

Development of Synthetic Aqueous Oil and Grease Standards for Determination of TOG in Produced Water: Evaluation of Alternative Methods for Application in an Offshore Environment

Vinnicius Ferraço Brant,* Rogério Mesquita de Carvalho, Márcio de Oliveira Martins, Flávia Ferreira de Carvalho Marques, and Antonio Augusto Fidalgo-Neto



Cite This: *ACS Omega* 2023, 8, 26317–26324



Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: Produced water is present in oil and natural gas reservoirs and is transported to the surface along with the oil. Total oil and grease content (TOG) is the main parameter evaluated in this waste disposal category. Today, the validation of methods in the laboratory is not done using petroleum. The objective of this work was to develop synthetic oily water standards that can be applied for internalization and validation in the laboratory. Oil weighing protocols, the influence of volatile compounds, and a procedure for preparing oily water with high reproducibility were studied. Synthetic oily water standards were prepared for TOG determination by gravimetric and infrared methods. Repeatability of 3.8 and 11% and accuracy of 85 and 105% were obtained using gravimetric and infrared methods. These results indicate that with the development of these standards, it is possible to validate methodologies for TOG determination using petroleum.



1. INTRODUCTION

Produced water refers to the effluent generated in the extraction of oil and natural gas, which can be found in the reservoirs, carried to the surface, and then discharged into the sea. This water is resulted from two possible oil and gas industry processes: (i) from the extraction itself that can result in a mixture of water and oil, sourced from the seawater surrounding the well and (ii) from the water injected into the oilfield to push the deep oil to the surface. Based on the origin, produced water can be classified as produced water from natural gas, oilfield, or coal bed methane.^{1,2}

Due to the complexity of its chemical constitution, the disposal of produced water is controlled and standardized by environmental agencies. Improper disposal can cause changes in seawater quality due to the increased concentration of pollutants in the water column and contamination of the marine sediment.¹

Aromatic hydrocarbons presented in the dissolved oil in produced water may be found under concentrations enough to cause bioaccumulation and toxicity. In this way, the determination of oil in produced water in onshore and offshore wells is fundamental owing to its deleterious effects to the environment and marine animals.³

The analysis of oil and grease has been historically used to monitor the operational efficiency of produced water in the treatment systems since it is an important parameter for water quality and safety. Regulatory agencies worldwide set limits to control the total oil and grease content (TOG) that enters in

the water reservoirs or in the sea through industrial discharges and also limits the amounts present in drinking water.⁴

The determination of TOG content in water is quite important, mainly for the petroleum industry that produces a relatively high amount of water along with oil. And according to Brazilian regulations,⁵ TOG should not exceed a monthly average of up to 29 mg L⁻¹, with daily peaks of up to 42 mg L⁻¹.⁶

Several methods have been applied in the determination of TOG in produced water, including gravimetry,^{7,8} infrared,^{4,9–14} fluorimetry,^{15–17} X-ray fluorescence,¹⁸ UV–vis spectrophotometry,^{19,20} gas chromatography with flame ionization detection,²¹ total organic carbon analyzer,²² and microemulsification-based methods.³

Despite the existence of many methodologies for TOG determination, their validation is not done with oil but with isolated substances since there is no oily water standard applicable to all techniques.

The gravimetric method uses n-hexane as the extraction solvent and stearic acid and hexadecane solutions for quality

Received: April 24, 2023

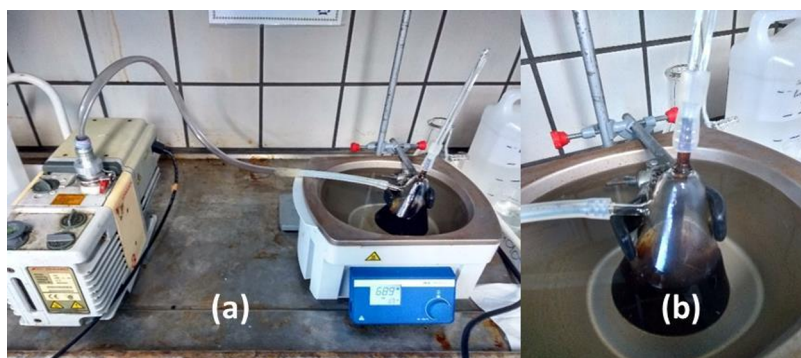
Accepted: June 21, 2023

Published: July 12, 2023



Table 1. Reference Substances Used in the Calibration of Different Methods to the Determination of TOG Content in Produced Water

reference substances	technique	reference
<i>n</i> -decane, <i>n</i> -eicosane and <i>n</i> -hexadecane, pristane and toluene	IR spectroscopy	9
<i>n</i> -hexadecane		10
isooctane and <i>n</i> -hexadecane		22
tetracontane		14
octanoic acid and isooctane		23
isooctane, <i>n</i> -hexadecane and benzene	gravimetry	24, 25
stearic acid and <i>n</i> -hexadecane		7, 8
isooctane, <i>n</i> -hexadecane and benzene	spectrophotometry UV–vis	19
synthetic oil		26
gasoline		27
mixture of diesel oil and lubricant	chromatography	21

**Figure 1.** (a) Apparatus used in the volatile oil depletion protocol. (b) Detail of the adapted Kitasato flask for carrying out the oil depletion procedure.

control.^{7,8} However, it is extremely laborious, takes a long time to be performed, provokes great losses of material, produces relatively large standard deviations, and cannot be used in offshore platforms since it requires material weighing, loss of constituents that volatilize, and the need of evaporation of the extract.⁴

Spectroscopy methods, such as infrared and ultraviolet, can be used as a simpler alternative to measure TOG, as all of them require calibration. In the methodology proposed by ASTM D 7678,¹⁴ calibration and standardization are carried out using tetracontane solution (between 0.5 and 1000 mg L⁻¹). In the methodology proposed by ASTM D 7066, calibration and standardization are carried out using a solution of octanoic acid and isooctane.²³ The method proposed by ASTM D 7575¹² is solvent-free and uses ClearShot technology, in which the samples are percolated into the cartridge to retain the oil content. Quantification is achieved by correlating the oil spectrum retained in the cartridge with a reference spectrum obtained from Orono Spectral Solutions, which is provided by the Calibration Standard Device Extractor.

The chromatographic method²¹ recommends the use of an alkane mixture, with a boiling point between 36 and 69 °C, which is used as the extraction solvent. The calibration is carried out by weighing equal amounts of two different types of mineral oil, both without additives.

The different principles for measuring TOG content in water samples require different standards for implementation and validation steps. Infrared methods are based on the measurements of carboxyl stretches and require octanoic acid, stearic acid, and hexadecane as validation standards. ISO 9322-2 proposes a mixture of diesel oil and lubricant without

additives as a calibration standard. Furthermore, some UV–vis methodologies employ synthetic oil, gasoline, and paraffin to prepare quantification standards. Table 1 summarizes the substances used in the calibration of the methods discussed above.

Given the complexity and low repeatability in the preparation, works using oil or oil/water in the validation step of instrumental analytical methods for TOG determination are not reported in the literature. In this context, considering the lack of a reference material that can be used in all techniques to the determination of TOG content, this work aims the development of an oil-in-water standard that can be used in several methodologies for determining TOG in water. The possibility of developing standards using oil dispersed in water enables the validation of TOG determination methodologies in the laboratory with greater representativeness of the matrix. It confers to the methodologies' greater accuracy and robustness in the determination of TOG, minimizing errors in the disposal of the oil industry and increasing the preservation of the marine environment.

2. EXPERIMENTAL SECTION

2.1. Preparation of Synthetic Oily Water. *2.1.1. Assessment of the Influence of Environmental Conditions on the Weight Loss of Oils.* The loss of volatiles under atmospheric pressure and ambient temperature was studied for four types of oils, namely, P52, LBV2001606, LBV2000706, and V2001B1705. Aliquots of approximately 25 g of oil were kept at a controlled temperature of 25 °C and under atmospheric pressure. Mass loss was observed for 8 h measured on an analytical balance (model AU202, Shimadzu).

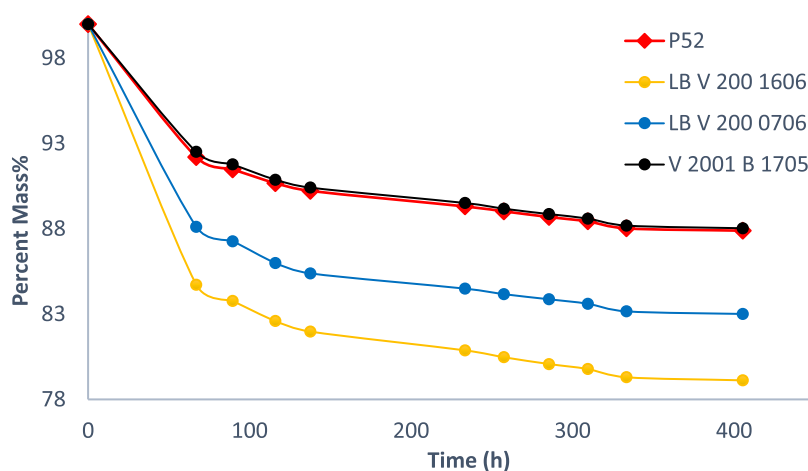


Figure 2. Study of the variation in oil mass under room temperature and atmospheric pressure conditions.

2.1.2. Evaluation of the Influence of Vacuum on Oil Mass Loss. A comparison between the loss of mass of the P52 oil under atmospheric pressure and under a vacuum of 0.5 atm was done.

Two aliquots of the oil (1 g) were measured on a precision analytical balance of ± 0.01 mg, model AUY-220 (Shimadzu). The first aliquot was kept at a controlled temperature of 25 °C and under atmospheric pressure. The second aliquot was kept in a desiccator under a vacuum of 0.5 atm. The variation of the mass, in both conditions, was evaluated by weighing in intervals of 5 min between them.

2.1.3. Mass Stability Study after Depletion Procedure. In an adapted Kitasato flask (Figure 1), about 20 g of P52 oil was fractionated. The upper part was sealed with the aid of a glass baton. The outlet side was connected to an Edwards Model RV3 vacuum pump under a 1 atm vacuum. A glass vial was kept at 70 ± 1 °C in a heating bath (IKA, model HB-10). The system was maintained under these conditions for 1 h. It was then allowed to stand in a desiccator with a desiccant for 1 h. After the resting time, the mass of the system was measured on an analytical balance (model AUY202, Shimadzu), with an interval of 5 min between weighings, over a period of 2–5 h. During oil weighing, the stability of the scale was accompanied by the measurement of the mass of a certified reference material of 100 g.

2.1.4. Oily Water Standard Preparation. Two forms of oily water preparation were evaluated. In the first, the oil aliquots were weighed in a high-density polyethylene bottle allocated on an analytical balance (model AUY202, Shimadzu). Masses between 4 and 300 mg of oil were measured. Then, 900 mL of 3.5% (w/v) NaCl (P.A.) (Sigma-Aldrich) solution was added. The pH was adjusted to 2 with 37% HCl (Sigma-Aldrich). The system was homogenized in an ultra-turrax model T25 (IKA, Staufen, Germany) at 25,000 rpm for 10 min to promote further dispersion of the oil in water. After that, the synthetic patterns of oily water were analyzed.

In the second procedure, a bed of 31.5 g of NaCl (P.A.) (Sigma-Aldrich) was prepared in a porcelain vessel. Then, masses from 4 to 300 mg of oil were measured on a salt bed. After weighing, the crucible contents were quantitatively transferred to an amber glass vial containing 900 mL of water with the pH adjusted to 2 with 37% HCl (Sigma-Aldrich). After that, the system was homogenized on a shaker table (IKA, Staufen, Germany) for 3 min at 5000 rpm. The

choice of the shaking table was intended to prevent oil losses in the ultra-turrax.

2.2. Analysis of the Total Oil and Grease Content in Synthetic Oily Water. **2.2.1. Gravimetric Method.** The synthetic standards were transferred to a 1000 mL separation funnel, and then 3 extractions were performed with 30 mL of hexane P.A. (Merck). At each extraction, the extracts were percolated by a bed of anhydrous sodium sulfate (Spectrum) and then transferred to a glass vial at a constant weight. At the end, the extracts were completely dried in a 70 °C water bath and weighed until constant weight (model AUY202, Shimadzu).

2.2.2. Infrared Spectroscopy. Synthetic samples ($n = 5$) with a TOG concentration of 40 mg L⁻¹ were prepared and analyzed by the ASTM D 8193 method.¹¹ The synthetic standards into a separation funnel and extraction with 50 mL of cyclohexane were performed. The extracts were analyzed in an Eracheck model ECO (Eralytics).

The calibration curve was made from oily water standards prepared following the procedure developed in this work. The extraction of the P52 oil followed the procedure described above. The correlation was conducted between 11 and 220 mg L⁻¹ TOG, with the standards prepared in six replicates at each level.

Linearity was ensured through the hypothesis tests for data normality (Anderson–Darling) and homoscedasticity (Breuch–Pagan) obtained using the software Action Stat.

3. RESULTS AND DISCUSSION

The procedure for preparing oily water standards involves weighing oil and then adding it to water. Due to a possible variability in the oil weighings, a study of the variation in oil mass under room temperature and atmospheric pressure conditions was conducted.

3.1. Oil Preparation. **3.1.1. Effect of Atmospheric Conditions on Oil Mass Variation.** Figure 2 shows the results found for the four oils evaluated. It is possible to divide the mass loss kinetics into three steps. The first occurs until around 125 h, when there is a significant mass loss rate, probably evidencing the loss of the most volatile compounds. Although still pronounced, the volatile loss rate reduces between 125 and 325 h compared to the previous step. From 350 h on, the loss of mass is reduced to a rate that probably refers to loss by evaporation, demonstrating the onset of stability. Tests under

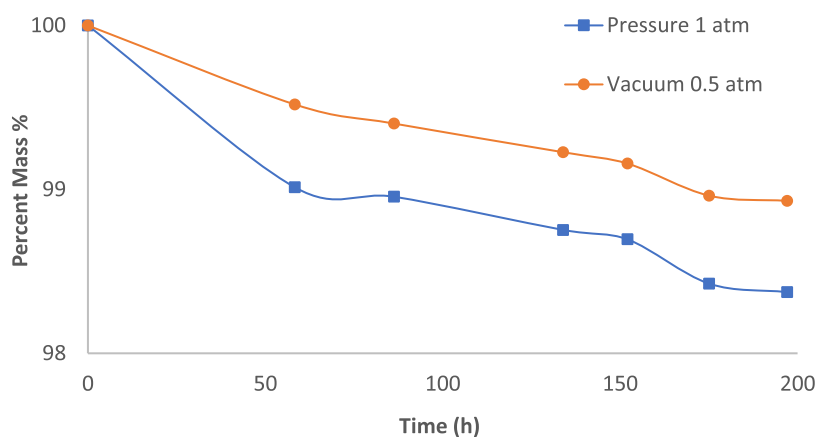


Figure 3. Study of the variation in oil mass under room temperature and vacuum conditions. Oil (P52) was heated for 2 h at 70 °C under a vacuum of 0.5 and 1 atm.

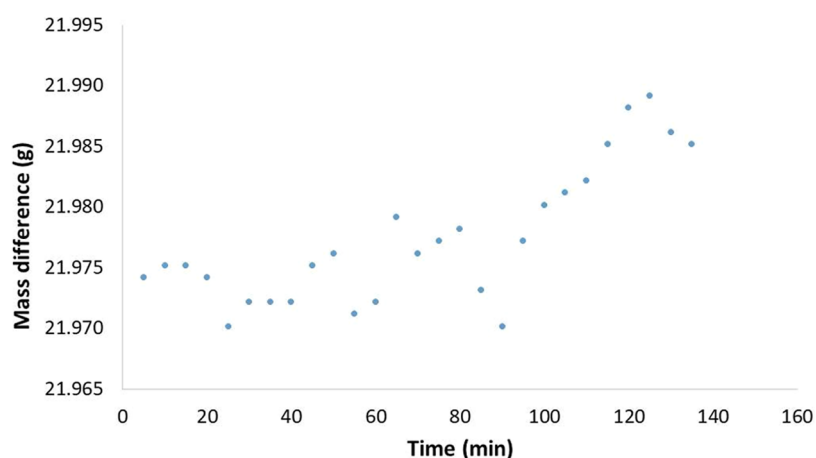


Figure 4. Stability study of the oil P52 after depletion procedure. Conditions: Oil (P52) was heated for 1 h at 70 °C, under a vacuum of 1 atm, rested for 1 h after depletion and mass loss accompanied for 2.5 h.

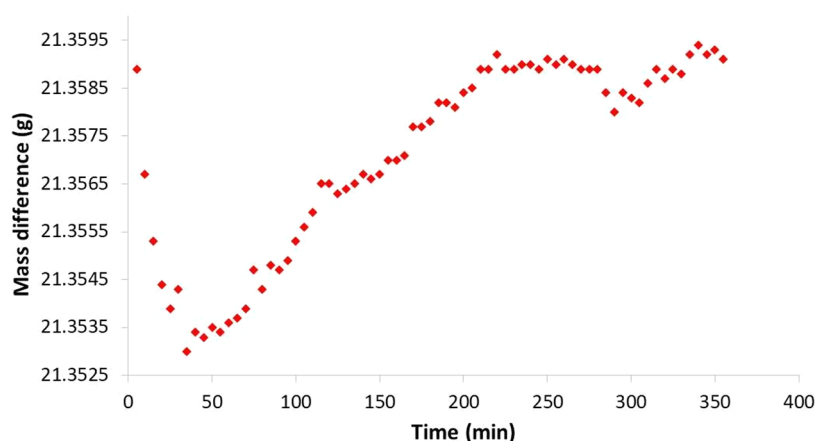


Figure 5. Stability study after oil depletion. Conditions: Oil (P52) was heated for 1 h at 70 °C, under a vacuum of 1 atm, rested for 1 h after depletion and mass loss accompanied for 5 h.

atmospheric conditions would simulate possible oscillations of masses during the weighing of the oils to prepare the standards.

The highest mass loss rate occurs in the first few hours of fractioning, which caused significant oscillation in the mass of standards. Therefore, these results indicate that the direct weighing of oil is not feasible. Thus, the kinetics of loss of mass was evaluated by exposing the oil to a vacuum system.

3.1.2. Effect of Vacuum and Temperature on Oil Mass Variation. Due to the difficulty of controlling the environmental conditions for this experiment, the exclusive use of P52 oil was preferred over other oils due to its faster kinetics.

Although the application of a vacuum of 0.5 atm in a glass desiccator was able to accelerate the kinetics of oil stabilization, it was not sufficient to eliminate the mass variation. Since the

vacuum limit in the desiccator was 0.5 atm, unfortunately, it was not possible to explore other conditions (Figure 3).

Once the favorable contribution of the vacuum was established, an oil depletion procedure was implemented, in which the vacuum intensity was increased from 0.5 to 1 atm, to accelerate the loss of volatiles. Further, the oil was heated to 70 °C, which is a temperature that can eliminate volatiles without causing degradation of other compounds. After the heating step, the oil rested to stabilize the steam–oil equilibrium. After this interval, the oil mass was weighed for 2.5 h to verify that equilibrium was really reached. Figure 4 shows the results of oil mass loss.

The results indicate that the depletion procedure promoted considerable loss of the most volatile compounds. In depletion procedure, mass loss kinetics is favored by controlled heating at 70 °C and a vacuum of 1 atm. It was possible to identify that after 1 h of rest and during the 2 h of mass loss evaluation, the vapor phase equilibrium was not reached. There was an increase in mass after 80 min. This phenomenon may have been caused by the influence of water vapor from the environment on the vapor equilibrium of the oil.

3.1.3. Phase Equilibrium Effect (Vapor–Oil) in Oil Mass Variation. This test evaluated whether 5 h of rest after depletion would already be sufficient to stabilize the mass of the oil. This evaluation aimed to optimize the preparation of synthetic standards. Figure 5 shows the obtained results.

These results showed that the oil stability window occurred 3 h after the first weighing. From that moment, it can be understood that the vapor–oil equilibrium has been reached. This result points to a greater accuracy in weighing the oil for the preparation of the standards. Table 2 summarizes the depletion and stabilization conditions for further weighing.

Table 2. Summary of Oil Depletion Conditions for the Elimination of Volatile Compounds

conditions	values
heating time	1 h
heating temperature	70 °C
waiting time after depletion	4 h

3.2. Oily Water Standard Preparation. **3.2.1. Selection of the Recipient to Weigh the Oily Water.** In order to prepare the oily water, a mass of the P52 oil was weighed in a plastic bottle with the subsequent addition of a 3.5% (w/v) NaCl solution at pH 2, and then, it was homogenized in a turrax mixer. The use of NaCl reports the seawater salinity, and the acid pH simulates the conservation of the sample made on the platform, where hydrochloric acid is added to the sample until this pH condition.

The performance evaluation of this procedure was conducted by preparing standards of 40 mg L⁻¹ TOG (*n* = 5). The quantification was performed using the gravimetric method, which is indicated for the determination of TOG content in Brazil.⁶ The oil contained in the hexane extract after evaporation of the solvent was compared with the mass of oil weighed during the preparation of 40 mg L⁻¹ standards. The results are presented in Table 3.

The results indicated a loss in the accuracy of the method since the recovery values were under 50%. This can be explained by the loss of oil due to adherence to the plastic bottle and its dispersion during homogenization. In this step, the ultra-turrax rod was immersed in the oily water standards.

Table 3. Results of Oil Recovery in Synthetic Oily Water Standards (40 mg L⁻¹ TOG) Prepared in a Polymeric Flask and in the Salt Bed^a

standards of TOG	mass of oil used to prepare the standards (mg)	mass of oil recovered in the extraction (mg)	recovery oil (%)	average oil recovery (%)	coefficient of variation (%)
Polymeric Bottle					
1	36.333	10.355	28.5	37.04	17.8
2	36.444	15.051	41.3		
3	36.222	16.191	44.7		
4	36.548	11.805	32.3		
5	36.222	13.909	38.4		
Bed of NaCl					
1	36.258	30.602	84.4	84.86	3.3
2	36.222	29.774	82.2		
3	36.485	31.742	87.0		
4	36.333	29.902	82.3		
5	36.521	32.285	88.4		

^aTOG content was determined by the gravimetric method.

After homogenization, when the rod was removed, some of the oil was lost.

A new form was then developed for the preparation of oily water. In this one, the oil was weighed directly into a bed of NaCl, and then, 900 mL of water at pH 2, adjusted with 37% HCl, was added. Homogenization was carried out on a vibrating table in preference to a turrax mixer. After preparation, gravimetric analyses were carried out on the synthetic samples. Table 3 presents the obtained results of oil recovery after determination of TOG content by the gravimetric method in 40 mg L⁻¹ TOG synthetic oily water standards prepared by weighing oil directly into a polymer bottle and bed of NaCl.

As the results of weighing the oil in the NaCl bed offered higher oil recoveries than the results obtained by weighing the oil directly in a polymeric vial, this preparation strategy was consolidated.

For the validation of the developed procedure, accuracy and precision were evaluated over a wide range of concentrations. The studies were performed with five replicates, and the TOG concentrations ranged from 5.5 to 72 mg L⁻¹. The accuracy was calculated through the oil content contained in the hexane extract, after evaporation of the solvent, and compared with the mass of oil weighed during the preparation of the standards. The precision in the preparation of the standards was evaluated in terms of the coefficient of variation of TOG content between the replicates prepared for each concentration level. Table 4 shows the obtained results.

The variation between the replicates of the prepared standards was between 3.8 and 11%, with the minor concentration levels presenting the most variation. Recovery values ranged from 70 to 85% and an apparent division into two groups can be seen. Applying the *t*-Student's test, it was identified that the two sets are statistically different, confirming that increasing the concentration in the samples causes a loss in recovery. The variation can be explained by a possible oil loss in the extraction step. The result was unexpected. However, there are no reports in the literature of validation of a gravimetric method for determining the content of oils and greases in water using oil as a standard. Accuracy evaluations by the gravimetric method have been reported in patent

Table 4. Results of the Evaluation of Accuracy and Precision in the Preparation of Oily Water Standards from the Developed Procedure^a

TOG theoretical concentration (mg L ⁻¹)	average oil recovery (%)	coefficient of variation (%) (n = 5)
5	85.0	7.1
10	83.0	11.0
30	87.0	5.0
40	75.0	6.2
60	73.0	3.8
70	70.0	5.9

^aDetermination of the TOG content was made by the gravimetric method.

5,294,553²⁸ and in the work of Biazon and co-workers.²⁹ In both works, recovery is studied only up to the 30 mg L⁻¹ concentration range, not covering the range of this work. At this concentration, the recovery is about 80%, confirming the values found in the developed procedure at this work.

It can be explained by the possible loss of light compounds, not expelled in the depletion, which, when solvated by hexane, are lost in the drying step. Very low-molecular-weight compounds can be lost due to volatilization, while very high-molecular-weight compounds are often not recovered well in liquid/liquid extractions.³⁰

As the results of accuracy and precision were satisfactory with gravimetric determination, the applicability of the oily water standards in other TOG determination methodologies was studied, applying the infrared method.

3.2.2. Determination of TOG in the Oily Water Standards by Infrared Spectroscopy. The oily water samples (n = 5), with a theoretical TOG concentration of 40 mg L⁻¹, were prepared with the P52 oil and analyzed by the ASTM D 8193 method in order to apply the synthetic standards in a methodology for TOG determination by infrared spectroscopy.

The choice of the alternative method for evaluating the produced oily water standards as the infrared method presented in this standard was justified by the possibility of applying the equipment Eracheck in an offshore environment.

Because it is an indirect method, a calibration curve (Figure 6) was constructed for oily water standards corresponding to the TOG content between 12 and 220 mg L⁻¹.

The statistical tests indicated that the data composing the calibration curve follow normal distribution (Anderson–

Darling: *p*-value = 0.148; as *p*-value > 0.05, H₀ is accepted). Similarly, the residuals follow homoscedastic behavior (Breusch–Pagan: *p*-value = 0.786; as *p*-value > 0.05, H₀ is accepted).

After the IR linearity study employing the oily water synthetic standards, 5 synthetic standards (theoretical TOG 40 mg L⁻¹) were prepared for recovery study.

The recovery was calculated based on the oil content contained in cyclohexane extract and compared with the mass of oil weighed during the preparation of the standard (40 mg L⁻¹ TOG). Table 5 shows the recovery results after extracting the synthetic standards from oil–water with cyclohexane.

Table 5. Oil Recovery Results Obtained in the Synthetic Samples Prepared with the P52 oil after Determination of TOG Content Using the ASTM D 8193 Method with Quantification Done Using the Calibration Curve Prepared with Oily Water Synthetic Standards

replicas	oil recovery (%)	average recovery (%)	coefficient of variation (n = 5) (%)
1	107.7		
2	108.5		
3	100.6	105.2	4.0
4	108.5		
5	100.6		

The application of synthetic standards for TOG analysis per ASTM D 8193 showed recovery results of 105.2% with reproducibility of 4.0%. These results were better than the values given in the standard: recovery between 70 and 130% and precision of 10%. Recovery values higher than 100% may be associated with the variability caused by the heterogeneity of the oil matrix.

This behavior indicates that the use of oily water standards in the validation step of the IR methodology did not compromise the accuracy and precision limits when compared to the values indicated in the ASTM D 8193 standard (obtained using a tetradecane solution).

Recoveries around 100% indicate that the procedure developed for the generation of synthetic standards for oily water is applicable not only to the gravimetric method but also to the spectroscopic methods.

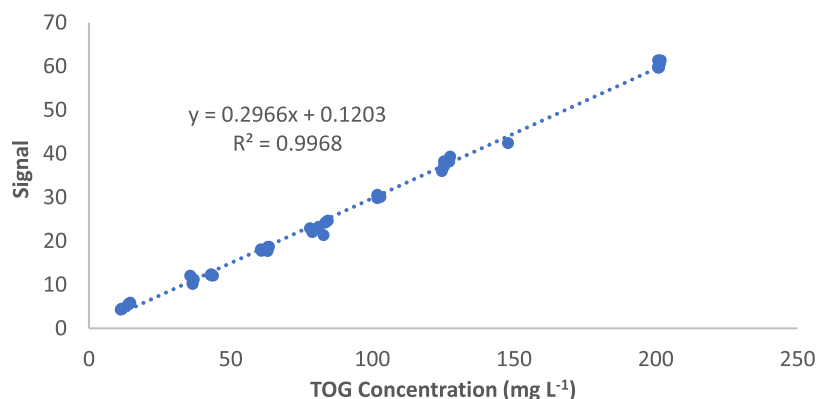


Figure 6. Calibration curve for TOG content determination by the ASTM Method D 8193, constructed using synthetic oily water standards prepared with the P52 oil containing between 12 and 220 mg L⁻¹ TOG.

4. CONCLUSIONS

Oily water standards have been successfully developed to validate analytical methodologies for determining TOG content. Accuracy and precision studies were performed using the gravimetric method, required by Brazilian regulations, and an alternative spectroscopic method.

A study was carried out on the interference of volatile compounds in oil weighing, in the progress of standard preparation, created in the development of an oil depletion procedure.

The prepared standards demonstrated high reproducibility and accuracy. The results were similar to those found in the ASTM D 8193 standard, which presents the acceptance limits for validating the methodologies.

The development of water-dispersed oil standards allowed the validation of gravimetric and IR methodologies using the oil itself. With this strategy, the complexity of the oil matrix was brought into the context of validation applied to more robust TOG determinations.

Other studies must be addressed to obtain reference material certificates. Furthermore, the influence on the results before the reduction of volatile compounds caused by the stripping procedure should also be investigated.

AUTHOR INFORMATION

Corresponding Author

Vinnicius Ferração Brant – SENAI Innovation Institute for Green Chemistry, FIRJAN, 20271-030 Rio de Janeiro, RJ, Brazil; Department of Analytical Chemistry—Fundamental and Applied Analytical Chemistry Laboratory, Institute of Chemistry, Fluminense Federal University, 24020-141 Niterói, RJ, Brazil; orcid.org/0000-0001-7572-5645; Email: vbrant@id.uff.br

Authors

Rogério Mesquita de Carvalho – Petrobras, 21949-900 Rio de Janeiro, RJ, Brazil

Márcio de Oliveira Martins – Petrobras, 21949-900 Rio de Janeiro, RJ, Brazil

Flávia Ferreira de Carvalho Marques – Department of Analytical Chemistry—Fundamental and Applied Analytical Chemistry Laboratory, Institute of Chemistry, Fluminense Federal University, 24020-141 Niterói, RJ, Brazil

Antonio Augusto Fidalgo-Neto – SENAI Innovation Institute for Green Chemistry, FIRJAN, 20271-030 Rio de Janeiro, RJ, Brazil

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.3c02718>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Petrobras and ANP (Brazil's National Oil, Natural Gas, and Biofuels Agency) through the R&D levy regulation.

REFERENCES

- (1) Al-Ghouti, M. A.; Al-Kaabi, M. A.; Ashfaq, M. Y.; Adel Da'na, D. Produced water characteristics, treatment and reuse: A review. *J. Water Process Eng.* **2019**, *28*, 222–239.
- (2) Fraser, G. S.; Ellis, J. The Canada-Newfoundland Atlantic Accord Implementation Act: Transparency of the environmental

management of the offshore oil and gas industry. *Mar. Policy* **2009**, *33*, 312–316.

- (3) de Oliveira, R. A.; Carvalho, R. M.; Gobbi, A. L.; Lima, R. S. Microemulsification-based method enables field-deployable quantification of oil in produced water. *Fuel* **2022**, *308*, No. 121960.

- (4) Farmaki, E.; Kaloudisa, T.; Dimitroua, K.; Thanasoulis, N.; Thana, N.; Kousouris, L.; Tzoumerkasc, F. Validation of a FT-IR method for the determination of oils and grease in water using tetrachloroethylene as the extraction solvent. *Desalination* **2007**, *210*, 52–60.

- (5) Fakhru'l-Razi, A.; Pendashteh, A.; Abdullah, L. C.; Biak, D. R. A.; Madaeni, S. S.; Abidin, Z. Z. Review of technologies for oil and gas produced water treatment. *J. Hazard. Mater.* **2009**, *170*, 530–551.

- (6) CONAMA. Resolução 393 do CONSELHO NACIONAL DO MEIO AMBIENTE. *Diário Oficial da União Brasil* **2007**, *1*, 72–73.

- (7) SM: 5520-B. *Standard Methods For the Examination of Water and Wastewater*; American Journal of Public Health and the Nations Health, 2018.

- (8) USEPA: 1664. *U.S. Environmental Protection Agency Office of Water, Method 1664, Revision B: n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry*; USEPA, 2010.

- (9) Ramsey, E. D. Determination of oil-in-water using automated direct aqueous supercritical fluid extraction interfaced to infrared spectroscopy. *J. Supercrit. Fluids* **2008**, *44*, 201–210.

- (10) Romero, M. T.; Ferrer, N. Determination of oil and grease by solid phase extraction and infrared spectroscopy. *Anal. Chim. Acta* **1999**, *395*, 77–84.

- (11) ASTM: 8193. *Standard Test Method for Total Oil and Grease (TOG) and Total Petroleum Hydrocarbon (TPH) in Water and Wastewater with Solvent Extraction Using Non-Dispersive Mid-IR Transmission Spectroscopy*; ASTM, 2018.

- (12) ASTM: 7575. *Standard Test Method for Solvent-Free Membrane Recoverable Oil and Grease by Infrared Determination*; ASTM, 2011.

- (13) ASTM: 7678. *Standard Test Method for Total Petroleum Hydrocarbons (TPH) in Water and Wastewater with Solvent Extraction using Mid-IR Laser Spectroscopy*; ASTM, 2011.

- (14) ASTM: 7678. *Standard Test Method for Total Petroleum Hydrocarbons (TPH) in Water and Wastewater with Solvent Extraction using Mid-IR Laser Spectroscopy*; ASTM, 2011.

- (15) Motta, A.; Borges, C.; Esquerre, K.; Kiperstok, A. Oil Produced Water treatment for oil removal by an integration of coalescer bed and microfiltration membrane processes. *J. Membr. Sci.* **2014**, *469*, 371–378.

- (16) Malkov, V.; Sievert, D. Applications of Submersible Fluorescence Sensors for Monitoring Hydrocarbons in Treated and Untreated Waters: Methods and Applications. In *Fluorescence in Industry*, Pedras, B., Ed.; Springer: Cham, 2019; Vol. 1, pp 135–171.

- (17) da Silva, C. M. F.; da Silva, A.; Melchuna, A.; Arinelli, L.; Hori, E. S.; Lucas, E. F. Correlation between Methods to Determine Total Oil and Grease in Synthetic Oily Water Using Heavy Oil: Gravimetry vs Fluorimetry. *Ind. Eng. Chem. Res.* **2022**, *61*, 18243–18249.

- (18) Reus, U. Determination of trace elements in oils and greases with total reflection X-ray fluorescence: sample preparation methods. *Spectrochim. Acta, Part B* **1991**, *46*, 1403–1411.

- (19) Khorshid, Z. B.; Doroodmand, M. M.; Abdollahi, S. UV-Vis. spectrophotometric method for oil and grease determination in water, soil and different mediates based on emulsion. *Microchem. J.* **2010**, *160*, No. 105620.

- (20) Costa, J. A.; Farias, N. C.; Queirós, Y. G. C.; Mansur, C. R. Determination of oil-in-water using nanoemulsions as solvents and UV visible and total organic carbon detection methods. *Talanta* **2013**, *107*, 304–311.

- (21) ISO: 9377-2. *Water Quality—Determination of Hydrocarbon Oil Index Part 2-Method Using Solvent Extraction and Gas Chromatography*; ISO: Switzerland.

- (22) Bucci, R.; Tafani, S.; Tarol, A. M.; Girelli, A. M. Oils and grease determination by FT-IR and n-hexane as extraction solvent. *J. Anal. Chem.* **2015**, *70*, 316–319.
- (23) ASTM D: 7066. *Standard Test Method for Dimer/Trimer of Chlorotrifluoroethylene (S-316) Recoverable Oil and Grease and Nonpolar Material by Infrared Determination*; ASTM, 2004.
- (24) Daghbouche, Y.; Garrigues, S.; Morales-Rubio, A.; Guardia, M. d. I. Evaluation of extraction alternatives for Fourier transform infrared spectrometric determination of oil and greases in water. *Anal. Chim. Acta* **1997**, *345*, 161–171.
- (25) Almeida, C. M. M.; Silvério, S.; Silva, C.; Paulino, A.; Nascimento, S.; Revez, C. A. Optimization and validation of FTIR method with tetrachloroethylene for determination of oils and grease in water matrices. *J. Braz. Chem. Soc.* **2013**, *24*, 1403–1413.
- (26) Costa, J. A.; Farias, N. C.; Queirós, Y. G. C.; Mansur, C. R. E. Determination of oil-in-water using nanoemulsions as solvents and UV visible and total organic carbon detection methods. *Talanta* **2013**, *107*, 304–311.
- (27) Winkler, I.; Agapova, N. Determination of water pollution by the oil products through UV photometry. *Environ. Monit. Assess.* **2010**, *168*, 115–119.
- (28) Kawahara, F. K. Method for the Gravimetric Determination of Oil and Grease. U.S. Patent US5294553A1994.
- (29) de Oliveira, E. C.; Biazon, C. L.; Moreira, R. M.; Filho, P. L. Uncertainty evaluation in the determination of oil and grease content in produced water by colorimetric method using Monte Carlo Simulation. *Pet. Sci. Technol.* **2019**, *37*, 436–442.
- (30) Stenstrom, M. K.; Fam, S.; Silverman, G. S. Analytical methods for quantitative and qualitative determination of hydrocarbons and oil and grease in water and wastewater. *Environ. Technol. Lett.* **1986**, *7*, 625–636.