quantifying oil and grease. Only one such instrument was located and it does not have a long history of application. Therefore, this instrument was not included in this study.

After eliminating the measurement methods discussed above, only three technologies (see Table 3.1) remained. Two were chosen to be studied in this project: those based on IR absorbance and UV fluorescence. These were chosen based on the reasoning explained in Section 1. Testing of technologies based on these two measurement principles will illustrate the problems that must be addressed in the evaluation of any oil and grease measurement technology. Since there appears to be no single technology clearly superior to all the others, it is important to illustrate the differences between these two and to explore their strengths and weaknesses so that operators can have a basis for choosing an instrument that best fits their needs.

EPA Method 1664 (EPA, 1995) provides the basis for the definition of oil and grease. Potential replacements for the IR method used by many operators for the last 20 years will be compared with this defining method. The property used to measure oil and grease under Method 1664 is its weight. That is, this method uses gravimetry as the quantifying parameter. From the three measurement methods remaining after eliminating those that do not fit the requirements of this study two will be chosen for further evaluation. These all rely on a spectrophotometric measurement and a comparison is shown in Table 3-1. Each measurement method has limitations caused by both the technology itself and by the intended application.

In the measurement of oil and grease in produced water, the impact of the properties and peculiarities of produced water on the analytical technology need to be considered. The measurement principles of the chosen technologies are already well understood (Silverstein, et al., 1974; Brost, 1996) and this review will focus on applications to produced water. Furthermore, only off-line analysis of discrete samples will be considered. On-line instrumentation is not within the scope of this study. Depending on the technology used, the sample analysis may be done with or without the use of an extraction solvent. From the measurement principles listed, two were selected (see discussion in Section 4) for application to produced water, and in turn an instrument using the chosen principle is recommended (see Section 4) for the laboratory testing phase.

Table 3-1. Analytical Measurement Principles for Oil and Grease Concentration

Comments	IR Absorbance	UV Absorbance	UV Fluorescence
Target Material	C-H Aliphatic Hydrocarbons	Aromatic Compounds	Aromatic Compounds
Advantages	Measures the major oil components directly; calibrates to most oils; widely used	Can be solvent free; can use hydrocarbon solvents including hexane; ease of use	Can be solvent free; can use hydrocarbon solvents including hexane; ease of use
Limitations	Requires C-H free solvent or complete solvent removal	Non oils may absorb (e.g., iron); requires constant aromatic/oil ratio	Non oil interferences (e.g., treating chemicals); requires constant aromatic/oil ratio

DISCUSSION OF ACCEPTABLE MEASUREMENT PRINCIPLES

Infrared (IR) Absorbance

Carbon-Hydrogen bonds (C-H bonds) absorb electromagnetic energy at a wavelength of 3.4 micrometers (microns). The more bonds present, the more energy that is absorbed. Since all components of oil and grease contain these bonds, the measured IR absorbance at 3.4 microns is proportional to the concentration of oil and grease. This proportionality, however, is not constant for all compositions of oil and grease. Unfortunately, water also absorbs energy at this wavelength. Before an analysis can be made, the components of oil and grease must first be extracted from water into a solvent that does not absorb IR energy. Alternatively, the extraction can be made using a solvent of suitable volatility and then the solvent is evaporated and the oil and grease residue is placed on a surface that is transparent to IR energy. The absorption of IR by this oil and grease residue can then be determined.

The distinct advantage of this technique is that it detects **ALL** of the major oil components. Since some components of oil and grease also contain carbon-carbon double bonds, oxygen or nitrogen, an exact measurement is not possible without a calibration relationship that depends on the exact composition of the oil and grease. For example, octane (C_8H_{18}) has a different number of C-H bonds for unit weight than does octanoic acid ($C_8H_{16}OOH$). Therefore, IR absorbance is not a direct method for oil and grease and must depend on a calibration curve that relates IR instrument measurements to the defined oil and grease concentration. For most produced waters, calibration curves will be similar. The largest difference is between heavy oil production and gas condensate production. With the right calibration curve, total oil is measured including either insoluble or dispersed oil and water soluble oil including water soluble organics (WSO).

Limitations include the requirement for an IR transparent solvent or the need to completely evaporate the solvent from the residue. Separation of insoluble or dispersed oil from WSO such as organic acids would require the use of additional sample treatment techniques such as filtration and/or absorption, or more than one wavelength for the measurement (e.g., 3.4 microns for the C-H hydrocarbon band, and 6.0 microns for the C=O carbonyl band).

Ultraviolet (UV) Absorbance

The ultraviolet absorbance method of measurement is based on the absorbance of light in the ultraviolet region of the spectrum (200 - 450 nanometers) by the material being analyzed. The material is dissolved in a solution that is transparent or has low absorption of light at the UV wavelength of the measurement. For the analysis of oil and grease in water, the technique generally involves either direct analysis of the water sample (a non UV absorbing surfactant can be added to the water sample to solubilize all the oil), or extraction of the acidified sample with a solvent that is sufficiently transparent in the UV spectral region. The chemical species that absorb at 200 to 450 nanometer wavelengths are usually aromatic compounds. Since most of the components of oil and grease are not aromatic compounds, it must be assumed that the ratio of aromatic compounds to total oil is constant. Not all aromatic compounds absorbs UV energy with the same efficiency. For example, single ring compounds do not absorb as strongly as multi-ring compounds. Therefore, one must be careful about drawing general conclusions about the effect of composition on oil and grease concentration measurements without specific experimental data. As is the case for IR absorbance, a calibration curve must be developed between the instrument readings and the defined oil and grease concentration for the specific site.

Advantages of this technique include high sensitivity and selectivity (e.g., aromatics in the oil can be detected in the presence of saturated hydrocarbons, which include solvents such as n-hexane). Direct analysis, without solvent extraction of the water sample, can also be a major advantage when interferences are not a problem. If the ratio of fluorophors to the other components remains constant, then both insoluble and dispersed oil and water soluble oil can be correlated.

Limitations include the requirement for constant ratio of aromatic hydrocarbons to oil and grease present, and potential interferences from non-oil UV absorbers, for example, iron (III). Turbidity could also be an interference when using the direct measurement mode.

Ultraviolet (UV) Fluorescence

The ultraviolet fluorescence method of measurement is based on the absorbance of light in the ultraviolet region and subsequent fluorescent emission of light at discrete wavelengths by the material being analyzed. The material is dissolved in a solution that is transparent or has low absorption of light at the UV wavelength of the measurement. The technique generally involves either direct analysis of the water sample (a non fluorescent surfactant can be added to the water sample to solubilize all the oil), or extraction of the acidified sample with a suitable non-fluorescent solvent that is sufficiently transparent in the UV spectral region. The aromatic hydrocarbons in the oil absorb light and then emit fluorescent light, which is detected and measured using a suitable calibrant; thus for the analysis of oil and grease in water, the aromatic hydrocarbons in the oil are measured.

Advantages of this technique include high sensitivity and selectivity (also, aromatics in the oil can be detected in the presence of saturated hydrocarbon solvents such as n-hexane). Direct analysis without solvent extraction of the water sample can also be advantageous when interferences are not a problem. Either insoluble or dispersed oil and water soluble oil can be correlated. This method has less sensitivity to the presence of iron in the water than UV absorbance.

Limitations include the requirement for constant ratio of aromatic hydrocarbons to oil and grease present. In addition, if the direct non-solvent technique is used, errors can arise from potential interferences from non-oil fluorescent substances and other materials such as, for example, humic materials, and highly turbid waters.

SELECTION OF TECHNOLOGIES FOR FURTHER STUDY

There is no technology that could universally be termed the best choice for measuring oil and grease in the field. Technologies using all three of the measurement techniques listed above have been successfully applied somewhere. Two technologies were chosen to be tested in this study:

- those using IR absorbance, and
- those using UV fluorescence.

All the others except UV absorbance were eliminated for the reasons discussed above. Since there is no unique best field method the objective of the study is to show the impact of produced water composition and properties on these two types of measurement technology and examine their advantages and disadvantages. The use of these two technologies allows a comparison of:

- IR versus UV,
- Absorbance versus fluorescence,
- Extraction versus in-situ measurements,
- Direct detection of oil and grease components versus detection of proportional surrogates, and
- Evaporation of extraction solvent versus no measurement in extractant.

Test data taken using the two selected technologies, both on synthetic produced waters and actual produced waters, not only provide information on the specific technologies tested, but will give information on the impact of the factors listed above on any technology using the same measurement principle. This will aid operators in doing their own tests of instruments they wish to evaluate.

Section 4
ANALYTICAL INSTRUMENTATION FOR OIL AND GREASE MEASUREMENT

SELECTION OF ANALYTICAL INSTRUMENTS FOR FURTHER STUDY

After selection of the measurement methods and technologies using them (Section 3), the next step was to locate commercial instruments that apply these technologies to the measurement of oil and grease in produced water. There are several suppliers of instruments that use each of the selected technologies. It is not possible to determine the best two instruments for this study since such a determination is subjective and depends on specific local needs, preferences, and operability considerations as well as the technical limitations of the technology. For example, an instrument that was extremely easy for field personnel to operate might be more desirable to an operator than an instrument that was more widely applicable and gave results that are more direct. It is also important that little waste material for disposal is produced. It is also important to consider instruments that produced acceptable results that allowed the operators to control their treatment processes and determined whether or not they were maintaining compliance with discharge limits reliably at a specific discharge point.

Two specific instruments are recommended for the planned laboratory and field evaluations, Instrument 1 and Instrument 4 in Table 4-1. These instruments were chosen not because they are the best representatives of their technology, but because they are the most convenient instruments to study of the ones examined. They meet the criteria listed below. The criteria used in this selection are:

- representative of currently acceptable technology for this application,
- availability of manufacturer technical support for the instrument,
- availability of manufacturer/suppliers field support for the instrument,
- suitability of the instrument for field work (size, weight, reliability, operability).

Most of the instruments examined acceptably meet these criteria and are worthy of consideration by users of this equipment. However, the two instruments selected are apparently the most convenient for use in this study.

ANALYTICAL INSTRUMENTS

Numerous instruments using the selected technologies and from a number of manufacturers can be applied to the measurement of oil and grease. It is not the purpose of this review to provide a comprehensive list of all the available instrumentation, but rather to demonstrate a representative set of the available instrumentation for the various technologies discussed above. A selection of instruments that meet the criteria are described in Table 4.1.

Table 4-1. Analytical Instruments for Oil and Grease Measurement

Instrument	Instrument 1	Instrument 2	Instrument 3	Instrument 4	Instrument 5
Technology	IR Absorbance	UV Absorbance	UV Absorbance	UV Fluorescence	UV Fluorescence
Target Material Measured	Aliphatic C-H bonds	Aromatic compounds	Aromatic compounds	Aromatic compounds	Aromatic compounds
Method	Hexane extraction; Evaporation on plate or card; IR unit	Extraction or surfactant addition; fiber optic UV probe	Extraction or surfactant addition; UV cell	Extraction or surfactant addition; UV cell	Extraction or surfactant addition; UV cell
Calibration: Instrument Correlation	Produced oil or standard oil; 1664 or other	Produced oil or standard oil; 1664 or other	Produced oil or standard oil; 1664 or other	Proprietary compound; Produced oil or standard oil; 1664 or other	Produced oil or standard oil; 1664 or other
Nominal Detection Limit	10 mg/l **	1 mg/l	1 mg/l	1 mg/l	1 mg/l
Footprint Weight	6x6x4 in. < 5 lb.	4x13x15 in. 5 lb.	16.5x11x6 in. 20 lb.	9x11x8 in. 13 lb.	15x10.5x5.5 5 lb.
Tech Support	good tech o.k. field	? tech good field	good tech. ? field	Good tech. o.k. field	? tech. ? field

** Dependent on the extraction ratio used and the mass loading of the extract to the sample volume. May be as low as 5 mg/l.

The instruments discussed are all capable of measuring oil and grease in produced water. While both off-line and on-line instruments are available, only off-line instruments considered suitable for field application are included. Safety and toxicity warnings for equipment and chemicals, which are used with the instrumentation described in this section, are supplied by the manufacturers.

IR-ABSORBANCE INSTRUMENTATION

Instrument 1

Measurement Principle: IR Absorbance

Size/Footprint/Power: A compact unit 6 x 6 x 4 inches and weighs less than 5 pounds. Runs on 12 volt dc. power supplies-requiring less than 20 watts. Supplied with a plug-in inverter to operate off normal 115 volt a/c. power.

Analytical Methodology: Oil is extracted from an acidified sample into n-hexane usually by applying a 10:1 sample to hexane ratio. A 50-100 micro-liter portion of the hexane extract is taken and placed on a sapphire plate, or alternative, both of which can be supplied by the manufacturer. The hexane is removed from the oil extract by evaporation at ambient temperature. The oil is measured by its absorption at 3.4 microns, and the concentration determined by comparison with a suitable calibration standard, the data for which may be stored internally in the instrument. Calibration standards, for example, could be a sample of the oil being determined in the sample or other selected oil, or possibly a hydrocarbon mixture such as iso-octane/toluene. The manufacturer can provide a detailed analytical procedure. Correlation to EPA Method 1664 is done by comparing the IR absorbance result to the oil concentration of the sample as measured by Method 1664.

Detectable Nominal Concentration Level: 10 mg/l

Potential Interferences: Residual hexane solvent measured as oil, if not completely removed.

Strengths: Hydrocarbons, the major oil components, are directly detected by their C-H bond absorption; the basic IR technology has been widely used in the past and its use has a large amount of historical experience in the oil and gas industry.

Weaknesses: Requires a compatible IR transparent (usually C-H free) solvent, or complete solvent removal. Non hydrocarbon organics and/or traces of water may distort the calibration if not properly accounted for. The effects of changing ratios of oxygenate fractions of oil and grease to total oil and grease on calibrations are not known.

UV-ABSORBANCE INSTRUMENTATION

Instrument 2

Measurement Principle: UV Absorbance of aromatic hydrocarbons

Size/Footprint/Power: The unit is 4 x 13 x 15 inches, and weighs less than 5 pounds; runs on 115 volt a/c. power.

Analytical Methodology: Oil is extracted from an acidified sample into n-hexane, or other UV transparent solvent. Absorbance is measured by placing a fiber-optic probe into the solvent extract. Alternatively, a solvent-free procedure can be used in which the sample is collected in a bottle that has been treated with acid and a non-UV-absorbing surfactant. A fiber-optic probe is placed into the treated water sample for the measurement. The concentration of oil in the extract (or sample, if no solvent extraction is done) is determined by comparison with the absorbance obtained for a suitable calibration standard. A crude oil of the type present in the water being analyzed can be used for calibration when the solvent extraction technique is used. However if the solvent-free technique is used, calibration is done by correlating the absorbance of the sample to the oil concentration of the sample as measured by another method, such as the gravimetric EPA Method 1664. A detailed analytical procedure can be provided by the manufacturer.

Detectable Nominal Concentration Level: 1 mg/l

Potential Interferences: Non-oil interferences, for example, iron (III) if present can interfere in the solvent-free mode; significant variations in the ratio of aromatic to total hydrocarbons in the sample; in the solvent-free mode, turbidity can cause interference in reading the sample absorbance thus requiring filtration of the surfactant treated sample before reading.

Strengths: Method can be run on most UV absorption spectrometers; sensitive to components of free oil and to water soluble organics. Can give separate absorbancies for each phase.

Weaknesses: The method is very dependent on maintaining a relatively constant relationship in the ratio of aromatic: total hydrocarbon (oil) in the calibrating solution, versus that which exists in the sample stream, over an extended time.

Instrument 3

Measurement Principle: UV Absorbance of aromatic hydrocarbons

Size/Footprint/Power: Unit is 16.5 x 11.4x 6.3 inches and weighs 20 pounds; AC line power selectable for 115/230 V a/c, 50/60 Hz.

Analytical Methodology: Oil is extracted from an acidified sample into n-hexane, or other UV transparent solvent. Absorbance is measured by placing the sample extract into a disposable plastic sample cell (six position Carousel available). Alternatively, a solvent-free procedure can be used in which the sample is collected in a bottle that has been treated with acid and a non-UV-absorbing surfactant. Since the manufacturer does not currently provide the surfactant, it would have to be obtained independently. The concentration of oil in the extract (or sample, if no solvent extraction is done) is determined by comparison with the absorbance obtained for a suitable calibration standard. A crude oil of the type present in the water being analyzed can be used for calibration when the solvent extraction technique is used. If the solvent-free technique is used, calibration is done by correlating the absorbance of the sample to the oil concentration of the sample as measured by another method, such as the gravimetric EPA Method 1664. A detailed analytical procedure specifically for oil and grease is not currently available from the supplier of this instrument.

Detectable Nominal Concentration Level: 1 mg/l

Potential Interferences: Non-oil interferences, for example, Iron III if present can interfere in the solvent-free mode; significant variations in the ratio of aromatic to total hydrocarbons in the sample; in the solvent-free mode, turbidity can cause interference in reading the sample absorbance thus requiring filtration of the surfactant treated sample before reading.

Strengths: Method can be run on most UV absorption spectrometers; sensitive to components of free oil and to water soluble organics. Can give separate absorbancies for each phase.

Weaknesses: Requires suitable aromatic/oil calibration, and a sufficiently constant aromatic to oil ratio between the time the instrument is calibrated and the time that the sample is analyzed. Calibration must be done by correlation to a separate method for oil and grease, for example, by gravimetry as in EPA Method 1664.

UV-FLUORESCENCE INSTRUMENTATION

Instrument 4

Measurement Principle: UV Fluorescence of aromatic hydrocarbons

Size/Footprint/Power: Unit is compact 9.25 x 11x 8.25 inches and weighs 13 pounds; External power supply, 100-240 V a/c, max 30 Watts.

Analytical Methodology: Oil is measured either directly in the produced water or in an extract of the sample. For extraction, the oil is extracted from an acidified sample into n-hexane, or other non-UV-fluorescing solvents. Absorbance is measured by placing the sample extract in a disposable plastic sample cell. Alternatively, a solvent-free procedure can be used. The concentration of oil in the extract (or sample, if no solvent extraction is done) is determined by comparison with the fluorescence obtained for a suitable calibration standard. A crude oil of the type present in the water being analyzed can be used for calibration when the solvent extraction technique is used. If the solvent-free technique is used, the manufacturer provides a proprietary compound for calibrations. Correlation to EPA Method 1664 is done by correlating the fluorescence of the sample to the oil concentration of the sample as measured by EPA Method 1664. A detailed analytical procedure for oil and grease is available from the supplier.

Detectable Nominal Concentration Level: 1 mg/l

Potential Interferences: Non-oil interferences, for example, in the solvent-free mode naturally occurring organic materials can fluoresce and interfere, and highly turbid samples (> 400 NTU) can interfere; varying amounts of aromatic to total hydrocarbons in the sample can result in error. Variations in dissolved oxygen and iron content can cause errors.

Strengths: Less susceptible to turbidity effects than UV absorbance; can be used in the solvent-free mode; sensitive to components of free oil and water soluble organics.

Weaknesses: Requires suitable aromatic/oil calibration, and a sufficiently constant aromatic to oil ratio between the time the instrument is calibrated and the time that the sample is analyzed. Calibration must be done by correlation to a separate method for oil and grease, for example, by gravimetry as in EPA Method 1664. Since fluorescence intensity can be affected by temperature, samples should be measured at constant temperature.

Instrument 5

Measurement Principle: UV Fluorescence of aromatic hydrocarbons

Size/Footprint/Power: Unit is 15 x 10.5 x 5.5 inches and weighs about 5 pounds; AC Power 115/230 V a/c, 50/60 Hz.

Analytical Methodology: A solvent-free procedure is used in which the sample is collected in a bottle that has been treated with a non-UV-fluorescent surfactant. Acid can be added to preserve the sample and to dissolve some types of suspended solids. The samples are placed in curettes for the measurement. The concentration of oil in the sample is determined by comparison of the fluorescence to the oil concentration of the sample as measured by another method, such as the gravimetric EPA Method 1664. A detailed analytical procedure can be provided by the manufacturer, as shown in the Appendix.

Detectable Nominal Concentration Level: 1 mg/l

Potential Interferences: Non-oil interferences, for example, naturally occurring organic materials can fluoresce and interfere, and highly turbid samples (> 400 NTU) can interfere; varying amounts of aromatic to total hydrocarbons in the sample can result in error. Variations in dissolved oxygen and iron content can cause errors.

Strengths: Less susceptible to turbidity effects than UV absorbance; can be used in the solvent-free mode; sensitive to components of free oil and water soluble organics.

Weaknesses: Requires suitable aromatic/oil calibration, and a sufficiently constant aromatic to oil ratio between the time the instrument is calibrated and the time that the sample is analyzed. Calibration must be done by correlation to a separate method for oil and grease, for example, by gravimetry as in EPA Method 1664. Since fluorescence intensity can be affected by temperature, samples should be measured at constant temperature.

Section 5

LABORATORY TESTING PROGRAM FOR SELECTED TECHNOLOGIES AND INSTRUMENTS

INTRODUCTION

The objective of the laboratory testing program is to:

- examine the response of the chosen instruments to known factors in produced water that might affect oil and grease determinations, and
- develop familiarity and hands-on experience with the instruments.

The factors recommended for inclusion in this program are:

- dispersed oil concentration,
- water soluble organic (WSO) concentration,
- aromatic component concentration, and
- interferences such as iron.

The laboratory testing program will evaluate the selected instruments and their technologies under controlled conditions that serve to manage and minimize interferences that might be encountered in the field. These include sampling and sample stability, oil and grease composition, produced water composition, matrix interferences, calibration and other variables. In addition, laboratory procedures made available by the manufacturers can be tested against the protocols outlined in this report.

The plan is to develop a sample matrix including the variables listed above, analyze the samples using both test instruments and the standard EPA Method 1664, and examine the data for trends that can be correlated to the test variables. The test samples will consist of the following, in various ratios (see Table 5-1):

- synthetic sea water with pH adjustment to 6.5,
- various concentrations of a crude oil (medium, 30-35° API gravity Gulf of Mexico crude oil),
- WSO (hexanoic acid, and 1-naphthalene acetic acid, 80/20 W%), and
- interferences (iron).

After laboratory testing of the synthetic produced water, samples will be collected from offshore platforms and analyzed in the laboratory to test the instrumental procedures on actual produced water samples. Three platforms will be used. They will be chosen according to the same guidelines developed for field site selection and testing (Section 6).

CALIBRATION

Calibration is a critical component of any analytical measurement. Appropriate calibration involves standardizing the instrument response, as well as the correlation of the analytical result to the true amount of the analyte of interest present in the sample. In the analysis for oil and grease, calibration is complicated by the fact that the analyte is not a single component, but is a multi-component material, which is defined by the method of analysis. In this case, oil and grease is defined by the EPA method of n-hexane solvent extraction-gravimetry.

As a means of clarification, the calibration procedure should be viewed as two separate, but equally important steps: (1) setting the instrument to yield reproducible numbers covering the range of interest, and (2) correlating the numbers yielded by the instrument to true oil and grease concentrations obtained using Method 1664. There is no technology or instrument that is not subject to both of these processes. Experience with field IR instruments in particular has fostered the idea that these instruments can be directly calibrated with the crude oil from the platform discharging the water. This false notion results from the mistaken belief that the oil in the produced water is crude oil. Rather, the oil in produced water contains varying levels and components of crude oil, depending on the type and level of treatment; it is never entirely made up of crude oil. Operators must correlate the readings gained in the field with the results of either EPA 413.1 or EPA 1664 methods to get the true concentrations of oil and grease measured. This use of Methods 413.1 and 1664 to ***define*** oil and grease is the single most important concept of this measurement. It is the only way of distinguishing oil and grease from all of the other organic components that can be present in produced water. All IR absorbance methods, UV absorbance methods and UV fluorescence methods share this same requirement. None has an advantage over another in this regard.

In setting the instrument, the objective is to make the instrument respond over the entire oil and grease concentration range of interest and to do it so that the readings can be reproduced. There is no single correct standard for setting instrument response. For IR instruments, the crude oil on the platform is acceptable since it contains C-H bonds. Single hydrocarbon components or mixtures of them can also be used. A standard crude oil representative of the oils produced in the area could also be used. It might be more convenient to use an artificial standard mixture similar to the ones discussed in the sample matrix below, that is, a mixture containing different amounts of crude oil, carboxylic acids, and aromatic compounds. For UV methods, it is important to choose a standard for setting the instrument that has UV absorbing and fluorescing compounds in a concentration range similar to those in produced water. This could be done using produced water extracts or an artificial mix. Unless the source of the oil being produced is relatively constant, the crude oil from the system producing the discharged water should not be used.

To convert the instrument readings to oil and grease concentrations, correlations must be made between the instrument readings (concentrations) and the results of method 1664 run on duplicate samples. For this calibration technique, duplicate samples of produced water are analyzed, where one sample set is analyzed by EPA 1664 and the other is analyzed by the method being calibrated. The results of these analyses are then correlated to give the relationship between the reference method and the method being calibrated.

INSTRUMENTATION, EQUIPMENT, AND REAGENTS

Instruments

The instruments chosen for comparative evaluation are:

- Instrument 1 (see Table 4-1) using IR absorbance measurements, and
- Instrument 4 using UV fluorescence measurements.

The instrument operating procedures used to do the laboratory work should follow the latest recommendations of the instrument supplier. These procedures should be fully documented and presented in the final report of this project. In addition, all the necessary equipment used with each instrument should be listed and its function explained.

Standards and Calibration Procedures

The specific calibration procedures for setting the instrument should be followed. Necessary modifications to the manufacturer's protocols should be agreed in advance. The following standards can be used for setting the instrument response subject to agreement with the manufacturer:

1) Instrument 1:

Crude Oil Standard in Hexane (COS-H): Prepare in n-hexane a concentration of 4 mg/ml of crude oil (Gulf of Mexico dark crude of 30-35 API Gravity). Place 400 +/- 4 mg crude oil in 100-ml volumetric flask and fill to the mark with n-hexane. Store refrigerated in a glass bottle with PTFE-lined screw cap. Working standards of this stock standard are prepared by dilution with n-hexane to make oil concentrations in n-hexane in the same range that would result from extraction of a water sample containing 10 to 100 mg/l oil.

Paraffinic Hydrocarbon Standard in Hexane (PHS-H): Prepare in n-hexane a concentration of 4 mg/ml of n-hexadecane. Place 400 +/- 4 mg of n-hexadecane in 100-ml volumetric flask and fill to the mark with n-hexane. Store refrigerated in a glass bottle with PTFE-lined screw cap. Working standards of this stock standard are prepared by dilution with n-hexane to make n-hexadecane concentrations in n-hexane in the same range that would result from extraction of a water sample containing 10 to 100 mg/l hydrocarbon.

These methods are intended to provide a calibration of instrument response. Once the data have been gathered, the manufacturer should be consulted on how to input the resulting calibration curve into the instrument memory. After instrument calibration, the instrument can then be used to collect data on the sample matrix. In addition to the instrument calibration methods listed above, the manufacturer's preferred procedure should also be considered.

2) Instrument 4:

Crude Oil Standard: Weigh 100 mg of Gulf of Mexico dark crude (30-35° API gravity) into a 100 ml volumetric flask. Add 1.0 ml of methylene chloride (DCM) and mix well. Make up to final volume (100 ml) with acetone. From this 1000 mg/L oil stock solution, make standards of 15, 30 and 60 mg/l by transferring an appropriate aliquot (volumetrically) to 100 ml flasks. Dilute the final volume with a synthetic sea water spiked with sodium chloride to a total dissolved solids (TDS) of 100,000 ppm which has been prepared using the method developed for work being done on the API project for the treatment of non produced fluids.

Aromatic Hydrocarbon Standard in Isopropanol (AHS-I): Prepare in isopropanol a concentration of 4 mg/ml of naphthalene. Place 400 +/- 4 mg of naphthalene in 100-ml volumetric flask and fill to the mark with isopropanol. Store refrigerated in a glass bottle with PTFE-lined screw cap. Working standards of this stock standard are prepared by dilution with synthetic seawater to make naphthalene concentrations in the range 10 mg/l to 100 mg/l.

Once the instrument calibration has been done it can be used for the laboratory sample matrix determinations. The manufacturer's preferred method should also be considered.

LABORATORY PREPARED TEST SAMPLES

The methods selected for testing will first be tested on synthetic produced water samples especially prepared to contain:

- Dispersed crude oil,
- Carboxylic acids, and
- An aromatic compound

at several concentration levels and ratios to each other. These synthetic samples will allow a study of the response of the instruments to changes in these produced water composition factors.

The synthetic produced water samples used in this study are prepared as follows:

The water is synthetic sea water with adjusted TDS levels to 100,000 ppm with sodium chloride and pH adjusted to 6.5 that is spiked with various levels of a Gulf of Mexico dark crude of 30-35 API Gravity. Also added are various levels of hexanoic acid and 1-naphthyl acetic acid as WSO components (in a ratio of 80/20 weight %). A stock solution of oil is first separately prepared using the method developed for work done on the API Non Produced Fluids Project. Samples are then prepared by adding appropriate concentrations of WSO and diluting with synthetic seawater to the concentration shown in Table 5.1. The produced water formulations are prepared at each test concentration in individual glass bottles with aluminum foil lined caps and mixed vigorously before sampling for analysis. The test samples are thus prepared as individual grab samples in the same way that actual samples are collected as grab samples. Samples should be freshly prepared at the beginning of the analyses. Sub-sampling of the formulation is not done because of the tendency of oil to adhere to the walls of the container. Sufficient sample sets are prepared to allow comparison testing of Instrument 1 and Instrument 4 as well as to carry out Method 1664, with appropriate sample sizes and containers for each method.

Table 5-1. Lab Prepared Produced Water Composition for Oil and Grease TestingOil\WSO, mg/l

60\0	60\15	60\30	60\60
45\0	45\15	45\30	45\60
30\0	30\15	30\30	30\60
15\0	15\15	15\30	15\60
0\0	0\15	0\30	0\60

Note:

Water Soluble Organic (WSO):

(Hexanoic Acid/1-Naphthalene Acetic Acid, 80/20 % Wt.)

Oil is a medium, 30-35 API Gravity Gulf of Mexico crude oil, low in WSO

Water is salt and pH adjusted water (seawater composition)

Test samples to assess potential interferences from iron are prepared by spiking the following Oil/WSO synthetic produced water formulations:

30/0 mg/l (Oil/WSO) spiked to contain 5 mg/l Iron (III)
30/0 mg/l (Oil/WSO) spiked to contain 50 mg/l Iron (III)
30/30 mg/l (Oil/WSO) spiked to contain 5 mg/l Iron (III)
30/30 mg/l (Oil/WSO) spiked to contain 50 mg/l Iron (III)

TESTING PROTOCOL

The proposed testing protocol is summarized in the matrix described in Table 5-2. Procedures should also follow operating instructions provided by each instrument manufacturer. In those cases, where the instrumental method can be used either directly on the sample without extraction (e.g., UV-fluorescence), or after extraction of the sample, both techniques should be evaluated using the matrix given below. As this proposed testing array proceeds, it could be modified as insight is gained into the importance of the factors being studied. If it is possible to drop some of the proposed analyses, then the savings in samples might be used to compare the methods under study with the IR method currently being used and in comparing IR analyses using Freon extraction and subsequent evaporation with the traditional method. The numbers of samples in the proposed Testing matrix are as follows:

20 concentrations X 3 methods (with extraction) X 2 duplicates = 120 samples
20 concentrations X 1 method (without extraction) X 2 duplicates = 40 samples
2 concentrations X 2 Iron (III) concentrations X 1 method (without extraction) X 2 duplicates = 8 samples
<u>Total = 168</u> samples

Table 5-2. Testing Protocol Matrix (mg/l Oil Measured)

Sample	Instrument 1	Instrument 4	Method 1664
Synthetic Produced Water 20 concentrations x 2 (duplicates)	E	E and D	E
Synthetic Produced Water Spiked with Iron (III) 2 x 2 concentrations X 2 (duplicates)	NA	D	NA

E = The sample is Extracted and the extract is tested.
D = The sample is tested Directly without extraction.
NA = not applicable

DATA ANALYSIS AND RESULTS

Results by all methods are evaluated by comparison to EPA Method 1664. A pooled relative standard deviation over all Oil\WSO concentrations for each instrumental method is compared to that for Method 1664 as a measure of precision. Percent recovery for each method when using crude oil for calibration is determined relative to results obtained by Method 1664. Potential iron interferences in the UV method being tested are assessed by comparing results with and without extraction. The performance evaluation results for the instrumentation and methods should be summarized in table form. The table should include a comparison of precision (% RSD), accuracy (% Recovery), detection range, correlation to Method 1664, potential interferences, procedural complexity, field suitability and limitations. Graphical presentation comparing the impact of the various factors should also be done.

QUALITY CONTROL

The quality control procedures for the laboratory testing should follow good laboratory practices. Where applicable, the Quality Control sections of Method 1664 can serve as a guideline for the laboratory testing procedures conducted in this study. Quality control procedures provided by the manufacturers of the instrumentation being evaluated should also be followed. The PHS-H and AHS-I standards described earlier can be used as quality control check standards.

Section 6

GUIDELINES FOR FIELD SITE SELECTION AND FIELD TESTING

Once the laboratory testing phase is complete, the instruments chosen for study should be tested on location using actual produced water samples. This work will be done at a convenient onshore location. Samples will be collected and brought to a field laboratory where the instruments being tested will be set up and the analyses done. The objective of such tests is to explore the limits of the methods and instrumentation under dynamic field conditions. The two methods chosen for study are very different and each could react differently to a number of factors that vary over both time and discharge point in the field. In order to show the relative impacts of these factors on the two methods, it is important to choose sampling locations where one or both instruments will experience problems, if the potential for such problems exist. Table 6.1 contains a range of variables that might affect each of the instruments.

Table 6-1. Factors Affecting Analytical Instruments

Factor	Instrument 1	Instrument 4
Loss of oil on evaporation	Yes	No
Solvent measured as oil	Maybe	No
Variation of the ratio of measured species to total oil	Maybe	Yes
Calibration differences before & after flotation	Maybe	Maybe
Impact of WSOs	Maybe	Maybe
Impact of iron content of produced water	No	Maybe

Sampling at platforms with the following types of production will increase the chance of encountering the range of the above listed factors:

1. a gas platform that produces a light condensate and water with a low WSO content;
2. a single platform producing from a relatively few wells, some of which produce oil and some produce gas (mixed); water production from oil and gas wells should be comparable; and
3. an oil platform that produces medium grade crude and water with a high WSO content.

Produced water from each of these platforms should be sampled, both upstream and downstream of the water processing equipment. The processing equipment removes oil and grease from the produced water. Both instruments recommended for study are subject to potential variation in calibration due to changes in composition of the oil in produced water due to oil removal treatment. For IR measurements, the ratio of carboxylic acids to total oil may change during the treatment process. For UV measurements, the ratio of aromatics to total oil may change during the treatment process. Sampling and calibrating before and after the treatment process will allow determination of whether or not such changes make a significant difference in calibration factors.

Samples should be taken on two different occasions, with a minimal one-day to one-week interval between sampling events. On the first sampling day two types of samples will be collected: one type for developing a correlation between the field methods being studied and the defining method, EPA 1664, and the other type will be test samples for evaluating the instruments under changing conditions. On the second sampling day only test samples will be taken. Test samples should be taken at three different times on each of the sample days: once in the morning, once in the middle of the day, and once late in the day. The second sampling day should be made when the production mix is different from that sampled on the first trip, if possible.

The three types of test platforms listed above were chosen because they each exhibit some of the factors that can affect oil and grease determinations. The oil and grease from produced water on the gas platform will be light and this will affect methods which rely on evaporation of the solvent. Water from gas platforms usually contains aromatic materials that might affect UV methods. The oil platform chosen should be one that has produced water with a higher than average concentration of WSO materials in the oil and grease. WSO materials are not removed as efficiently in treatment processes as hydrocarbons and there is more chance that such a platform will have a different oil and grease composition upstream and downstream of the treatment system. The platform having both oil and gas production will provide an opportunity for variations in composition of the oil and grease in produced water. In this case, the gravity of the oil and grease can change, the aromatic content of the oil and grease can change, and the WSO content can change. These three types of platforms can present opportunities to test many of the factors that will affect oil and grease determinations in produced water.

CALIBRATION

Instrument calibration of both instruments will be done using crude oil from the structure being sampled. In addition, the calibration protocol for the UV instrument recommended by the manufacturer will be followed using the proprietary dye standard recommended by the manufacturer. Both of these instrument calibrations are entirely consistent with the way the currently used field IR units are calibrated. As discussed earlier, instrument calibrations serve to set the instrument so that its responses cover a useful range. Conversely, the correlation procedure discussed below serves to relate instrument responses to actual oil and grease concentrations.

CORRELATION TO DEFINING METHOD

The most important factor in choosing an instrument for measuring oil and grease in the field is the correlation of the instrument response to the defining method. First, one must be able to correlate the measurements made with the field instrument to the defining method and then this correlation must remain constant for a significant period. If you cannot trust the correlation then the field measurements are meaningless. Therefore, one of the major objectives of field testing instruments for measuring oil and grease is to show how well the correlation to the defining method is maintained. In order to be useful, a field instrument must consistently agree with the defining method and the correlation must hold over a significant period. If the correlation changes often, then the field instrument's usefulness decreases.

Changes in composition of the oil and grease cause most correlation problems. There are two factors that result in changes of composition of the oil and grease in produced water: treatment to remove oil and grease and changes over time due to changes in production rates or sources. Treatment systems can remove the various constituents of oil and grease at different efficiencies. For example, dispersed hydrocarbons are removed more efficiently than WSOs. Production rates and sources can change because wells are shut in or shut in wells are put back on production. The effect of such changes can be determined by testing discharge points in two ways: upstream and downstream of oil removal treatment systems and at widely separated points in time.

Correlations between EPA 413.1 (the original defining method) and the IR methods widely used in the field in the past were developed doing a field analysis every time a sample was submitted for a 413.1 analysis. The results of these 413.1 analyses were plotted against the results of the corresponding field analyses and a best fitting straight line was fitted to the plot using the method of least squares. After a time, enough analyses were accumulated to form a useful correlation. For the field studies done for this project, a faster, more reproducible correlating method is needed. One alternative for obtaining a set of calibration samples rapidly is to take samples from the upstream sampling point on the water treating system on each platform. The untreated produced water stream will usually have a high enough oil and grease concentration to develop a correlation range covering the oil and grease concentration in the treated produced water. Table 6-2 summarizes the samples needed to determine the correlation. Using this procedure, the following sequence of events would occur:

- Four sets of three replicate[1] samples would be taken upstream of the water treatment.
- Table 6-3 summarizes the samples in these sets of replicates. Each set of three replicates should be taken simultaneously to ensure as far as possible that they are identical.
- Each set of replicates will be a whole sample or one of three dilutions.
- One sample from each replicate set will be analyzed by Method 1664, one will be analyzed by the field IR instrument and the other would be analyzed by the field UV instrument.
- When all four sample sets have been analyzed, the resulting data will constitute three sets of analyses of four concentrations of produced water by the defining method and two field methods.

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[1] A replicate is one of a set of samples taken simultaneously. That is, a set of three samples taken at the same time from the same sample point are replicates.

The data obtained from analyses of the 12 samples taken from each sample point will be used to develop correlations between Method 1664 and the two field instruments being studied. The correlations developed can then be used in comparisons of field samples taken during the field sampling program.

Table 6-2. Samples Needed For Correlation to Method 1664
(A correlation requires a range of concentrations. These are achieved by taking four samples at each sample point and diluting three of them to 75%, 50%, and 25% of total produced water. These dilutions are done with sodium chloride made up to the salinity of the produced water on the platform ahead of time.)

Platform	**Gas**	**Mixed**	**Oil**
Sample Point	**Upstream**	**Upstream**	**Upstream**
PW Content	25% V	25% V	25% V
PW Content	50% V	50% V	50% V
PW Content	75% V	75% V	75% V
PW Content	100% V	100% V	100% V
	Number of Samples	Number of Samples	Number of Samples
Method 1664	XXXX	XXXX	XXXX
IR Instrument	XXXX	XXXX	XXXX
UV Instrument	XXXX	XXXX	XXXX
X = A Sample			
# Of Samples	12	12	12

Table 6-3. Sampling Matrix for Calibration Samples

Sample Number	**EPA 1664** **Sample Volumes (ml)**	**IR Samples** **Sample Volumes (ml)**	**UV Samples** **Sample Volumes (ml)**
1	1000	80	10.0
2	750	60	7.5
3	500	40	5.0
4	250	20	2.5

Samples 2 through 4 will be diluted with a sodium chloride solution of the same salinity as the sample, so that the volume of sodium chloride added to the sample brings the total volume of the diluted sample up to the volume of the first sample in each of the three sets. That is 1000, 80 and 10 ml, respectively.

FIELD SAMPLES FOR COMPARISONS

In addition to collecting samples for the calibration of each of the instruments, samples must also be collected for the actual method comparisons as shown in Table 6.4. The table shows the recommended sampling matrix.

Table 6-4. Sampling Matrix for Field Testing

Trip	**Platform**	**Sample Point**	**Replicates (one each morning, noon and afternoon at each point)**			
			Method			
			EPA 1664 (1000 ml)	**IR (80 ml)**	**UV (10 ml)**	**Number of sets per day**
1	Gas	Upstream	1	1	1	3
1	Gas	Downstream	1	1	1	3
1	Mixed	Upstream	1	1	1	3
1	Mixed	Downstream	1	1	1	3
1	Oil	Upstream	1	1	1	3
1	Oil	Downstream	1	1	1	3
2	Gas	Upstream	1	1	1	3
2	Gas	Downstream	1	1	1	3
2	Mixed	Upstream	1	1	1	3
2	Mixed	Downstream	1	1	1	3
2	Oil	Upstream	1	1	1	3
2	Oil	Downstream	1	1	1	3
Totals			12	12	12	
Grand Total						**108**

Each line of this table represents a replicate set. At each point, three such sets will be taken in day one, in the morning, one at mid day and one in the afternoon. Two separate sampling trips should be made separated by enough time that operating conditions can change. The samples for the first trip can be taken at the same time as the correlation samples discussed above. Having the second set (Trip 2) of samples gathered several days after the first set (Trip 1) will allow a determination of how the correlations to EPA 1664 hold over time. If possible, a time should be chosen when the mix of wells on production is different from that during the first trip.

FIELD SAMPLING PROTOCOL

Specific sampling instructions for gathering samples for the two field instruments being studied must be agreed on with the instrument suppliers. A method for collecting replicate samples must also be agreed on. This could be done with a sampling manifold and a set of sample containers arranged to collect simultaneously from this manifold. This could provide a set of three replicates for each sampling event: one replicate for each of the two instruments and one for the EPA 1664 method.

The following sampling protocol is based in part on a protocol submitted by an API member company (Brost, 1996).

1. Prepare 1-liter bottles for EPA 1664 by adding enough hydrochloric acid to reduce pH less than 2. Similarly, prepare smaller volume bottles (e.g., 100-ml) for the IR instrument and (10- ml) for the UV instrument methods.
2. Prepare replicate bottles as required for the analysis method under investigation (see Note 1).
3. Either use a sampling manifold or duct tape to strap the replicate bottles together. Fill the bottles simultaneously, by repeatedly alternating them under a flowing stream of water. Add about 10 % or less of total sample volume at a time to each bottle, and then proceed immediately to the next. Continue repeatedly adding to one bottle after another until all the bottles are full. Do not top off any of the bottles to bring them to full volume. Other devices, such as sampling manifolds, can be used that obtain representative grab samples of the stream into separate bottles of replicate samples.
4. After the sample set is collected, visually inspect all the bottles. Pay particular attention to the uniformity of color, clarity, and amounts of solids. If the samples appear significantly different, discard them, clean the bottles and start again.
5. Perform any post-sampling manipulations, if any are required for the method(s) under investigation (e.g., reagent additions, heating, filtration, etc.).

Note 1: Any pre-sampling procedures required by the method(s) being evaluated are done as needed. For example, the surfactant-assisted methods often work best when the surfactant is added to the bottle before the sample is collected. The surfactant prevents free oil from adhering to the cap and walls of the container. It also solubilizes the free oil immediately upon collection, while the oil is fresh and all the salts are still dissolved in the water. Once the samples are prepared in this manner, the water soluble organics and solubilized free oil usually remain stable for weeks.

Simple analytical tests recommended on-site at the time of sampling include Total Iron, Ferrous Iron, and Total Hardness, and any observed sample volatility. These data may be useful in explaining any anomalous results.

Using Method 1664 as a reference standard for evaluating field methods can present a problem. If oil and grease concentrations in the produced water from the discharge points used in the study are too low; there may not be a sufficient concentration range for determining the correlation slope and offset. This factor should be taken into account when choosing test sites.

DATA TREATMENT AND ANALYSIS OF RESULTS

One of the major objectives of the field sampling program is to investigate the impact of changing produced water composition and field operations on the behavior of the instruments. An instrument will always yield a number when it is applied to the analysis of produced water to determine oil and grease. The most important question is whether the correlation relationship between the field method and the official method remains valid for a significant period. If this relationship does not hold for a relatively long time then the field method is not reliable.

One way of testing the effect of oil and grease composition on these correlations is to compare the results of analyses on duplicate samples, one of which is analyzed by the defining method and the other analyzed using the field method with subsequent correlation to the defining method. The differences in these two analytical results can be used to check consistency. For example, the three sample results taken upstream of the water treating system on one of the test platforms are averaged. The average can be compared to similar averages for other sampling dates (checking for the effect of time). Alternatively, they can be compared to similar averages for samples taken downstream of the water treating system on the same platform (checking for the effect of changing composition). If the average differences change significantly, the correlation is not constant. Using the data from the sampling program outlined in Table 6-4 comparisons can be made for time and concentration changes on the three platforms, for the two sampling trips (time) as a function of the three types of production facility.

Section 7

GUIDELINES FOR OPERATORS WHO CONDUCT THEIR OWN EVALUATIONS

There are now a number of instruments on the market for determining oil and grease in produced water. The majority of these instruments use one of the five technologies discussed in Section 3. When this project was started, there were no other technologies that had a track record of successful application to produced water. Recently some operators have begun to apply several new technologies. Most of the instruments currently using the technologies chosen for study in this project will work adequately for measuring oil and grease in produced water. Some instruments using new novel technologies may also work well. It is not possible to say what the best instrument is in every case. The factors that enter this judgment include more than just the suitability of the technology itself. They include such things as operability, availability of technical and field support for the instrument, and other specific needs of the operator. Therefore, the best instrument for a particular operator, at a given site, is somewhat specific to that site, for that operator. If an operator wants to select an instrument and determine the feasibility of using that instrument on the water processing systems for monitoring oil and grease, the guidelines given below can be followed.

The first step in the evaluation is to understand exactly what the instrument is to measure. For the purpose of this discussion it will be assumed that oil and grease measurements monitor processing equipment to ensure that the equipment is performing the function for which it was intended, that is for removing oil and grease from the water as defined by the EPA 1664 method. Therefore, the technology used by the instrument should be one of the three identified in this study:

- Infrared (IR) absorbance,
- Ultraviolet fluorescence,
- Ultraviolet absorbance.

In addition to the technology that was selected for this study, it is also possible that the operator has identified a new technology for his or her particular application. Which technology is selected will depend on the nature of the produced water and personal preference. Both are important.

Next, the operator should identify the specific instruments to evaluate. This selection should be based on:

- an evaluation of the manufacturer's recommended procedure (as a measure of the operability features of interest),
- an evaluation of the manufacturer's ability to supply service,
- an evaluation of the manufacturer's ability to supply an expert that can explain the principles on which the instrument works, and
- other factors important to the operator.

A company that cannot supply the type of help and practical field application assistance you require should be eliminated from further consideration.

Once candidates are chosen for evaluation, examine the properties of the produced water and compare them to the known limitations and interferences that affect the performance of the instrument. Specifically, determine:

- the level of water soluble organics (WSOs), both before and after the treatment system,
- the level of fluorescence in the produced water, both before and after treatment,
- the turbidity of the water, and
- other factors known to affect the instruments of interest.

After the produced water properties are known, tests on laboratory prepared samples similar to the ones described in Section 5, Laboratory Testing of Selected Technologies, should be made. Concentrations of WSOs and fluorescing materials should be adjusted to cover those found in the water. This laboratory testing is important because it allows an evaluation of the effect of known interferences without the added effect of the other interferences in the water. The laboratory tests should be conducted using the instruments being evaluated and the defining method (EPA 1664). If no problems are identified in the lab testing, proceed to field evaluations.

Field evaluations should follow the general procedure given in Section 6, Guidelines for Field Site Selection and Field Testing. Each instrument should be calibrated against the defining method as shown in that section. Determinations made over a period and using the original calibration curve should then be compared to EPA 1664 results on duplicate samples. If the calibration holds, and the standard deviation of the replicates measured in each trial remains acceptably low, the method can be used. Experience with the instrument in the field should allow the user to determine if its operability is suitable and preferable to the alternatives.

Section 8

CONCLUSIONS AND RECOMMENDATIONS

The following are the conclusions and recommendations from this study:

- There is no single best replacement for the Freon-113® extraction IR method for analyzing oil and grease in the field.
- There are several technologies that are potentially suitable alternatives.
- This study was limited to those technologies for which there were already commercial instruments available when the study was proposed. Since that time, new instruments have been developed that use novel technology that may also be viable for this application. They have not been included in this study.
- It was concluded that three technologies showed promise for application to oil and grease measurements in the field:
    - ⇒ infrared absorbance (IR),
    - ⇒ ultraviolet absorbance, and
    - ⇒ ultraviolet fluorescence.
- One instrument using each technology was chosen for further study:
    - ⇒ One representing IR absorbance, and
    - ⇒ One representing UV Fluorescence.
- These two instruments represent the boundaries of a range of factors that affect oil and grease determinations in produced water:
    - ⇒ One is at one end of the optical portion of the electromagnetic spectrum and the other is at the other end.
    - ⇒ One must use extraction while the other may be used with or without extraction.
    - ⇒ One uses solvent evaporation and the other does not.
    - ⇒ One measures a factor present in all oil and grease constituents and the other measures a factor proportional to oil and grease constituents.
- Comparing both of these methods to the defining method for oil and grease (EPA Method 1664) will provide information that will help in the selection of any instrument that applies the three listed technologies. This comparison could be used to provide a strong foundation for further work.

- The properties of produced water that are most likely to impact oil and grease measurement by spectrophotometric technologies are:

    ⇒ aromatic (fluorescing) content,
    ⇒ water soluble organic (WSO) content, and
    ⇒ variability in these factors due to variability in oil and gas production operations.

- The recommended laboratory sample matrix discussed in Section 5 will show the relative impact of the properties of produced water on the performance of the instruments.

- Selection criteria were developed for field sites for use in field evaluations, and procedures for calibrating instruments and developing correlations are recommended. Three platforms are recommended:

    ⇒ a gas platform,
    ⇒ a platform producing both oil and gas, and
    ⇒ an oil platform discharging high concentrations of WSOs.

- Field sampling should be done on two different days, to allow parameters to vary over the time of the study.

- Guidelines are provided in Section 7 for individual operators who want to choose another technology or to do their own instrument study.

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