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The Analysis of Oil Products from Used Water through the Spectrophotometry of Absorption in IR Compared to the Gravimetric Method

Octav Pântea, Vasile Dumitrescu, Magdalena Maria Budeanu

Universitatea Petrol-Gaze din Ploiești, Bd. București 39, Ploiești, România,
email: vdumi@mail.upg-ploiesti.ro

Abstract:

The oil products existing in used water, resulted from the units of oil processing, cause these a certain degree of toxicity. In order to evaluate the degree of pollution of industrial waters, before and after the biological purification, a series of analytical methods have been elaborated as years passed.

The present article compares the results obtained from the gravimetric analysis broadly used in our country, on a large scale in the present and the spectrophotometric analysis in IR of used waters from certain refineries and petrochemical units.

According to the analysis of twelve samples, taken in different days, the results obtained through the spectrophotometric method of absorption in IR are several times bigger than the results obtained through the gravimetric method. These results lead to the conclusion that the gravimetric method isn't sufficiently precise, thus enforcing the usage of some modern methods of analyses with a high degree of precision in determining oil products.

Keywords: *water pollution, oil products, IR spectrophotometry, gravimetric method*

Introduction

The determination of contents in oil products from the surface and used waters can be done through several volumetric and gravimetric methods [1-4], as well as pycnometric [5-7], chromatographically [8-14] and spectrophotometric methods [15-20].

The spectrophotometric method of absorption in IR, compared to other methods, has the following advantages:

- it is selective, the selectivity depending on, among other factors the extraction method of the oil product so that interfering substances won't appear [10];
- it is more sensitive than the gravimetric and volumetric methods, having the same size as chromatographic method;
- it is more precise [6, 16];
- it is faster.

The disadvantages of the spectrophotometrical method consist of: the necessity of creating some curves of graduation [16], the lower precision in comparison with the chromatographical method in the case of the lightly volatile substances [6] and the high price of the equipment.

The aim of the paper is to comparatively show the results obtained through the spectrophotometrical method of absorption in IR and those obtained through the standardized gravimetical method, which are both applied to some samples of used waters resulted from the petrochemical units and refineries.

Experimental

The processing of samples in order to determine the concentration of the oil products is made as follows:

- the water sample is acidulated with HCl at pH = 5;
- the oil products and the other organic substances are extracted with CCl₄ and then separated from the watery phase.

Next, the preparation of the sample for analysis through both methods is different.

The gravimetical method consists in: making a distillation for removing the CCl₄, dissolving the residues in oil ether, removing the interfering substances by passing through an active alumina column and evaporating the resulted product to reach its constant mass.

In the case of the spectrophotometrical method the extract in CCl₄ is passed through a chromatographically column filled with active alumina in order to remove the interfering substances. The spectrum of the product in the domain 3300 - 2600 cm⁻¹ is recorded and then the band extinction from 2926 cm⁻¹ corresponding to the vibration of expansion (valence) ν_{C-H} from the group CH₂ is measured.

The choice of the CCl₄ as a solvent for the extraction was due to its transparency in the domain of spectrum recording, fact which allowed the using of the spectrophotometrical method to concentration lower than 0,1 mg/l, by enhancing the absorption layer (the cell's thickness).

Results and Discussions

For the quantitative determination of oil products through the spectrophotometrical method in IR, by using the Lambert-Beer law, the absorption coefficient was calculated through two methods: the first by using a known concentration mixture of hydrocarbon (C₁₅ - C₂₀) and the second by using the extract in CCl₄ from a sample of used water, taken when the majority of plants from a petrochemical unit functioned.

The extinction coefficients determined by the two methods have values of 1.56, by using the mixture of known concentration, and of 1.60, by using the extract in CCl₄. It has been noticed that the difference between the two values is not significant, this allowing the use of both ways of the extinction coefficient determination.

The results obtained when analyzing some samples of used water through the spectrophotometrical and gravimetical methods are shown in table 1.

The data reported in table 1 show that the results obtained through the spectrophotometrical method are a few times higher than the ones obtained through the gravimetical method.

These differences are due to the different ways of sample preparation. When using the gravimetical method there are losses of oil products in two phases of the sample preparation:

- at the distillation of CCl_4 , at the temperature of 74 - 76 °C, once the extraction solvent is removed, the hydrocarbons with the boiling point around the temperature of 75 °C are also removed;
- at evaporation of the oil ether, until it reaches a constant mass, when the evaporation of other oil products is also possible.

Table 1. The values of concentration of oil products from used waters, determined through the spectrophotometrical and gravimetrical method

No.	Spectrophotometrical method, mg/l	Gravimetrical method, mg/l
1	70.00	26.60
2	92.13	21.80
3	284.1	38.00
4	201.12	38.00
5	127.8	55.00
6	397.6	227.80
7	49.38	22.60
8	21.74	12.00
9	40.30	14.00
10	18.70	13.00
11	96.20	13.00
12	132.50	51.00

The differences which appear between the spectrophotometrical and the gravimetrical determinations are also shown by the absorption spectre in IR, from 3400 to 2600 cm^{-1} , recorded for the same sample, prepared in two ways (fig 1). Spectrum (a) represents the extract in CCl_4 recorded as such (the spectrophotometrical method), and spectrum (b) represents the extract from the same sample in conformity with the gravimetrical method and diluted in CCl_4 , at its initial concentration.

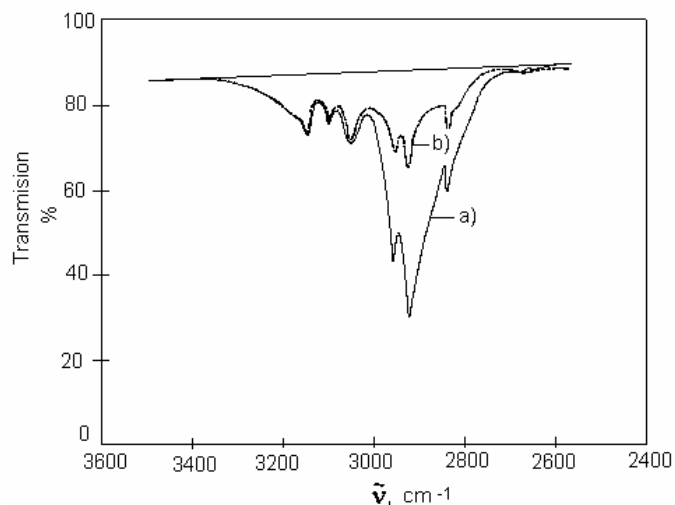


Fig.1. The IR spectrum of the oil products existing in used water

It is worth mentioning that both spectres were recorded in absorbance at the same thickness of the absorbent layer. It has been observed that the extract obtained through the gravimetric method has a lower concentration than the initial extract in CCl_4 .

To convince ourselves that the big differences of concentration resulted between the two methods are not due to the way of calculating the extinction coefficient two samples were taken after being analysed through the gravimetric method and dissolved in a constant volume of CCl_4 ; after that the absorption spectres in IR, in the conditions imposed by the spectrophotometrical method, were recorded. The results obtained were comparable as it can be observed in table 2.

Table 2. The values of the concentration of products from used waters, determined through the spectrophotometrical method after the determination through the gravimetric method and dilution in CCl_4

No.	Spectrophotometrical method, mg/1	Gravimetric method, mg/1
1	97.60	89.31
2	21.20	22.80

Conclusions

- The use of the gravimetric method leads to the appearance of some errors by the loss of oil products during the sample preparation.
- Through the spectrophotometrical method, the losses of easily volatile oil products are low and can be limited through the fast preparation of water samples.
- The superior limit of the concentration in oil products, which can be determined through the spectrophotometrical method, is unlimited to the possibility of sample dilution until it reaches a convenient concentration and the inferior limit can be expanded a lot under 0.1 mg/1, due to the transparency of CCl_4 in the domain of spectrum registration making possible that the thickness of the absorbent layer to be raised up to values of the centimetres order.
- The spectrophotometrical method is more simple and faster.

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Analiza unor produse din apă uzată prin spectrofotometria de absorbție în IR comparativ cu metoda gravimetrică

Rezumat

Produsele petroliere existente în apele uzate din instalațiile de prelucrare a țițeiului imprimă acestora un anumit grad de toxicitate. Toate platformele industriale chimice și petrochimice sunt dotate cu stații de epurare biologică a apelor infestate cu produse petroliere. Pentru aprecierea gradului de poluare a apelor industriale, înainte și după epurarea biologică, au fost elaborate, de-a lungul timpului, o serie de metode analitice.

În prezenta lucrare se face o comparație între rezultatele obținute prin analiza gravimetrică, utilizată pe scară largă la noi în țară în momentul de față și analiza spectrofotometrică în IR a apelor uzate din unele rafinării și platforme petrochimice.

S-a constatat că metoda spectrofotometrică de absorbție în IR prezintă avantaje majore față de metoda gravimetrică, cum ar fi: exprimarea cantitativă mai exactă a hidrocarburilor, timp de analiză mai mic, acuratețe a analizelor ridicată etc.

Prin analiza a 12 probe, recoltate în zile diferite, s-a constatat că rezultatele obținute prin metoda spectrofotometrică de absorbție în IR sunt de câteva ori mai mari decât rezultatele obținute prin metoda gravimetrică. Aceste rezultate conduc la concluzia că metoda gravimetrică de analiză a produselor petroliere din apele uzate nu este suficient de precisă, impunându-se astfel utilizarea unor metode moderne de analiză, cu un înalt grad de precizie în determinarea produselor petroliere.