

# OIL AND GREASE DETERMINATION IN PETROLEUM OPERATION WASTE WATER

by

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## ABSTRACT

A regulation concerning waste water quality for oil and gas activities in Indonesia has recently been issued in the State Minister for Environment Decree No. 42/MENLH/10/1996. Waste water quality for oil and gas activities is classified in this decree according to the type of activities, namely exploration and production activities, refineries, and petroleum product storage and distribution activities. Maximum permissible concentration of oil and grease in waste water varies depending on the activities and mode of discharges. The oil and grease concentration in operation waste water that ranges from 20 ppm for the refineries to 75 ppm for off shore production have led to the variation in determination methodologies.

Survey on oil and grease determination methods in Indonesia indicated that determination method ranges from gravimetric method that is unsuitable for light fraction to spectrometric method that depends on the oil standard. Moreover variation of solvent will give different result.

This paper describes an overview of oil and grease determination conducted by the Indonesian oil and gas companies informing the advantages and disadvantages of each method. The possible single method that can be utilized as a standard method as well as approaches in conducting correlation program is proposed.

## 1. INTRODUCTION

Produced water and waste water discharges for oil and gas activities in Indonesia are recently regulated under the State Minister for Environment Decree No.42/MENLH/10/1996<sup>(1)</sup>. The regulation classifies waste water quality according to the type of activities, namely exploration and production activities, refineries, and petroleum product storage and distribution activities. The recent regulation is intended as replacement for the previous one stating only one limitation for all activities. One of its provisions is that the concentration of oil and grease in effluent water for onshore production activities and for refineries be below 25 mg/L and 20 mg/L respectively, while for offshore production activities be below 50 mg/L (cf. Table 1).

The regulation does not indicate analytical methods to be used for determining oil and grease in the discharge waters. These may vary from gravimetric to spectrometric methods, and each laboratory could decide which method is suitable for this purpose. Not only could the different methods give different results, but using different solvent may change the specific analytical protocols and ultimately may have the potential of changing the result for a given sample. The petroleum industries are obviously concerned that a change in method could cause a

change in results and thereby in the status of permit compliance.

This paper describes an overview of oil and grease determination conducted by the Indonesian oil and gas companies informing the advantages and disadvantages of each method used. The possible single method that can

Table 1  
Effluent limitations for oil and  
grease concentration, mg/L

Activities	Maximum Concentration (mg/L)	
	A*	B**
Near offshore produced water	35	25
Far offshore produced water	75	50
Refinery effluent water	25	20
Petroleum product storage effluent water	-	25

(The State Minister for Environment Decree No.42/MENLH/10/1996)

\*) A : Water treatment processes or planning of water treatment processes of the industries have been developed before the Decree

\*\*) B : Planning of water treatment processes of the industries are being developed or has been developed after the Decree.

be utilized as a standard method is proposed. Correlation program of oil and grease determination in water samples is also discussed.

## II. TEST METHODS FOR OIL AND GREASE

### IN WATER

Numerous methods have been suggested for the purpose to determine oil and grease or oily material content in effluent waters of the petroleum industries. The development of the methods has been commenced in 1950's and in principle there is not much modification in analytical steps and determinations, except replacement of the chemicals due to their toxic properties or their impacts to the environment.

Three basic steps are generally involved in the test methods for oil and grease in water. These are sampling and preservation, separation of oily matter from water, and determination of separated oily matter with one of available determinative techniques. Although several methods of separation of oily matter from water have been proposed, such as adsorption on an adsorbent followed by solvent extraction of the adsorbed material, direct solvent extraction of oily matter from water sample seems to be the most popular nowadays.

In the determination of oil and grease, an absolute quantity of substance is not measured. Rather, groups of substances with similar physical characteristics are determined quantitatively on the basis of their common solubility in an organic extracting solvent. Besides, unlike some constituents that represent distinct chemical elements, ions, compounds or group of compounds, oils and greases are defined by the method used for their determination. Hence, two factors should be considered in the determination of oil and grease in water. Firstly, type of extracting solvents that will influence the recovery of oil and grease from the samples. Secondly, type of oils that will determine which standard should be used for calibration.

#### A. Sampling and Preservation

Generally, collection of water samples for oil and grease determination has to be done using a glass bottle equipped with a screw cap having a TFE-fluorocarbon liner. If analysis is to be delayed for more than two hours, sample should be preserved by refrigeration and acidifying them to pH 2 or lower. One method<sup>(5)</sup> uses 1 : 1 HCl, while another<sup>(6)</sup> uses 1 : 1 H<sub>2</sub>SO<sub>4</sub>.

To overcome the inhomogeneity of oil and grease in the water sample due to the possible adherence of oil to the

glass wall, the entire sample should be used and no portion should be removed for other test. The sample container should be rinsed with the extraction solvent, therefore, containers other than glass bottle are not recommended.

#### B. Extraction

Most methods use liquid-liquid extraction of oily matter from the water samples. Previously, carbon tetrachloride was used as the extraction solvent since carbon tetrachloride has superior solvent power to other solvents. Due to its carcinogenic and toxic properties some laboratories have replaced carbon tetrachloride with Freon 113 (1,1,2-trichloro-1,2,2-trifluoro ethane). Freon is an excellent solvent for this purpose because of its solvent power for oil and grease. Besides, because of its volatility that make it easy to evaporate from the oil and grease analyte, freon is very meaningful when gravimetry method is used as a determinative technique.

Although Freon 113 is adequate for extracting oily matter, however, it does readily dissolve undispersed viscous oil such as No. 6 Fuel Oil.<sup>(1)</sup> Freon 113 is therefore not recommended for preparing Infrared Standard solution of viscous oils. Another disadvantages of using Freon is that this solvent is one of the substances that will deplete the ozone layer in the upper atmosphere. According to the Montreal Protocol that calls for the reduction of use of these substances, some laboratories have replaced Freon with other solvent. For example, the US EPA<sup>(7)</sup> uses n-hexane as replacement solvent for extracting oil and grease in water followed by gravimetry determination in the Method 1664.

Replacement of the solvent in the analytical protocol does not mean that it would not create problems. One of many factors to be considered of using n-hexane is safety, since this solvent is quite flammable. More over n-hexane has a higher boiling point than Freon. This means that it will take longer to evaporate the solvent, and there is a greater likelihood of solvent remaining in the evaporation flasks at the weighing step. These tendencies could lead to erroneously high values for oil and grease determined by gravimetry method. Because n-hexane is less dense than water, it floats on top in the extraction funnel. This means that the entire water layer must be drained back into the sample bottle, then the n-hexane layer is drained in the flask. This entire procedure is repeated twice more with additional amount of hexane. This adds to the manipulations and to the cost of the analysis, not only are there concerns about longer analysis times, there are some additional safety concerns.

Another impact of using n-hexane as a solvent is that

the Infrared Method used on the most refineries and platforms for monitoring will no longer be available. The Infrared Method, as given by Standard Methods 5520C,<sup>(3)</sup> uses the characteristic frequency of the C-H bond on hydrocarbon molecules for the measurement of oil and grease. Since n-hexane is itself a hydrocarbon, it completely masks any infrared absorption due to a trace amount of oil and grease in the solvent. Continued use of the Infrared Method would depend on the availability of another solvent without C-H bonds that can be safely used and is not excessively expensive. Alternative solvents that can be used with Infrared Method should be selected. One of the alternative solvents that could be used for extracting oil and grease in water is perchloroethylene<sup>(2)</sup>. Selection of solvent for use in Infrared Method and or probability of using other methods would be an interesting matter to be discussed in this workshop. Criteria for the selection would include: easy of use, low capital cost, safety, low toxicity, minimal waste generation, etc.

### C. Calibration and Determination

The methods used by the petroleum laboratories for refinery and offshore discharge water analyses basically entail extraction of the oil and determination by one of four techniques, i.e. : gravimetric, infrared, ultraviolet, and colorimetric techniques. The accuracy of these techniques varies widely. Factors such as brine characteristic, physical and chemical properties of oil and standards used, all influence their accuracy. The extent to which each technique is affected is primarily governed by the oil constituents that are measured. Ideally, the determinative technique measures all, and only, the oil constituents. However, due to the complex chemical composition inherent to petroleum oil, each technique measures only some specific oil constituents. Table 2 lists the determinative techniques, the respective constituent measured and the primary factors influencing the accuracy of each technique.

Standards play a critical role in all but gravimetric technique. It appears, therefore, that this technique is more

universally applicable than the others. Its accuracy however is not on a par with the infrared technique.

One method<sup>(2)</sup> defines oil and grease as a "known oil" when a sample of oil and/or grease represents the only material of that type used or manufactured in the processes represented by a waste water. While an "unknown oil" is defined as one for which a representative sample of the oil or grease is not available for preparation of a standard. When the oil identity is unknown reference oil should be used as a standard. Several reference oils have been proposed as standards for use in Infrared Method. For example CONCAWE<sup>(4)</sup> method uses n-hexadecane as a standard and includes a factor of 0.664 in the calculation. Other standard<sup>(2)</sup> uses a mixture by volume of 37.5 % isooctane, 37.5 % hexadecane and 25.0 % benzene. Standard test method for oil and grease and Petroleum Hydrocarbons in water described by ASTM<sup>(6)</sup> uses a mixture of 50% isooctane and 50% cetane. Dating back to at least 1951<sup>(6)</sup>, for many years a mixture of isooctane, cetane and benzene was accepted as a standard for calibration. Concern regarding the hazards of exposure to benzene, which acts here only as a diluent having no contribution at 2930 cm<sup>-1</sup> has prompted elimination of this chemical as a component for calibration.

The merit of calibration or standardization is to measure the absorptivity value as stated by Beer-Bouguer Law:  $A=abc$ , where A is absorbency, a is absorptivity, b is cell path length and c is concentration. Use of the synthetic standard is based on the assumption that the infrared absorptivities of oils from different sources are very close and similar to the synthetic standard absorptivity. Gruenfeld<sup>(1)</sup> and the authors<sup>(2)</sup> have shown that the absorptivity of a large variety of oils are in fact very similar and close to the synthetic standard.

### III. PETROLEUM INDUSTRY PRACTICE

A survey was conducted to establish the test methods for oil and grease in water samples that are currently

Table 2  
Determinative techniques for oil and grease in water

Determinative techniques	Main constituent measured	Factors affecting measurement
Gravimetric	Non-volatile, residual oil constituents	Volatility of oil
Infrared	Paraffinic hydrocarbons	Standards used
Ultraviolet	Aromatic hydrocarbons	Standards used
Colorimetric	Dark colored oil constituents	Color of oil, standards used

**Table 3**  
**Test methods for oil and grease in water samples**  
**in Indonesia petroleum laboratories**

Laboratory	Method	Oil Standard	Solvent
1	Gravimetric (APHA-1985)	-	Freon-113
2	Infrared (ASTM D-3921)	-	CCl <sub>4</sub>
3	Infrared (APHA-1992)	a mixture of iso octane, hexadecane, and benzene	CCl <sub>4</sub>
4	Infrared (OCMA)	-	CCl <sub>4</sub>
5	Infrared	-	CCl <sub>4</sub>
6	Infrared	heavy oil	CCl <sub>4</sub>
7	Infrared (ASTM D-3921-85)	crude oil	Freon-113
8	Infrared (CONCAWE)	crude oil	CCl <sub>4</sub>
9	Infrared (ASTM D-3921-85)	crude oil	Freon-113
10	Infrared (ASTM D-3921-85)	-	CCl <sub>4</sub>
11	Infrared (CONCAWE)	hexadecane	CCl <sub>4</sub>
12	Colorimetry (HACH)	std. oil	Freon-113
13	Colorimetry (HACH)	-	Freon-113

used by the petroleum industries in Indonesia. Thirteen laboratories have responded the questionnaire, consisting one laboratory of petroleum product storage and distribution activities, five laboratories of refinery activities, five laboratories of production activities, one laboratory of training activities and one laboratory of research and development activities. The result of the survey is summarized in Table 3. Test method used can be classified as gravimetric method (one laboratory), infrared method (ten laboratories), and colorimetric method (two laboratories). Of ten laboratories using infrared method as the determinative technique, five are refinery laboratories, three are offshore production laboratories and one laboratory of each for training and research institute. Two laboratories that use colorimetric method (HACH Method) both are offshore production laboratories. It seems that HACH method is used with regards of portability, especially for off shore monitoring.

Regarding solvents required for extracting oil and grease in water, most laboratories are still using carbon tetrachloride (eight laboratories). Due to its carcinogenic and toxic properties, some laboratories have replaced of using carbon tetrachloride with Freon-113. There is no attempt to replace Freon-113 with other solvent yet.

#### IV. CORRELATION PROGRAM FOR OIL AND GREASE WATER

Unlike other parameters, such as heavy metals, phenol, chloride etc. that is soluble in water, oil and grease

in water are present in different forms of phase: dissolved, dispersed, and undispersed phase. When presence in dissolved or dispersed phase, such happens in very low concentration (e.g., 0.1 ppm) in sea water, determination of oil and grease in water samples would give a good precision due to the homogeneity of the samples. Regarding that effluent waters may contain oil and grease beyond the limits of its solubility, the homogeneity of the samples is questionable. Besides, when the samples can not be analyzed immediately, oil and grease may separate from the water and adhere to the wall of the container. This may result in difficulties in preparing water samples for correlation purposes.

The determination of oil and grease involves three basic steps: sampling, extraction, and determinative step. The error of the analytical results could come from any step and make data comparison difficult. There are several approaches that can be taken to ensure that all values from participating laboratories are comparable, at least in regard to the use of their determinative instruments, e.g., infrared spectrophotometers.

The first approach is by the distributing laboratory making and sending out solutions of petroleum and standard in organic solvent instead of water samples in small ampoules. The second approach is by sending only solutions of petroleum in organic solvent and lets the participating laboratories use their own standard. These approaches would overcome the inhomogeneity of water samples and major errors in extraction steps. Data comparison in these approaches would be very useful in evaluating precision

of the instrumental quantification techniques.

If these approaches are satisfactory, further approaches could be followed. These would include preparation of synthetic mixtures of oil and grease in water by adding exact amount of oil into each bottle containing sea water (ca. 100 ml) and sending out these samples to the participating laboratories. Standard oil could also be sent out together with the samples. These approaches are useful in determining the errors caused by extraction step. The last approaches, provided that the previous approaches are satisfactory, correlation of the samples from the actual effluent water could be performed.

## V. CONCLUSIONS AND RECOMMENDATIONS

### A. Conclusions

1. The survey on oil and grease determination method conducted by thirteen petroleum laboratories in Indonesia indicated that determination method includes gravimetric method (one laboratory), infrared method (ten laboratories), and colorimetric method (two laboratories). Most of the laboratories are still using carbon tetrachloride as extracting solvent (eight laboratories), while the rests have replaced the solvent with Freon-113.
2. Although the gravimetric technique does not require standards, its applicability is only in situations where the loss of volatile oil component does not affect the accuracy of results. The technique is not applicable to measurement of oils that contain significant amounts of petroleum compounds that volatilize at temperature below 70°C
3. To assure compliance with government limitation the infrared techniques seemingly provide more accurate results because a major class of oil components (paraffinic hydrocarbons) is measured. This method is, therefore, proposed as standard method to use in oil and grease determination in water.

### B. Recommendations

1. Most laboratories are still using carbon tetrachloride as extracting solvent and some have replaced with Freon-113. Due to its toxic and environmental impacts, an alternative solvent should be chosen for use with infrared method. The alternative solvent would be a matter of discussion and research among the petroleum laboratories of ASCOPE member countries. The criteria for the selection would include some consideration such as safety, low toxicity, inexpensive, etc.

2. Unlike other parameters that soluble in water, the error of oil and grease determination in water could be broken down into sampling, extraction, and determinative errors. The purpose of a correlation program is to quantify these so that we can determine which differences are truly significant. To conduct correlation program for oil and grease determination in water samples, therefore, it is recommended to start with very simple approaches using artificial oil sample in organic solvent, followed by artificial water sample containing exact amount of oil, and lastly true samples from effluent water.

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