

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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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 platforms;
- 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.

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

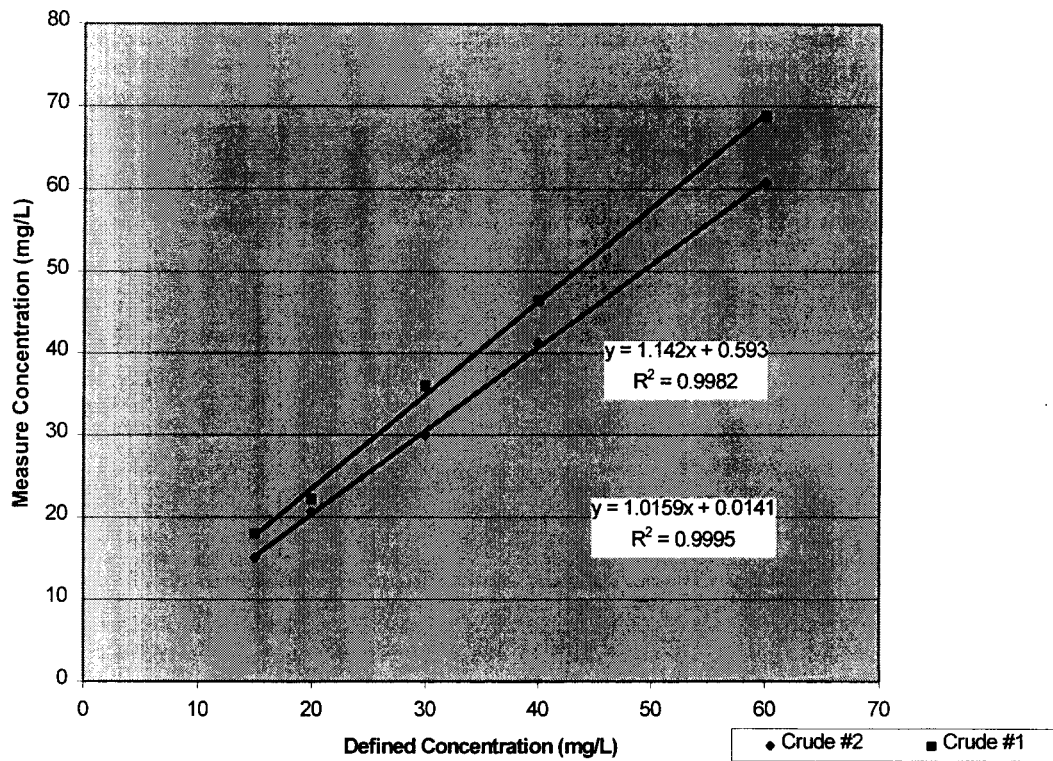
Defined Concentration (mg/L)	Measured Oil and Grease Concentration in Crude #2 Simulated Produced Water (mg/L)		Measured Oil and Grease Concentration in Crude #1 Simulated Produced Water (mg/L)	
	Instrument A	Instrument B	Instrument A	Instrument B
15	15.1	15.4	18.3	18.0
20	20.6	20.2	24.3	22.2
30	30.0	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

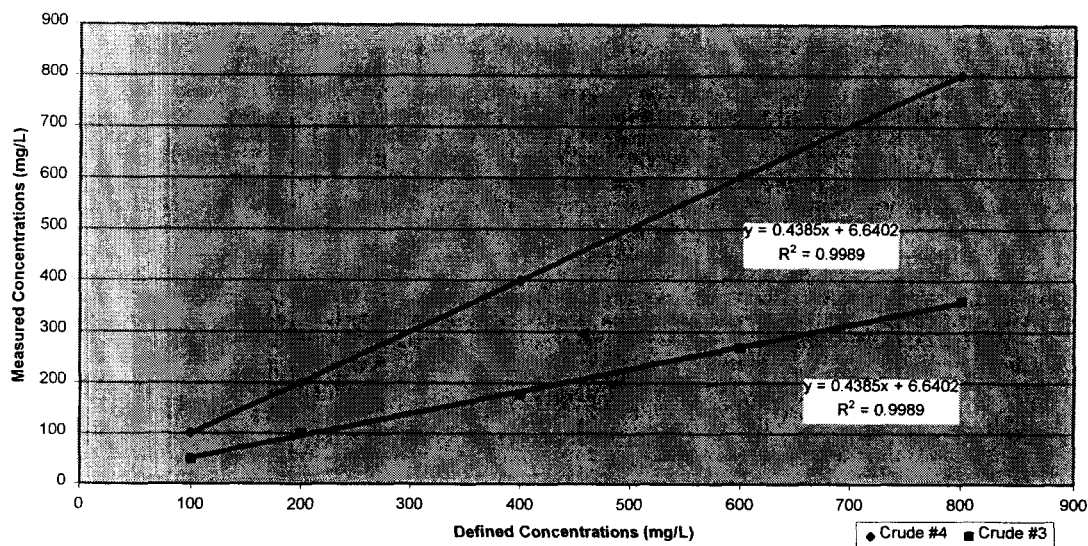
Defined Concentration (mg/L)	Measured Oil and Grease Concentration in Crude #4 Simulated Extract (mg/L)	Measured Oil and Grease Concentration in Crude #3 Simulated Extract (mg/L)
100	100	49
200	199	100
400	399	177
600	602	268
800	801	360

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



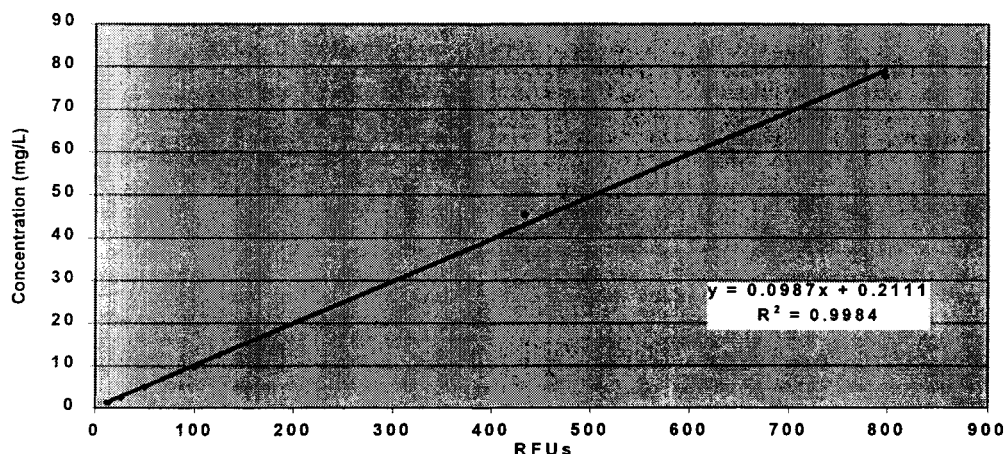
fluorescent units (RFUs) for a series of known oil and grease concentrations. A correlation can then be developed between RFUs and the oil and grease concentrations. Table 4-5 provides data from the calibration of Instrument A with a stock dye solution supplied by the instrument manufacturer. The RFU 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

Sample I.D.	Fluorescence Units			
	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

Defined Concentration (mg/L)	Crude #1		Crude #2	
	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

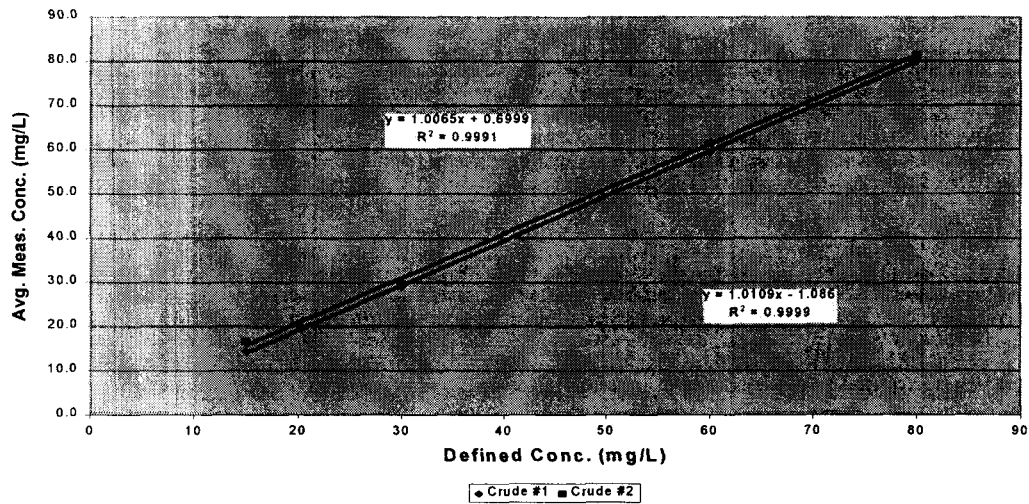
Defined Conc. (mg/L)	Oil and Grease Concentration from Simulated Extracts of Crude #1 in Hexane* (mg/L)			Oil and Grease Concentration from Simulated Extracts of Crude #2 in Hexane* (mg/L)		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
15	13	16	14	15	17	18
30	30	28	29	27	30	32
60	60	60	58	63	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

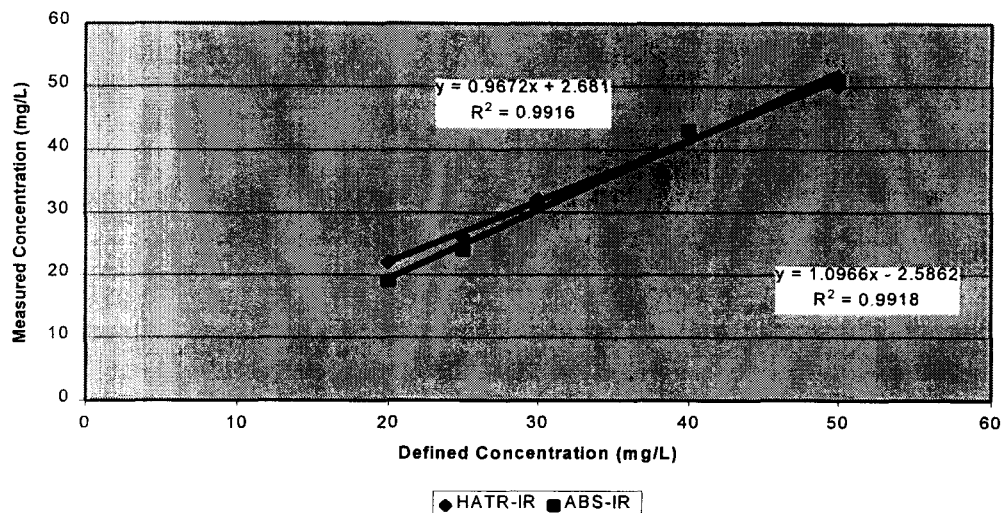
A comparison was made of IR-HATR and the IR-ABS methods in analyzing oil and grease in simulated produced water samples containing Crude #2, at defined concentrations of 20-50 mg/L. Oil and grease was extracted with hexane before analysis. For both methods, the instrument was calibrated using simulated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