Ilma Cirne[1], Jaime Boaventura[1], Yuri Guedes[2] and Elizabete Lucas[2]

METHODS FOR DETERMINATION OF OIL AND GREASE CONTENTS IN WASTEWATER FROM THE PETROLEUM INDUSTRY

*[1] Federal University of Bahia, Institute of Chemistry,
R. Barao Jeremoabo, 147, Ondina 40170-115, Salvador, Brazil
[2] Federal University of Rio de Janeiro, Institute of Macromolecules,
Av. Horacio Macedo 2030 - Ilha do Fundao, 21941598 Rio de Janeiro, Brazil*

Abstract. Infrared spectrometry and spectrofluorimetry methods were correlated in the measurement of oil concentration in produced water. Furthermore, we compared colorimetry and gravimetry techniques. Adsorption experiments were performed in synthetic oily wastewaters by polymer compounds based on poly(hydroxyethyl acrylamide and polypropylene. The residual oil content was used in the techniques correlation.

Keywords: oil, grease, produced water, petroleum, infrared spectroscopy, spectrofluorimetry, gravimetry technique.

1. Introduction

The production of oily water during extraction of oil and gas is a serious problem in the petroleum industry due to the high volume generated and the chemical nature (toxicity and solubility) of the contaminants contained in this water [1]. Large quantities of contaminated water are also generated during oil refining [2]. The oil present in these wastewaters can be classified as free, dispersed, emulsified or dissolved [3]. In untreated wastewater, the total oil and grease (TOG) concentration can vary between 100 to 2,000 ppm [4]. In Brazil, the rules issued by the National Environmental Council (CONAMA) limit the TOG level in discharged wastewater to 20 ppm [5]. The problem of monitoring the pollution caused by wastewater containing oily contaminants is not only measurement of their concentration, but also analyzing the chemical transformations of petroleum hydrocarbons in the environment. The methods generally employed to measure the TOG in the oil industry are gravimetry and infrared spectrometry [6, 7].

Gravimetric methods, such as Method 413.1 and Standard Method 5520B from the U.S. Environmental Protection Agency (EPA), involve liquid-liquid extraction (LLE) from oily water samples using 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113), a compound that severely depletes ozone in the atmosphere.

A new gravimetric procedure, Method 1664, which uses hexane as an alternative extraction solvent, has been developed by the EPA specifically to measure the oil, grease and total petroleum hydrocarbons (TPH) in aqueous samples. The idea behind this development was to provide a low-cost and less environmentally harmful method than LLE to determine the oil, grease and TPH in wastewater samples. This method is performance-based, thus permitting the use of different solvent concentrations and extraction techniques, such as solid-phase extraction (SPE). The SPE procedure enables faster analysis, even though additional steps are necessary to prevent the clogging of SPE cartridges when used on aqueous samples containing high levels of particles. Therefore, successful application of Method 1664 depends on satisfying many quality control parameters, which are hard to achieve.

The method for measurement of TOG by infrared spectrometry typically uses a Horiba OCMA-350 analyzer, which is designed to measure contamination by hydrocarbons in samples of fresh and salt water as well as soil [8]. This instrument operates on the technique of energy absorption in the infrared spectrum, with a wavelength range from 3.4 to 3.5 micrometers. According to the operating principle of this device, the quantity of energy absorbed is correlated with the concentration of hydrocarbons present in the sample, that is, it only measures C-H bonds. Since water also absorbs energy in the range from 3.4 to 3.5 micrometers, it is necessary to extract the hydrocarbons present in the sample with a solvent that is insoluble in water and that also does not

absorb energy in this wavelength range. Horiba recommended the S-316 solvent (an oligomer based on poly(trifluoroethylene)), which has the drawback of being very expensive. Carbon tetrachloride, which is much less expensive, can be used in place of S-316 in these analyses, but it is highly toxic and its use is no longer allowed in Brazil. Also, the device must be calibrated to assure reliable results. For this, it is necessary to prepare a calibration solution with the standard formulation supplied by the manufacturer and to define the calibration range (0–50 or 0–200 mg/l). Therefore, it is worthwhile evaluating other techniques to determine TOG concentration.

Due to the wide range of chemical and physico-chemical components of crude oil, there are several other techniques that can be used to determine TOG levels in water, such as colorimetry, spectrofluorimetry, gas chromatography combined with mass spectrometry and high-performance liquid chromatography (HPLC) [9]. Each of these techniques can detect all or some of the constituents of the wastewater produced by the petroleum industry.

Gas chromatography is an instrumental chemical analysis method that permits the separation, identification and measurement of the concentration of chemical components in complex mixtures. The separation is based on the differences in the speed with which these components are carried in the fixed phase by the flow of a mobile liquid or gas phase. The stationary phase is immobilized in a column with the function of separating different components, causing each of them to leave the column at different time (retention time). A detector is used to monitor the outflow from the column. At the moment that each chemical compound leaves the column, it is detected and identified electronically, and the quantity can also be determined. Generally the substances are identified (qualitatively) by the order in which they emerge (elute) from the column and by the retention time of the column.

The colorimetry, or visible spectrophotometry, technique measures the absorption of electromagnetic radiation in the Uv-visible region by a solution. Therefore, it is possible to obtain information about a sample or measures the concentration of chemical species contained in the sample. A spectrophotometer is a spectroscopic device that uses a monochromator or polychromator together with a transducer to convert radiant intensities into electrical signals, enabling measuring the ratio between the intensity of two light beams by calculating the absorbance ($A = \log(P_0/P)$, where $P_0 = P_{solvent}$ and $P = P_{solution}$). Photometers employ a filter, together with a transducer, to select the wavelength with a suitable radiation. Spectrophotometers have a considerable advantage because the wavelength can be continuously altered, making it possible to record an absorption spectrum. On the other hand, photometers have the advantage of simplicity, robustness and low cost. The majority of spectrophotometers cover the UV-visible region, while photometers are almost exclusively used in the visible region. Photometers are widely used as detectors for chromatography, electrophoresis, immunoassays or continuous flow analysis. Both photometers and spectrophotometers can be found as single-beam or dual-beam variety.

The spectrofluorimetry technique is based on the quantification of fluorescent compounds in oil, such as aromatics and alkyl-aromatics, through the incidence of a light beam with a determined wavelength, causing certain components to become excited and emit this energy in another wavelength range, which is detected by the device [10, 11]. The fluorometer is relatively easy to use, provided an appropriate wavelength range is selected for the intended analysis. The instrument excites the molecules between wavelengths of 360 ± 30 nm, and its florescence filter observes this phenomenon in a wavelength range of 360 to 900 nm, enabling quantification of aromatic and polyaromatic compounds.

In this study we used four methods to measure the concentration of oily contaminants in water and compared the results: gravimetry, infrared spectrometry, spectrofluorimetry and colorimetry, pointing out the advantages and limitations of each method. Besides this, we performed experiments of adsorption of oil in synthetic oily wastewaters by a polymer compound based on post-consumed poly(hydroxyethyl acrylamide) (PHMAA) and polypropylene (PP) [12]. These experiments were conducted using a batch method (liquid-solid extraction), varying the contact time. They were used to determine the correlation of the adsorption percentage between the infrared and spectrofluorimetry techniques.

2. Experimental

2.1. Materials

Three types of crude oil with different compositions (Table 1) were supplied by Petrobras Research Center (CENPES, Rio de Janeiro). The solvent S-316 (oligomer based on chlorotrifluoroethylene) and standard calibration solution were supplied by Horiba (São Paulo). Hexane P.A., sodium chloride P.A. and calcium chloride P.A. were supplied by Vetec Química Fina Ltda. (Duque de Caxias). The adsorbent P01, composed of post-consumed poly(hydroxyethyl acrylamide) and polypropylene in mass proportion of 35:65, was synthesized as described in a previous work. All the materials were used as received [12].

Table 1

Composition and characteristics of crude oil samples*

Properties	Oil A	Oil B	Oil C
Asphaltenes, % m/m	1.6	2.45	6.2
Paraffin, % m/m	3.86	4.17	0.83
°API	22.5	19.7	13.0
Density, g/cm^3	0.9150	-	0.9759

Note: *as informed by Petrobras

2.2. Preparation of the Synthetic Oily Water

We first prepared a saline solution of 55,000 ppm with distilled and deionized water containing NaCl and CaCl2 (10:1). The selected crude oil sample was added to 400 ml of this synthetic brine, using an IKA Ultra-Turrax homogenizer (model T-25) operating at 13,000 rpm. The oil was added with a micro-syringe with a long tip to assure good homogenization of the oily water. After adding the oil, the homogenizer's rotation was increased to 15,000 rpm for 15 min, and then another 600 ml of brine was added, with rotation of 11,000 rpm for 1 min more [13].

2.3. Meausurement of the Total Oil and Grease (TOG) Concentration by Four Techniques

2.3.1. Gravimetry by adsorption in silica

This technique involves the extraction by solvents of the organic phase from the aqueous phase using *n*-hexane (EPA method 1664). In this step, the following quantities of *n*-hexane were used: three portions of 30 ml for the extraction of 400 ml of oily water, and one of 20 ml for final rinsing. The organic phase was drained through an analytic funnel containing filter paper and 10 g of anhydrous sodium moistened with *n*-hexane and collected in an Erlenmeyer flask. The flask with the extract was then placed over a stirrer plate and its color was observed. The extract had a light yellowish hue, so procedure A was used for the gravimetric analysis. This procedure as applied here consisted of the following steps: (1) The Erlenmeyer flask was placed under magnetic stirring for 5 min with silica gel (3.0 g). (2) The extract was then filtered and collected in a previously weighed round-bottom distillation flask. (3) This flask was placed in an IKA RV 05 Basic 1-B rotary evaporator to eliminate the solvent, after which the remaining sample was left for 1 h under nitrogen flow. After this period, the flask was weighed again. (4) At the end of the extraction, the total oil and grease content was calculated by Eq. (1):

$$TOG = 1{,}000{,}000 \cdot (\text{final mass} - \text{initial mass})/\text{sample volume} \qquad (1)$$

where final mass is mass of the flask and its content after extraction; initial mass is mass of the empty flask; and sample volume is volume of the sample analyzed.

2.3.2. Infrared spectrometry

For this process, the oil must first be extracted from the aqueous phase by an organic solvent, here S-316. For this step, three portions of S-316 were used: 40, 30 and 20 ml for extraction from 70 ml of oily water. The organic phase was drained through a funnel containing filter paper and 10 g of anhydrous sodium sulfate moistened with S-316 and was collected in 100 ml round-bottom beaker. After the extraction step, the oil and grease content present in the sample was calculated using the value indicated by the device (Horiba OCMA-350 content analyzer) and the dilution factors were used during the extraction step, according to Eq. (2):

$$C_{solution} = (\text{reading} \cdot V_{flask} \cdot R_{dilution})/V_{sample} \qquad (2)$$

where $C_{solution}$ is the concentration of the sample analyzed, mg/l; V_{sample} is the original volume of the sample, measured in a graduated cylinder, ml; V_{flask} is the volume of the flask (100 ml); and $R_{dilution}$ is the dilution ratio used.

2.3.3. Colorimetry

The colorimetry technique consists of extraction by solvents of the organic phase from the aqueous phase using chloroform (Petrobras Manual, 2000). This involves the use of three portions of chloroform: one of 20 ml and two of 30 ml for extraction of oil and grease from 400 ml of oily water. The organic phase was drained through a funnel containing filter paper and 10 g of anhydrous sodium sulfate and collected in 100 ml round-bottom flask. The colorimeter was set to zero with a portion of clean chloroform. The sample was placed in a cuvette and the concentration was read in a CELM model E225D spectrophotometer with a calibration curve already inserted (concentrations were 5, 25, 50, 100 and 200 ppm) at a wavelength of 400 nm. The TOG value was calculated by Eq. (3):

$$TOG = (\text{reading} \cdot \text{sample volume in the flask})/\text{sample volume from the separation funnel} \qquad (3)$$

2.3.4. Spectrofluorimetry

This analysis presents a quick result for the synthetic oily water samples, by extraction with *n*-hexane (Turner Designs Manual, 1997). The measurements were initially obtained with a Turner Designs TD-360 fluorometer using microcuvettes previously rinsed with n-hexane and then filled with the organic phase. Each cuvette containing the organic solution was placed in the instrument compartment and the concentration in ppm was readily obtained. The calibration curve has two critical points, one referring to the pure *n*-hexane solvent (blank) and the other referring to the curve's maximum concentration (225 ppm). Subsequent measurements were carried out with a Varian Carry Eclipse fluorescence spectrophotometer and the values read from the instrument were converted into TOG with the use of another calibration curve, obtained for dispersions with different oil concentrations. All the experiments were carried out in duplicate and the results presented are the average of the readings.

The wavelength used to excite the sample was 350 nm and the range of the emission spectrum was 360–750 nm. The wavelengths for the oily water were 402.0 and 440.0 nm.

For use of this spectrophotometer, we constructed a standard curve for the purpose of correlating the emission intensity of the samples with their oil concentration, obtained by testing solutions with various known concentrations. These solutions were prepared with the same Ultra Turrax T-25 homogenizer.

The oil samples extracted by *n*-hexane were placed in cuvettes and the corresponding emission values were read. The analytic curve was constructed by plotting the concentrations of the prepared oily water (TOG) versus the intensity of the signal produced by the instrument, as presented in Fig. 1. The curve was composed of six points and deviated from linearity at high concentrations, which is associated with the deviation from the L'Ambert Beer law.

We first obtained standard curves of absorption intensity in function of oil concentration in the oily water,

varying the known concentration from 5 to 200 ppm and using two wavelengths (402 and 440 nm). Fig. 1 presents the curves obtained.

At both these wavelengths, the fluorescence intensity showed the significant linear correlation with the concentration over the wavelength range tested. However, we selected the wavelength of 440 nm because it presented the highest linear correlation ($R = 1.000$). The equation obtained was $y = 11.437x + 4.230$ and the equation used to infer the concentrations was $C = (i - 4.230)/11.437$, where C is the concentration and i is the emission intensity read from the instrument at 440 nm.

2.4. Analysis of the Adsorbent Performance: Comparison of Spectroscopic Techniques

The polymer composite was evaluated for its oil adsorption capacity by the infrared and fluorescence techniques, to obtain a correlation between the measurement methods.

The infrared and fluorescence methods used to measure the quantity of oil adsorbed to the composite, by batch liquid-solid extraction, were both preceded by placing the mass of the composite in an Erlenmeyer flask and then adding 50 ml of the recently prepared stock solution at known concentration. The flasks were then placed in a thermostatically controlled IKA shaker bath, designed for dynamic adsorption studies, with adjustment of speed and temperature.

To choose the best method for determining TOG, we varied the contact time between the adsorbent and oily water (2, 5, 10, 16, 20 and 24 h), while maintaining the same sorbent mass (0.3 g) and temperature (298 K). In these procedures, the quantity of oil adsorbed by the composite is calculated by comparing the oil concentration in the solution before and after adsorption. The extraction solvents used were S-316 and hexane, respectively for the infrared analyzer (Horiba OCMA-350) and fluorescence spectrophotometer (Varian Carry Eclipse).
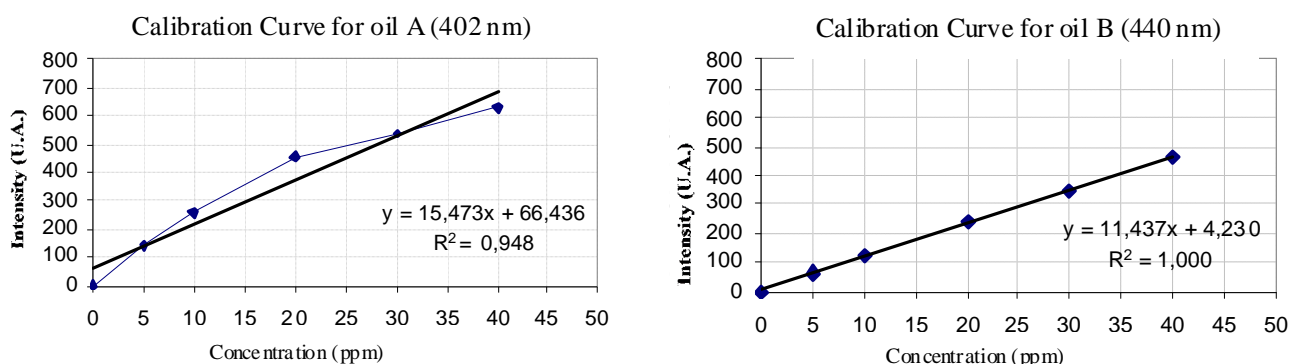

Fig. 1. Calibration curve of intensity *vs.* concentration obtained by spectrofluorometer at 402 and 440 nm

The methods differed to obtain the aliquots for analysis of the oil quantity after adsorption. For the fluorescence method, after the contact time between the adsorbent composite and oily water solution, 45 ml of the latter was removed from each Erlenmeyer flask and transferred to 50 ml graduated test tube, to which 5 ml of the solvent *n*-hexane was added. This mixture was shaken vigorously for five minutes for extraction of the oil by *n*-hexane. The organic phase extracted in each tube was placed in a quartz cuvette with the capacity of 3.0 ml. Each cuvette was then placed in the appropriate compartment of the instrument for analysis of the oil. The values read were transformed into TOG with the use of a calibration curve.

When using infrared spectrophotometry, the oil was extracted from the oily solution by the organic solvent S-316 and by filtration after the samples were shaken in the Erlenmeyer flask. Then the organic phase was placed in cuvettes in the spectrometer compartment for analysis of oil. To obtain the total oil and grease (TOG) values, Eq. (2) was used.

3. Results and Discussion

This study was carried out in two steps. The first one involved preparing three types of synthetic oily water, from three types of dispersed crude oil (A, B or C), which TOG values were determined by gravimetry, infrared spectrometry, colorimetry and fluorescence spectrometry. The results were mutually compared and the advantages and disadvantages of each technique were noted. In the second step, oily water prepared from petroleum sample A was treated with a polymeric adsorbent and the removal efficiency was monitored by infrared spectrometry and fluorometry.

3.1. Analysis of TOG for Oil Dispersions in Solvent and in Synthetic Oily Water using Four Techniques

Table 2 reports the TOG values for the dispersions prepared directly in the pure solvent obtained by different techniques. Table 3 reports the TOG values for the synthetic oily water. In both investigations theoretical concentrations of 40 and 120 ppm were used.

Comparison between the results obtained by analyzing the dispersions of oil in the solvent (Table 2) and in the salt water (Table 3), it can be seen that in general the TOG values obtained were lower for the synthetic oily waters. This can be explained by the possible occurrence of losses during the solvent extraction of the oil contained in the oily water.

The techniques that provided the mutually closest concentration values and the ones nearest to the theoretical concentration were infrared spectrometry and colorimetry, though the latter, in general, produced values slightly farther from the theoretical values. These differences can be explained by the differences in the detection principles of these two techniques and the diverse composition of the petroleum samples. The Horiba OCMA-350 instrument analyzes compounds that absorb energy in a limited range of 3.4–3.5 µm, *i.e.*, compounds that present C–H bonds, so it is expected that this device analyzes all the compounds in crude oil. Hence this technique supplies concentration results very near to the theoretical values. In the case of colorimetry, the only compounds detected are those that absorb energy necessary to excite the electrons to more excited states $(n \rightarrow \pi*)$ and $(\pi \rightarrow \pi*)$, in a given wavelength, which can fail to analyze some components of the oil dispersed in the solvent or oily water.

The TOG values obtained by fluorometry were significantly lower than the theoretical concentrations, and in general were also significantly lower than those obtained by infrared spectrometry and colorimetry. This result is due to the principle behind the fluorescence spectrometry technique, which mainly detects aromatic and polyaromatic compounds in the composition of petroleum. With the exception of the concentration obtained for the oil in the solvent at the theoretical concentration of 120 ppm, the other results presented higher TOG values for petroleum C than A and B. These results are in accordance with the composition of these oil samples (Table 1): petroleum C contains the highest content of asphaltenes (polyaromatic compounds) and the lowest content of paraffinic compounds.

Table 2

Content of oil and grease (TOG) determined by each of the techniques
for different types of oil dissolved in the analysis solvent at different concentrations

Oil type	Theoretical concentration, ppm	Content of oil and grease (TOG), ppm		
		Infrared (I)	Colorimetry (C)	Fluorimetry (F)
Crude oil A	40	64 (0.6)	88 (0.4)	11 (3.6)
	120	123 (1.0)	168 (0.7)	18 (6.7)
Crude oil B	40	50 (0.8)	87 (0.5)	12 (3.3)
	120	100 (1.2)	154 (0.8)	22 (5.4)
Crude oil C	40	62 (0.6)	56 (0.7)	17 (2.4)
	120	63 (1.9)	125 (1.0)	18 (6.7)

Note: values in brackets refer to the ratio between the theoretical and measured values

Table 3

**Content of oil and grease (ppm) determined by each of the techniques
for synthetic water prepared with different types of crude oil at different concentrations**

Oil type	Theoretical concentration, ppm	Content of oil and grease (TOG), ppm			
		Infrared (I)	Colorimetry (C)	Fluorimetry (F)	Gravimetry (G)
Crude oil A	40	50 (0.8)	53 (0.8)	16 (2.5)	53 (0.8)
	120	107 (1.1)	175 (0.7)	37 (3.2)	159 (0.8)
Crude oil B	40	35 (1.1)	67 (0.6)	12 (3.3)	15 (2.7)
	120	110 (1.1)	98 (1.2)	37 (3.2)	71 (1.7)
Crude oil C	40	60 (0.7)	15 (2.7)	23 (1.7)	17 (2.4)
	120	115 (1.0)	110 (1.1)	56 (2.1)	149 (0.8)

Note: values in brackets refer to the ratio between the theoretical and measured values

The gravimetry technique was the most laborious one, requiring great care in material preparation and final sample analysis, as well as taking longer. This method does not characterize the composition of the oil and also fails to quantify the volatile hydrocarbon species, which are lost during extraction from the solvent by a rotary evaporation.

The infrared spectrometry technique, using the Horiba OCMA-350 instrument, is highly reliable in measuring the TOG level, but is laborious regarding preparation of the calibration solutions (which has to be done daily) and expensive due to the high cost of the solvent (S-316) used to extract the oil and grease from the oily water. It is not possible to substitute S-316 with carbon tetrachloride because the latter is highly toxic. Therefore, it is desirable to establish a method that can be used in place of infrared spectrometry. Between infrared spectrometry and fluorometry, although the results varied in function of the petroleum sample, the differences were not substantial at the two concentrations analyzed: The TOG ratios obtained by infrared spectrometry and fluorometry (I/F) were 5.7, 4.0 and 3.6 for the systems prepared with crude oils A, B and C at the theoretical concentration of 40 ppm, and 6.7, 4.5 and 3.5 when using the theoretical concentration of 120 ppm. The spectrofluorometry technique uses a relatively inexpensive solvent (*n*-hexane) and requires a much shorter time, with simple calibration. Besides this, the technique uses a portable instrument of easy operation. Nevertheless, for studies to compare the TOG of systems containing crude oils of different origins, it is necessary to establish previously a standard for correlation between the infrared spectrometry and fluorometry techniques.

Therefore, the second part of the study involved evaluation of a polymeric composite with adsorbent properties using infrared spectrometry (Horiba OCMA-350 analyzer) and fluorometry (Varian Cary Eclipse fluorescence spectrophotometer).

3.2. Comparison between Spectroscopic Techniques: Infrared Spectrometry *versus* Fluorometry

As observed in the first part the study, there was reasonable linearity between the results obtained by infrared spectrometry and spectrofluorometry. However, the correlation factor can vary in function of the compositional characteristics of the crude oil present in the aqueous phase. To compare these two techniques for assessing the performance of oil adsorbents, we conducted tests varying the contact time between the adsorbent polymer and oily water, measuring the adsorption efficiency. The assays applying both techniques were conducted with 0.3 g oily water prepared with petroleum A (adsorbent P01), at the theoretical concentration of 40 ppm and temperature of 298 K, with contact time of 2, 5, 7, 10, 16, 20 and 24 h.

The results obtained by two methods are shown in Fig. 2. It can be seen that for contact time of 2 h, the efficiencies were around 50 and 60 % when using infrared spectrometry and spectrofluorometry, respectively. After 5 h, there was an increase in both efficiencies, reaching 87 % in the case of spectrofluorometry and 70 % when measured by infrared spectrometry. In the period between 5 and 7 h, the efficiency remained constant in the case of infrared spectrometry and increased very slightly when measured by spectrofluorometry. From 7 to 16 h, the measured efficiency levels basically remained the same, while from 16 h onward they diminished steadily with time until 24 h [14].

The increase in efficiency with longer contact time is attributed to the time necessary for the oil to be adsorbed from all the surface area of 0.3 g mass of the polymer. The reason for approximately constant efficiencies at some time intervals is due to the saturation of the polymer surface area. After 16 h the adsorption efficiency declines due to the possible desorption, attributed to the adsorption of the solvent at specific sites [14].

Based on the above results, it can be stated that the adsorption efficiency curves behaved similarly between the infrared spectrometry and spectrofluorometry techniques, despite a slight shift between them. This shift is related to the difference in the operational principle of each technique, but both are fully reliable for the purposes in question.
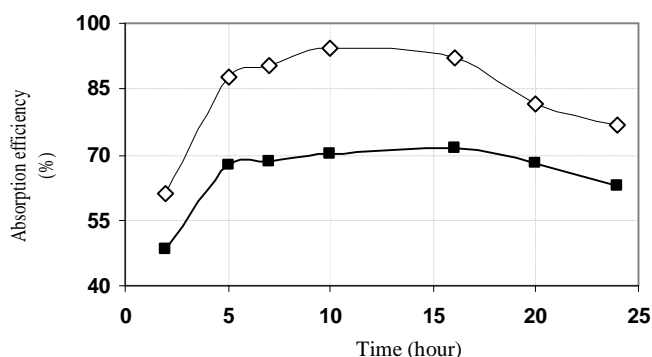
3.3. Correlation between Two Methods

The infrared spectrometry technique, using the Horiba OCMA-350 instrument, was highly effective in measuring the TOG level. However, it has restrictions regarding preparation of the calibration solutions (which has to be done daily) and regarding the solvent employed to extract the oil and grease from the oily water sample. Since two possible solvents indicated are CCl4, which is prohibited by international rules, and S-316, which is very expensive, we sought to validate the use of spectrofluorometry (Varian Cary Eclipse device), because this instrument is simpler to operate, provides faster TOG

results and uses a relatively inexpensive solvent, *n*-hexane. We therefore sought to correlate the TOG values obtained from two devices.

For this purpose, we tested two techniques for an adsorption equilibrium time of five hours. This interval, besides enabling the TOG reading on the same day, is also the time necessary to obtain an efficiency value near the maximum, *i.e.* the equilibrium time where the polymer adsorption is maximum. The TOG measurement should be carried out, whenever possible, within a single day to avoid evaporation of the solvent, and consequently errors in reading the concentration.

The data obtained are presented in Table 4 and correlated in Fig. 3. There was satisfactory linear correlation between the efficiency values obtained by infrared spectrometry and spectrofluorometry (linear correlation coefficient $R = 0.9578$), although there was an average difference of 18.93 ± 5.77 in the efficiency measurement. Therefore, these results validate the use of spectrofluorometry in the tests carried out in this work.

Fig. 2. Adsorption efficiency *vs.* time using OCMA-350 and spectrofluorometer: –◊– fluorescence; –■– infrared. Polymer P01, 0.3 g, 298 K, oily water concentration is 40 ppm, oil A
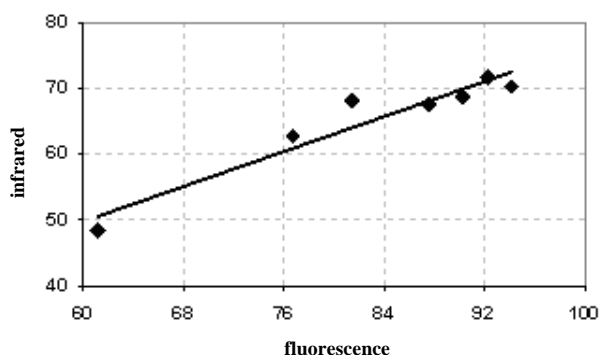
Fig. 3. Linear correlation between the results obtained by infrared spectrometry and spectrofluorometry: $y = 0.685x + 10.430$; $R^2 = 0.9174$; Polymer P01, 0.3 g, 298 K, oily water concentration is 40 ppm [15]

Table 4

Correlation between readings in the IR methods (OCMA-350) and spectrofluorimetry

Time, h	Adsorption, %		Difference between measurements
	Spectrofluorimetry	OCMA-350	
2.00	61.10	48.42	12.68
5.00	87.57	67.52	20.05
7.00	90.35	68.63	27.72
10.00	94.16	70.23	23.93
16.00	92.23	71.56	20.67
20.00	81.44	68.15	13.29
24.00	76.75	62.58	14.17

4. Conclusions

The similarity found when comparing the curves produced by infrared spectrometry *versus* spectrofluorometry techniques demonstrates that both methods are reproducible and reliable. This similarity between the curves was expected, since the experiments were carried out under the same time, temperature and sample mass conditions.

The fluorescence method has advantages over infrared spectrometry (OCMA-350), because it uses a relatively inexpensive and less toxic solvent and the analysis time is shorter.

Acknowledgements

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МЕТОДИ ВИЗНАЧЕННЯ ВМІСТУ НАФТИ І МАСТИЛА В СТІЧНИХ ВОДАХ НАФТОВОЇ ПРОМИСЛОВОСТІ

Анотація. За допомогою інфрачервоної спектрометрії і спектрофлуориметрії визначено концентрацію нафти в промислових водах. Проведено порівняння колориметричних і гравіметричних методів. Досліджено адсорбцію шкідливих компонентів із синтетичних нафтозабруднених стічних вод полімерними сполуками на основі полі(гідроксиетил)акриламіду і поліпропілену. Для кореляції методу використано показник залишкового вмісту нафти.

Ключові слова: нафта, мастило, промислова вода, бензин, інфрачервона спектроскопія, спектрофлуориметрія, гравіметрія.