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Determination of oil-in-water using nanoemulsions as solvents and UV visible and total organic carbon detection methods

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ABSTRACT

The aim of this study was to investigate the application of oil in water (O/W) nanoemulsion as solvent in the extraction step for determination of oil content in oily water, measured using a UV visible spectrophotometer (UV–vis) and a total organic carbon (TOC) analyzer. The optical micrographs and distribution size curves showed that the use of a small amount of nanoemulsion was capable of transforming the oily water in a colloidal dispersion that can be read in the UV–vis and TOC-VCHS devices. The oil content results obtained showed great accuracy between the measurements, with very low average standard deviation (~5%) for both UV–vis and TOC-VCHS. The new methods suggested in this work are very promising, since they allow simple, quick and accurate analyses, and especially require a lower volume of solvent (less than 1%) compared to those used in conventional analytic methods.

1. Introduction

The increasing exploration and production of oil in deep waters has raised environmental concerns among authorities and the public, especially regarding the quality of the wastewater discharged from this type of activity.

Specific rules from the environmental agencies of several countries limit the oil content in water to a monthly average of 29 mg L^{-1} and the methods for determining this content are established in standards [1,2]. The big problem is that these analytic methods have limitations that affect the accuracy and precision of the results. Additionally, they consume enormous amounts of toxic solvents that need to be recovered [3–5].

The study results of methods to determine the oil content of wastewater conducted in 205 laboratories located only in Nordic countries showed that 300,000 measurements were made in 2001 alone. This represented the use of about 1.75 t of toxic solvents, which are also considered to deplete the ozone layer [6].

The test methods most widely used involve gravity and infrared spectrometry (IR) and employ Freon-113 (1,1,2-trichloro-1,2,2-trifluoroethane) in the sample preparation stage for liquid phase extraction (LLE). With Decision XI/15 of the Parties to the Montreal Protocol, which ended the manufacture of Freon-113 on January 1, 2002, several alternative methods have been introduced using different solvents in the extraction step in the liquid phase [7].

For the gravimetric method, in the revision of the standard (EPA method 1664-A, 2009), the solvent employed in liquid–liquid extraction (LLE) is now *n*-hexane instead of Freon-113. Although this method is simple and cheaper, It has disadvantages such as low sensitivity (detection limits are usually 5–10 mg L^{-1}), loss of components, which volatilize at temperatures higher than those used for the evaporation of the solvent, high time and possibility of the inclusion of compounds other than oils and grease that are extracted by the solvent and as such contribute to the final weight [8,9].

In order to validate the methods using the IR technique, Horiba developed the solvent S-316 (1,2,3,4-tetrachloro-1,1,2,3,4,4-hexafluorobutane) and ASTM approved and published the ASTM D 7066 method (2004), allowing the use of S-316 as a solvent in extraction phase for oil content analysis using IR spectrometry, at a wavelength of 2930 cm^{-1}. Despite its relative availability, the solvent S-316 is a clorofluorcarbon (CFC) and is suspected of being an ozone depleting solvent [6]. Farmaki et al. [10] proposed validating the method by using IR and tetrachlorethylene (TTCE) as the extractor solvent, since the infrared technique is simple and has high sensitivity for a large number of analytes. The results showed that the method is robust and presented acceptable levels of accuracy and recovery of the analyte, with detection limits of about 0.0001 mg mL^{-1}. However, the use of TTCE does not provide a long-term solution, since it is on the Montreal Protocol list of substances to be banned in 2030 [11].

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The International Organization for Standardization (ISO) had already introduced Gas Chromatography (GC) method ISO 9377-2 in 2000. In this version of the standard, *n*-hexane is used to extract oil from water and hydrocarbon species are measured using flame ionization detection (FID). This method is suitable for surface waters, industrial effluents and water from sewage treatment, by allowing determination of the index of hydrocarbon at concentrations from 0.1 mg L^{-1}. This index is determined by the sum of compounds with retention times between the compounds *n*-decane and *n*-tetracontane [6,12].

Since ISO 9377-2 (2000) is not applicable to hydrocarbons with chain lengths below C10, a modification of the method was proposed by the OSPAR Commission (Oslo and Paris Convention for Protection of the Marine Environment of the North), to include certain hydrocarbons having smaller chain lengths for measuring the concentration of hydrocarbons in produced water.

OSPAR changed the ISO 9377-2 (2000) standard, so that *n*-pentane is used also in the ELL step, which allows adding the concentrations of the extracts of compounds which are not adsorbed by treatment with silica gel (TMS), whose retention time varies among the compounds *n*-heptane (C_7H_{16}) and *n*-tetracontane (*n*-$C_{40}H_{82}$). The total peak area in the retention time range, excluding the concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX), is used to calculate the level of oil in water.

The ISO 9377-2 (2000) method, as altered by OSPAR, became the standard reference method for measuring oil in water for the OSPAR countries from January 1, 2007. However, the report generated from an independent survey sponsored by United Kingdom Department of Trade and Industry (DTI) and a consortium of eight oil companies concluded that the GC-FID Method (ISO 9377-2), as altered by OSPAR, would be difficult to implement and suggested that an alternative method using simpler parameters and more familiar techniques should be considered. Based on the trial report OSPAR has acknowledged that the modified version of ISO 9377-2 which uses complex GC instrumentation with difficult total integration parameters may limit or even prevent implementation on certain offshore installations and considers that the use of simpler methods would be useful [13].

Nanoemulsions are liquid dispersions in which droplets of one liquid with nanometric diameters are dispersed in the continuous phase of another liquid, so that they present the classic behavior of colloids [14,15].

In order to minimize the use of toxic solvents and to evaluate other techniques for determining oil content in produced water, this study evaluated the application of oil-in-water (O/W) nanoemulsion as the solvent in the extraction step and the use of an ultraviolet–visible (UV–vis) spectrophotometer and a total organic carbon analyzer (TOC).

2. Experimental

2.1. Materials

We used the nonionic surfactant ethoxylated lauryl ether (ULTROL® L70), obtained from Oxiteno-Brazil, with seven ethylene oxide (EO) units in its chain, to prepare the oil-in-water nanoemulsion. As the oil phase, we used Solbrax Eco 175/225. This is a solvent produced by Petrobras and was donated by its distribution subsidiary, BR Distribuidora, Brazil. It is mainly composed of aliphatic and naphthenic hydrocarbons with a distillation range between 175 and 225 °C.

The crude oil used came from Brazilian well and was donated by the Petrobras Research Center. It had the following characteristics: =21.2° API; saturates content=40.7%, aromatics content=34.1%; resins content=22.9% and asphaltenes content =2.4%.

2.2. Obtaining nanoemulsion based on Solbrax

The O/W nanoemulsion used was prepared by the high-energy method in an Emulsiflex C5—Avastin high-pressure homogenizer (HPH).

Initially, we prepared emulsions (saltwater/Solbrax/L70) from the Eco Solbrax solvent mixture with the ethoxylated surfactant (ULTROL L70), and subsequent addition of brine.

The content of the oil phase (Eco-Solbrax) was varied between 5 and 10 wt%, with surfactant concentrations of 10 and 12 wt%. The brine was prepared by adding NaCl and $CaCl_2$ (10:1) in deionized distilled water. The total concentration of salts in water was 55,000 mg L^{-1}.

All samples were processed in the HPH at a pressure of 15,000 psi and 3 cycles of operation, since in the previous study [16,17] these were the best conditions for obtaining the most stable nanoemulsions and smaller droplet sizes. They were characterized regarding droplet size and size distribution as well as stability, by the light dynamic backscattering in a Malvern Zetasizer Nano ZS [18].

2.3. Preparation of synthetic oily water

The same saline solution used to obtain the nanoemulsion was also used to prepare the synthetic oily water. 200 μL of oil was added slowly to 1 L of brine by means of a micropipette with long stem and using an Ultra Turrax mixer (model T-25), at 13,000 rpm. The synthetic oily water was then allowed to stand for one hour and was analyzed for droplet size and size distribution in the same Zetasizer Nano ZS and under an S2H10 optical microscope. This oily water, containing an oil content of 200 mg L^{-1} (theoretical), was considered here as the ceiling. The same procedure was used to prepare oily water containing 10 mg L^{-1} (theoretical), which was considered the minimum.

2.4. Determining oil-in-water by extraction with solvents and by solubilization in o/w nanoemulsions using the UV–vis spectrophotometer

Initially, we performed solubility tests by adding 0.1 wt% of crude oil in the O/W nanoemulsions, at room temperature. For the nanoemulsion that presented the best solubilization of crude oil, we did saturation tests, by adding concentrations ranging from 0.001 to 10 wt% of crude oil in the nanoemulsion.

Later, we carried out solubility tests of crude oil dispersed in synthetic oily water by addition of the nanoemulsion in the oily water samples in the following ratios: 1:1, 1:0.5, 1:0.2, 1:0.1, 1:0.02 and 1:0.01. The droplet size and size distribution were measured in the Zetasizer Nano ZS. Analyzes were also made in the S2H10 optical microscope in order to observe the behavior of the nanoemulsion before and after adding the oil. From these tests, we determined the saturation point of the nanoemulsion with crude oil and selected the mixing ratio able to transform the oily water in a colloidal dispersion. This ratio was then used as a standard to obtain the calibration curve of crude oil in the nanoemulsion.

2.4.1. Obtaining calibration curves using the solvents n-hexane, Solbrax-Eco and the nanoemulsion

For the solvents *n*-hexane and Solbrax, solutions were prepared at concentration of 1 wt% of crude oil and were diluted to concentrations from 10 to 10,000 mg L^{-1}. For the nanoemulsion,

Table 1
Composition and stability of nanoemulsions based on Solbrax.

Solbrax (wt%)	Ultrol L70 (wt%)	
	10	12
7	Stable/+120 days	Stable/+120 days
8	Stable/30 days	Stable/+120 days
9	Unstable	Stable/8 days
10	Unstable	Unstable

solutions of 5 wt% of crude oil were prepared and were diluted to concentrations from 10 to 50,000 mg L^{-1}. These solutions were diluted in brine using the mixing ratio established as standard. For all solutions, scan readings were performed at wavelengths between 200 and 800 nm, in a Varian Cary 50 UV–vis spectrophotometer, equipped with 5 and 10 mm fiber optic probes.

2.4.2. Extraction of crude oil from synthetic oily water with the solvents n-hexane and Solbrax and determining oil content

For the extraction of crude oil from the synthetic oily water, 10 mL of each solvent was added to 100 mL of the oily water samples. These mixtures were stirred and then kept at rest as usual in liquid–liquid extraction procedure. Aliquots of the solvent phase (hexane and Solbrax) were brought to the equipment for UV absorbance reading, determined under the same conditions as used to obtain the calibration curves. The oil content was obtained with the aid of the calibration curves of the oil in the respective solvent.

2.4.3. Preparation of nanoemulsion in synthetic oily water mixture and determination of oil-in-water

Aliquots of the nanoemulsion were added to 100 mL of synthetic oily water samples, in the ratio established as standard. UV absorbance reading was carried out under the same conditions used for plotting the calibration curve of the oil in the nanoemulsion. The oil content was determined with the help of the calibration curve obtained for the crude oil in the nanoemulsion.

2.5. Determination of oil-in-water by solubilization in o/w nanoemulsion using the total organic carbon (TOC) analyzer

To assess the measurement accuracy and precision of the carbon content measured by the analyzer (TOC-VCSH, Shimadzu), we initially prepared solutions of ethanol and butanol in deionized water at a concentration of 5000 mg L^{-1}. These solutions were diluted to 200 and 400 mg L^{-1} in order to the TOC values obtained were within the calibration curves of the equipment. Then the experimental values were compared to theoretical values.

We later determined the mean TOC value of the pure nanoemulsion diluted in saline water in different proportions, also obeying the limits of the calibration curve plotted for the equipment.

To determine the oil content of the oily water in samples containing 10 mg L^{-1} (minimum detection limit) and 200 mg L^{-1} (maximum detection limit), aliquots of 25 μL or 0.5 mL of the nanoemulsion samples were added in 100 mL of synthetic oily water previously prepared. These samples were then placed in the TOC-VCHS equipment and the oil content was obtained by converting the difference between the TOC of the oily water samples containing the nanoemulsion and the average TOC of the pure nanoemulsion diluted in saline water. For this we used a conversion factor obtained from the ratio between the molar mass of the carbon and average molar mass of saturated hydrocarbons in a range between *n*-heptane (C_7H_{16}) and tetracontane ($C_{40}H_{82}$) (considered here as the main constituents of crude oil).

A calibration curve of the crude oil content in the nanoemulsion was obtained as a function of TOC values at concentrations ranging from 0.1 to 10%. This curve was used to determine the crude oil content in oily water of 200 mg L^{-1}.

All analyses of this study were performed in duplicate by two different lab technicians.

3. Results and discussion

3.1. Formation and stability of nanoemulsion based on Solbrax

For formation of the nanoemulsions, the Solbrax solvent was selected as oil phase because it has good affinity with crude oil, since it is basically composed of a mixture of aliphatic hydrocarbon naphtha extracted and treated by the catalytic hydrocracking process. This reduces its aromatics content to less than 1%, presenting low toxicity [19]. The ethoxylated surfactant Utrol L70 was used to stabilize these nanoemulsions [20].

For the compositions containing 5 to 6 wt% oil phase (Solbrax) and 10 to 12 wt% of surfactant (ULTROL L70) was not necessary to use any method of high energy, such as high-shear stirring, high-pressure homogenizers and ultrasound generators for preparation of nanoemulsion [21]. The oil phase concentration was increased to 7–10 wt% and the surfactant concentration was maintained (10 and 12 wt%) and for these systems the nanoemulsions were obtained in the high-pressure homogenizer.

Table 1 shows the composition and size range (between 5 and 20 nm) of nanoemulsions formed and the times they remained stable. The photo in Fig. 1a shows the transparency of the nanoemulsion containing 8 wt% Solbrax and 12 wt% surfactant. This is due to the tiny size of the droplets. In comparison, the nanoemulsion that lost size stability had a milky appearance. Fig. 1b shows the nanoemulsion droplet size distribution curves in the period of 120 days, and with above 90% of sample volume in the size range between 5 and 20 nm. Fig. 1c shows an optical micrograph of the same solution.

3.2. Synthetic oily water

Fig. 2a shows the size distribution curve of the crude oil droplets dispersed in the synthetic oily water (oil concentration of 200 mg L^{-1}) prepared by the method described in Section 2.3. It can be seen that these droplets showed size in the range between 700 and 2000 nm. Fig. 2b contains the optical micrograph, which shows the dispersed droplets of crude oil.

3.3. Determining oil-in-water by extraction with solvents and by solubilization in o/w nanoemulsions using the UV–vis spectrophotometer

3.3.1. Extraction with solvents and reading in the UV–vis spectrophotometer

The determination of the oil content in the oily water by extraction with *n*-hexane and reading in the UV–vis spectrophotometer was performed only to serve as a comparative parameter with the new proposed method using the nanoemulsion, since this solvent has been used in standard methods to determine the oil content in oily water [22]. The use of Solbrax in the extraction step was also for comparative purpose, since this solvent was used as the oil phase of the nanoemulsion. Thus, the analysis was performed only for the theoretical synthetic oily water concentration of 200 mg L^{-1}. The calibration curves used in

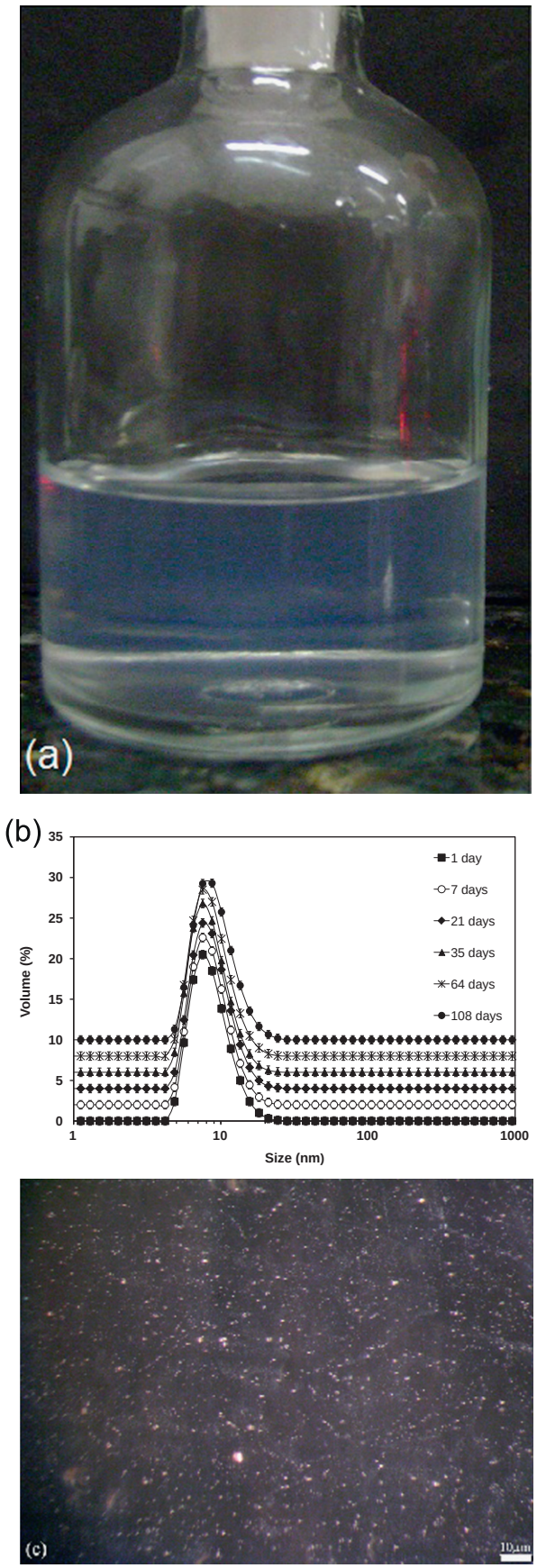

Fig. 1. Nanoemulsion based on Solbrax and ULTROL L70, which remained stable for over 120 days: (a) photograph (b) droplet size distribution curve and (c) optical micrograph.

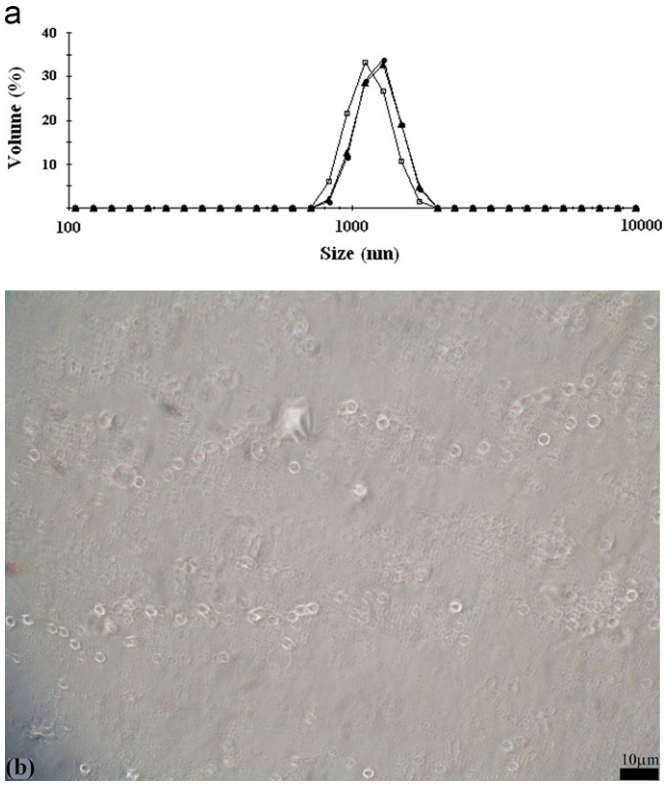

Fig. 2. Synthetic oily water: (a) crude oil droplet size distribution curves and (b) optical micrograph of the dispersion.

this study were constructed for the absorption at a wavelength of 400 nm and the optical path of the probe of 5 mm, since they showed the best correlation coefficients of the linear equations with standard deviation less than 3%. Fig. 3a and b show the calibration curves of the crude oil in *n*-hexane and Solbrax, respectively. Table 2 shows the mean and standard deviation of the oil content of the synthetic oily water obtained using the extraction method with *n*-hexane and Solbrax and the UV–vis reading.

The average oil content of the synthetic oily water shown on Table 2 agrees with expected experimental value, since it was prepared with a theoretical crude oil concentration of 200 mg L^{-1} and during its preparation there were oil losses in the stem of Ultra Turrax stirrer and the walls of the backer. Furthermore, with Solbrax as the solvent, the oil content was lower. This can be explained because Solbrax has lower affinity for the heavier petroleum fractions, such as resins and asphaltenes (substances that have higher UV–vis absorption) than the *n*-hexane solvent, since it is basically a mixture of saturated hydrocarbons of higher molar weights.

3.3.2. Study of the solubilization and saturation of crude oil in the nanoemulsions

The study of the solubility and saturation of crude oil in the nanoemulsions was performed by optical microscopy and particle size analysis.

Initially, the crude oil (at concentration of 0.1 wt%) was added in nanoemulsions, and for all nanoemulsions the results demonstrated that the entire oil mass had migrated into nanoemulsion drops distributed evenly, producing a homogeneous dispersion, with above 80% of sample volume without significant size variation. This way was selected for this study the stable nanoemulsion containing the highest level of oil phase (Sobrax—8 wt%) and

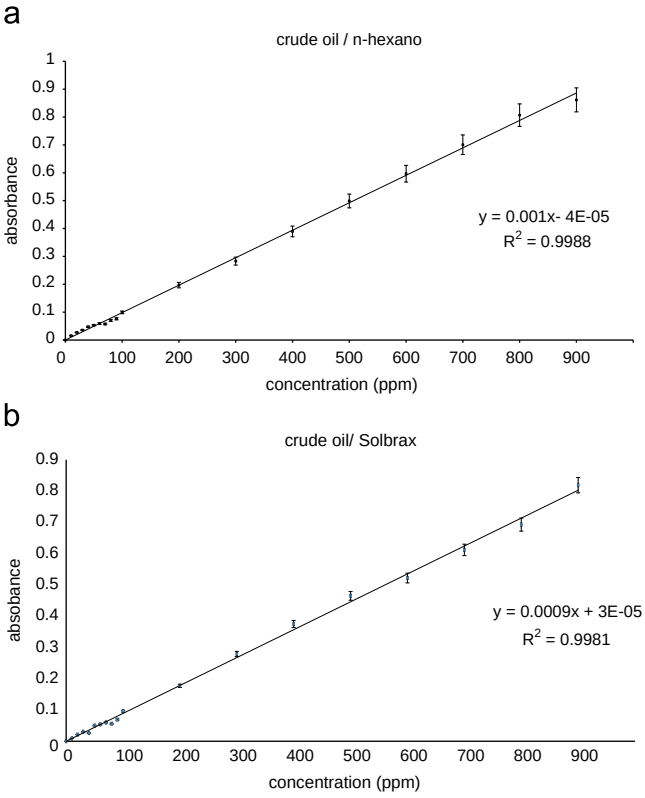

Fig. 3. Calibration curves of crude oil plotted for the wavelength of 400 nm from the reading probe of 5 mm in the UV–vis spectrophotometer with (a) hexane and (b) Solbrax.

Table 2
Oil content values of synthetic oily water obtained by extraction with *n*-hexane and Solbrax solvents, read in the UV–vis spectrophotometer.

Samples	*n*-Hexane			Solbrax		
	Average absorbance	Standard deviation	Content o/w (mg L^{-1})	Average absorbance	Standard deviation	Content o/w (mg L^{-1})
1	0.361346	0.021589	256 ± 17	0.344102	0.037477	254 ± 41
2	0.330983	0.006408	225 ± 3	0.251244	0.008952	149 ± 11
3	0.245246	0.036461	137 ± 36	0.248058	0.010545	146 ± 12
4	0.23677	0.040699	129 ± 39	0.248968	0.01009	147 ± 12
5	0.29169	0.013238	185 ± 10	0.228485	0.020332	124 ± 23
6	0.293056	0.012555	187 ± 9	0.232581	0.018283	128 ± 22
7	0.240342	0.038913	141 ± 29	0.253975	0.007586	152 ± 10
Average	**0.285633**	**0.024266**	**180 ± 20**	**0.269148**	**0.018947**	**170 ± 20**

the Ultrol L70 surfactant at 12 wt%, in which the crude oil was more easily solubilized. Fig. 4a–c show a photo of the nanoemulsion containing crude oil, the oil droplet size distribution curves and optical micrograph, respectively. The graph in Fig. 4b shows that the size distribution curve is similar to the curve of Fig. 1b (pure nanoemulsion), indicating no significant change in the droplet size of nanoemulsion with solubilization of crude oil in the nanoemulsion. The optical micrograph in Fig. 4c shows the droplets of nanoemulsion containing crude oil.

The optical micrographs shown in Fig. 5 indicate the onset of saturation at a concentration of 10 wt%, in which the droplets size exceeds the ceiling (6000 nm) of the Zetasizer Nano ZS equipment and the droplets begin to lose their spherical shape but not yet showing visual phase separation of the nanoemulsion.

The study of the solubility of crude oil dispersed in synthetic oily water by addition of the nanoemulsion showed that for all

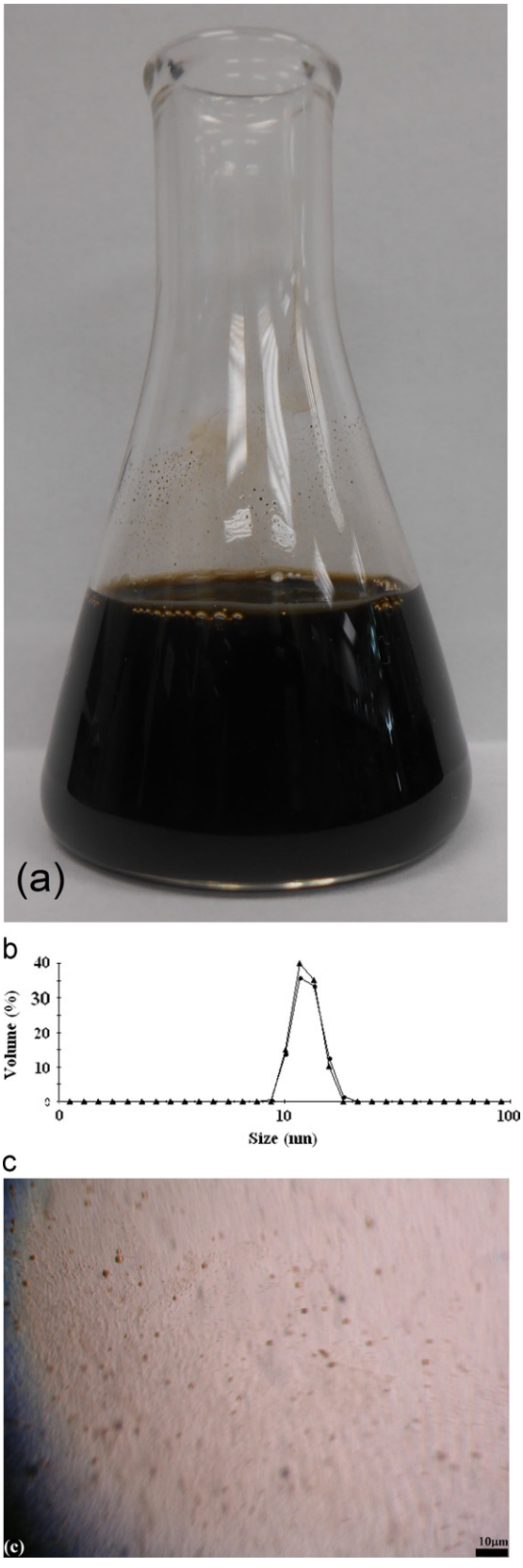

Fig. 4. Dispersion of crude oil in the nanoemulsion: (a) photograph, (b) size distribution curve and (c) optical micrograph.

proportions the oil dispersed in the oily water, initially with sizes in the range between 700 and 2000 nm (Fig. 2a), migrated into the droplets of the nanoemulsion, as can be observed in the size

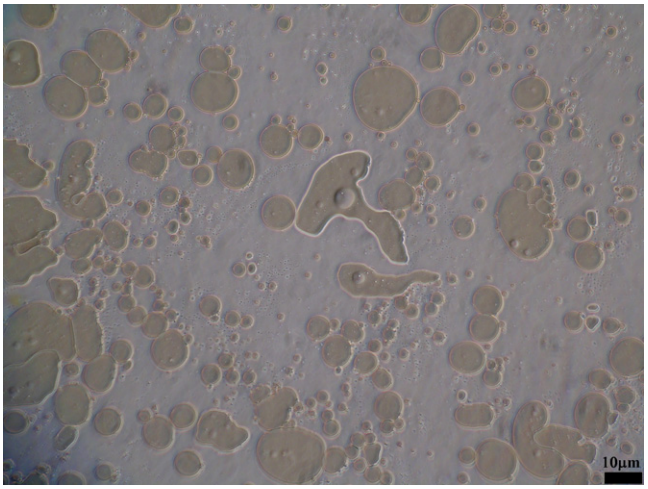

Fig. 5. Optical micrographs of solutions of crude oil in nanoemulsion: 10 wt%.

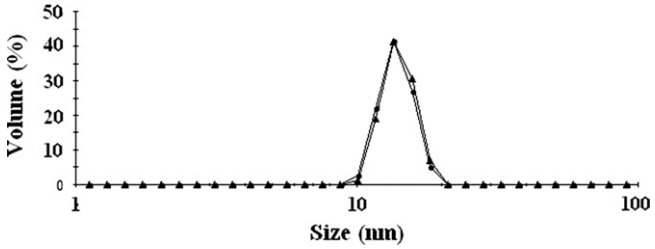

Fig. 6. Mixture of oily water and nanoemulsion 1:0.01: (a) optical micrograph and (b) size distribution curve.

distribution curve shown in Fig. 6a with range between 10 and 20 nm.

Since size distribution curves of all the different mixing ratios showed the same droplet size range, we selected the mixture 1:0.01 for determination of the oil content by UV spectrometry. This choice was mainly due to the advantage of using the minimum amount of nanoemulsion capable of transforming the dispersion (oily water) into a colloidal dispersion that can be read on the spectrophotometer. Furthermore, the nanoemulsion was prepared in the same brine used in preparing the synthetic oily water, with 80 wt% concentration. The concentrations of Ultrol L70 and Solbrax in these systems are negligible. It is also noteworthy that at this mixing ratio, the concentration of crude oil from the oily water that migrated to the nanoemulsion was around 2 wt%, not reaching the saturation point.

3.3.3. *Obtaining the calibration curve of crude oil in the nanoemulsion*

The nanoemulsion was transparent and did not interfere in the UV reading. The curve in Fig. 7 shows the calibration curve of crude oil in the nanoemulsion diluted with brine at the ratio of 0.01:1. The maximum of this curve was in 3 wt% of crude oil in the nanoemulsion or 300 mg L^{-1} of crude oil in brine after dilution, which is in line with the Lambert–Beer law for the wavelength of 400 and 5 mm pathlength. The standard deviation between the measurements points was around 1%.

Table 3 shows the mean oil content obtained by the solubilization of the nanoemulsion in oily water with the aid of the calibration curve (Fig. 7).

Although the average oil content obtained for the oily water at 200 mg L^{-1} by means of solubilization in the nanoemulsion

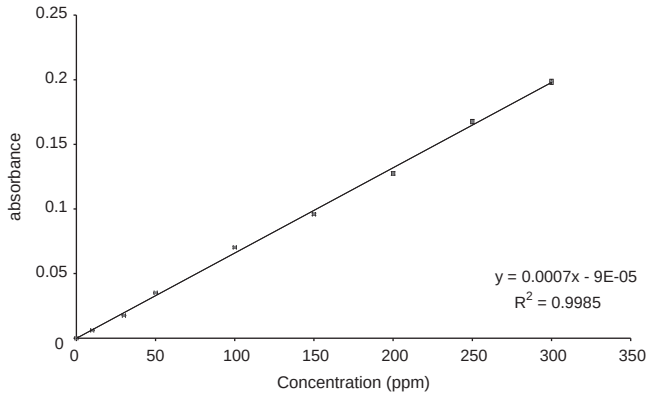

Fig. 7. Calibration curve of crude oil in the nanoemulsion for wavelength of 400 nm from the optical path reading with a probe of 5 mm.

Table 3
Oil content of synthetic oily water samples (200 and 10 mg L^{-1}) obtained by solubilization of the nanoemulsion in the oily dispersion and reading in the UV–vis spectrophotometer.

Samples	Oily water (200 mg L^{-1})			Oily water (10 mg L^{-1})		
	Average absorbance	Standard deviation	Content (o/w)	Average absorbance	Standard deviation	Content (o/w)
1	0.342693	0.005462	160 ± 7	0.23498	0.00121	5 ± 2
2	0.341203	0.002087	157 ± 1	0.23671	0.00193	8 ± 2
3	0.344441	0.00719	162 ± 10	0.23691	0.00043	8 ± 1
4	0.355975	0.005075	178 ± 7	0.23716	0.00135	8 ± 2
5	0.329191	0.007663	140 ± 10	0.23816	0.00365	10 ± 5
6	0.339911	0.00068	155 ± 1	0.233603	0.00112	3 ± 2
7	0.340659	0.004731	156 ± 7	0.233809	0.00089	3 ± 2
8	0.330036	0.005225	141 ± 7	0.23581	0.00113	6 ± 2
Average	**0.340514**	**0.004764**	**156 ± 7**	**0.235906**	**0.001464**	**7 ± 2**

presented a lower value than that obtained by means of extraction with the solvents, the average standard deviation for each sample was much lower (~5%), showing greater accuracy between the measurements, both for oily water at 200 and 10 mg L^{-1}. In this case, we can also attribute these results to the oil losses on the beaker and stem of Ultra Turrax, which was more visible for the oily water at 200 mg L^{-1}.

3.4. *Determining oil-in-water by solubilization in the nanoemulsion and reading in the TOC-VCHS analyzer*

Although measurement of dissolved organic matter (DOM) involving direct injection of liquid samples and combustion at high temperature for conversion of organic matter into CO_2 was first studied in the 1960s, it was not until the last decade that this became the preferred technique for measurement of DOM in seawater [23].

The main advantages of modern high-temperature catalytic combustion analyzers are the elimination of the extraction step, the use of very small sample volumes (~200 μL), rapid and high oxidation efficiency by incorporating sensitive CO_2 and automatic operation [24,25]

However, for determining oil-in-water it is necessary to measure not only the dissolved organic matter, but also the free and emulsified oil, which is not homogeneously distributed in the sample. Therefore, TOC-VCHS analysis provides unsatisfactory results.

The use of a nanoemulsion can distribute the free and emulsified oil uniformly, to form a homogeneous colloidal dispersion. Thus, we also measured the oil content by using the nanoemulsion and reading in the TOC-VCHS analyzer.

Table 4
Experimental and theoretical values of TOC obtained for ethanol and butanol diluted in distilled and deionized water in the TOC-VCHS analyzer.

Content (mg L^{-1})	Ethanol		Butanol	
	TOC theoretical (mg L^{-1})	TOC experimental (mg L^{-1})	TOC theoretical (mg L^{-1})	TOC experimental (mg L^{-1})
200	104.3	104.9	129.8	128.3
400	208.7	207.1	259.5	261.7
600	313.0	312.9	389.2	390.0

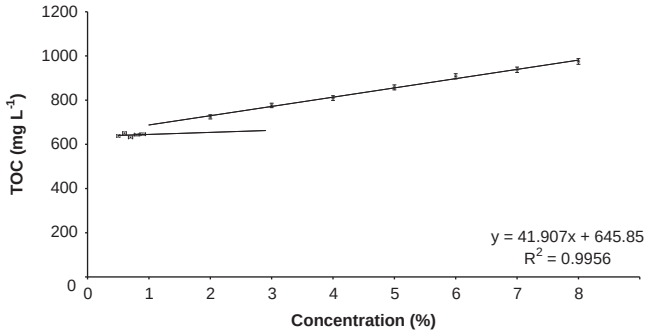

Fig. 8. Total organic carbon content of crude oil in nanoemulsion diluted in brine as a function of concentration.

The precision and accuracy of the analyzer are shown in Table 4. It can be seen that the theoretical total organic carbon (TOC) values calculated for the ethanol and butanol solvents diluted in water showed less than 1% error when compared with the experimental measurements made in the TOC-VCHS analyzer. These tests were performed to check for errors involved in the measurement of carbon when using the nanoemulsion, which it was composed of polymeric surfactant and an oily phase composed of a mixture of saturated hydrocarbons. Moreover, the nanoemulsion droplets also have a size distribution range, so the experimental TOC value is also an average.

In order to identify the required amount of nanoemulsion which must be added to oily water so that the oil concentration in the nanoemulsion can be distinguished, we plotted the calibration curve of the oil in the nanoemulsion from the TOC-VCHS readings (Fig. 8). It can be seen that only when the oil concentration in the nanoemulsion reached 2% could the TOC in the oil be distinguished from that in the nanoemulsion. The TOC values of the samples with concentrations of oil in the nanoemulsion below 1% were very close to the average value TOC for the nanoemulsion pure. Thus was obtained only a short straight line shown in Fig. 8. Thus, for the samples of 100 mL of water oily at 200 and 10 mg L^{-1}, we added to aliquots of 0.5 mL and 25 μL of nanoemulsion, respectively, representing a concentration of oil in the nanoemulsion of around 4% in both cases. The average TOC value for samples of 25 μL and 0.5 mL of pure nanoemulsion in 100 mL of brine were about 56.45 and 646 mg L^{-1}, respectively, with an average percent deviation of around 1%. From this calibration curve, it was only possible to directly determine the oil concentration in the oily water of 200 mg L^{-1}.

Eqs. (1) and (2) show the calculation method for converting TOC value into oil content of oily water.

$$TOC_{(O/W)} = TOC_{(N/OW)} - TOC_N \quad (1)$$

$$C_{(O/W)} = 1.18 \times TOC_{(O/W)} \quad (2)$$

where, $C_{(O/W)}$ is the mean oil content in the oily water and $TOC_{(O/W)}$, $TOC_{(N/OW)}$ and TOC_N are the TOC in oily water, the oily water/nanoemulsion mixture and nanoemulsion in brine, respectively.

Table 5
Average oil content of oily water at 200 and 10 mg L^{-1} obtained by calibration curve and by direct conversion of the TOC supplied by the TOC-VCHS analyzer.

Samples	Oily water (200 mg L^{-1})			Oily water (10 mg L^{-1})	
	TOC	$C_{(O/W)}$ Direct conversion	$C_{(O/W)}$ Calibration curve	TOC	$C_{(O/W)}$ Direct conversion
1	717.00	83.76	84.89	59.16	2.70
2	698.67	62.13	63.02	59.46	3.01
3	723.67	91.63	92.84	58.43	1.97

The value of 1.18 is a conversion factor obtained from a mean ratio between the weight of saturated hydrocarbons (C n H $2n+2$) and carbon molar mass of hydrocarbons, ranging from 7 to 40.

Table 5 shows the mean oil contents in the oily water samples at 10 and 200 mg L^{-1} obtained by calculating the conversion of TOC into oil content directly and also obtained from the calibration curve for oil in nanoemulsion calculated from the TOC-VCHS readings.

The $C_{(O/W)}$ values obtained from the TOC-VCHS analyzer were lower than expected for the samples of synthetic oily water with concentrations of 200 and 10 mg L^{-1}, compared to the method using the UV spectrophotometer, but with very small deviations in the two methods to determine the oil content (direct conversion and response curve). This device allows obtaining absolute values of TOG and showed high sensitivity and accuracy for samples containing soluble carbon, as can be seen in Table 4.

Thus, it can be concluded that methods of analyzes using different detection techniques can not be compared, since they present significant alterations related to the final result. The UV spectrophotometer only identifies compounds such as aromatics, resins and asphaltenes in oil, which give color to the solution, but do not represent the largest oil fraction. This may explain the higher oil content obtained by UV–vis spectrometry with extraction using hexane compared to that obtained with extraction using Solbrax and dilution in the nanoemulsion based on Solbrax, since this solvent is composed mainly of saturated hydrocarbons. The low oil content obtained by dilution in the nanoemulsion and reading by the TOC-VCHS analyzer can be explained by the fact that the losses on the beaker walls and Ultra Turrax mixer during preparation of the oily water are higher for saturates, which are essentially insoluble in water. Therefore, it may be necessary to identify and quantify the losses to establish a new conversion factor and establish more precise methods.

4. Conclusion

The new methods suggested in this work using nanoemulsion based on Solbrax as solvent in the extraction phase and detection in a UV–vis spectrophotometer or total organic carbon analyzer show great promise, since they allow performing analyses simply, quickly and accurately, with a lower volume of solvent (less than 1%) compared to that used in the analyses by conventional methods.

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References

[1] F. Ahmadun, A. Pendashteha, L.C. Abdullaha, D.R.A. Biaka, S.S. Madaenic, Z.Z. Abidina, J. Hazard. Mater. 170 (2009) 530–551.
[2] Conselho Nacional do Meio Ambiente (CONAMA). Dispõe sobre o descarte contínuo de água de processo ou de produção em plataformas marítimas de petróleo e gás natural, e dá outras providências. Resolução n. 393, de 8 de agosto de 2007.
[3] J.C.F. Menéndez, S.M.L. Fernández, Anal. Chim. Acta 415 (2000) 9–20.
[4] D. Patra, A.K. Miishra, Talanta 55 (2001) 143–153.
[5] M.T. Romero, N. Ferrer, Anal. Chim. Acta 395 (1999) 77–84.
[6] Nordic Council of Ministers, Use of Ozone Depleting Substances in Laboratories. Copenhagen: Ekspressen Tryk & Kopicenter (2003).
[7] United Nations Environment Programme, Report of the 11th Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer, Decision XI/15, Beijing, 1999, in: Handbook for Montreal Protocol on Substances that Deplete the Ozone Layer, eighth ed., Nairobi, UNON, 2009. p. 123.
[8] F.K. Kawahara, US patent 5,294,553, 1994.
[9] S. Stokes, US patent 6,727,438 B1, 2004.
[10] E. Farmaki, T. Kaloudis, K. Dimitrou, N. Thanasoulias, L. Kousouris, F. Tzoumerkas, Desalination 210 (2007) 52–60.
[11] S. Rintoul, World Oil Mag. 227 (2006) 1–4.
[12] D.A. Skoog, F.J. Holler, T.A. Nieman, Princípios de análises Experimental, in: quinta (Ed.), Bookman, Porto Alegre, 2002.
[13] E.D. Ramsey, J. Supercrit. Fluids 44 (2008) 201–210.
[14] J.L. Burguera, M. Burguera, Talanta 96 (2012) 11–20.
[15] C. Solans, P. Izquierdo, J. Nolla, N. Azemar, M.J. Garcia-Celma, Curr. Opin. Colloid Interface Sci. 10 (2005) 102.
[16] L. Kourniatis, L. Spinelli, G. Gonzales, C. Mansur, New Mag. Chem. 33 (2010) 295–300.
[17] L. Kourniatis, L. Spinelli, C. Piombini, C. Mansur, Colloid J. 72 (2010) 396–402.
[18] V. Souza, S. Almeida, L. Spinelli, C. Mansur, J. Nanosci. Nanotechnol. 11 (2011) 2237–2243.
[19] M. Fortuny, Quím. Nova 31 (2008) 6.
[20] P. Oliveira, L. Spinelli, C. Mansur, J. Nanosci. Nanotechnol. 12 (2012) 4081–4087.
[21] C. Solans, P. Izquierdo, J. Nolla, N. Azemar, M.J. Garcia-Celma, Curr. Opin. Colloid Interface Sci. 10 (2005) 102–110.
[22] ENVIRONMENTAL PROTECTION AGENCY Method 1664 Revision A: *n*-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel *n*-Hexane Extractable Material (SGT-HEM; Non-Polar Material) by Extraction and Gravity. USA: EPA, 2009.
[23] J.H. Sharp, C.A. Carlson, E.T. Peltzer, D.M. Castle-Ward, K.B. Savidge, K.R. Rinker, J.H. SHARP, Mar. Chem. 77 (2002) 239–253.
[24] M.L. Peterson, S.Q. Lang, A.K. Aufdenkampe, J.I. Hedges, Mar. Chem. 81 (2003) 89–104.
[25] W. Chen, Z. Zhao, E. Koprivnjak, M. Perdue, Mar. Chem. 78 (2002) 185–196.