

SPECTROFLUOROMETRIC DETERMINATION OF MINERAL OIL CONTENT IN WASTE WATERS

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The continuous and reliable control of the mineral oil content in natural waters and in industrial waste waters is very important from the aspect of environmental protection. Several analytical methods are known for the quantitative determination of oil contamination in water. For the determination of higher oil contents, the simple gravimetric method can also be used, however, in certain cases the reliability of the results obtained is questionable. On the other hand, the method is unsuitable for the determination of very low oil content.

In the ppm—ppb region, only modern instrumental analytical methods, such as e.g. spectrophotometry, gas chromatography, IR spectrometry and spectrofluorometry can be taken into consideration.

As compared to the other methods, the spectrofluorescent method has several advantages. First of all, the high sensitivity of the method must be mentioned. The sensitivity of spectrofluorescent oil content determination is as high as 1 $\mu\text{g/l}$ oil concentration [1]. A further advantage of the method, as compared to spectrophotometry is that quantitative determinations can be carried out in a broader concentration range, and moreover, it furnishes two kinds of information on the test sample: the excitation spectrum and the emission spectrum. Owing to these advantages, the analytical importance of the spectrofluorescent method steadily gains ground.

In recent years, several papers discussed the extraction of the oil content of waste waters and sea water with organic solvents, and the subsequent fluorescent determination of oil concentration [1—4].

According to the method, from the intensity of the fluorescent light, emitted by the luminescent compounds to be found in the oil products investigated, conclusions can be drawn on the oil content present. It can be established in general that in the case of most of the mineral oils the luminescent compounds mentioned give the strongest fluorescent light emission, when an excitation light beam of 310—365 nm wavelength is used. Therefore, in the analytical procedure published so far, the authors always used the excitation wavelengths mentioned.

However, the intensity of emitted light changes with the different mineral oils, and particularly with the distillates. In the determination of mineral oil concentration, the fact that mineral oils and oil distillates of identical concentration but of different origin emit light of different intensity, may cause substantial errors. The selection of the standard is very important in the reduction of this error. If the origin, the type of the contaminating oil or fraction is exactly known, the error of determination can be reduced to a minimum. In the contrary case, the relative error may be as large as several hundred per cent.

The object of our work was to determine on the basis of the fluorescent spectra of the various oil fractions the distribution of the luminescent compound present in mineral oil between the single fractions, and to establish which are those distillates, which can actually be measured by spectrofluorescent determinations.

In the course of the analysis of emission spectra, recorded at various excitation wavelengths, parameters were to be found, at which the difference between the fluorescent light intensity of various distillates of identical concentration is the smallest.

Material and apparatus

Oil samples used for the investigation were Soviet mineral oil supplied to Hungary and fractions of different boiling point, prepared from it.

The distillation temperature intervals of the distillates investigated, pressure values belonging to them, and the results of the visual observations of fluorescence are summarized in Table 1.

Table 1

The fluorescence of the 1000 ppm solutions of mineral oils in n-heptane, produced by UV light

Distillates	Distillation temperature (°C)	Distillation pressure (mm Hg)	Fluorescence of 1000 ppm solution in n-heptane under an UV lamp
Gasoline	60—170	760	—
Kerosene	140—240	760	—
Light gas oil	170—300	760	—
Heavy gas oil	220—370	760	weak blue light luminescence
Light paraffin distillate	180—280	10	weak blue light luminescence
Medium paraffin distillate	210—310	10	strong blue light luminescence
Heavy paraffin distillate	280—350	10	strong blue light luminescence
Goudron	350	10	strong diffuse light
Mineral oil	—	—	strong diffuse light

For the spectrofluorometric investigations, solutions of identical concentration (10 ppm) have been prepared from the different oil fractions. The solvent used was n-heptane of "alt" purity, which has been previously further purified by repeated distillation.

A spectrofluorometer Model HITACHI MPF—2A was used for the spectrofluorometric investigations. Spectra presented are uncorrected.

Results and discussion

1. Fluorescent spectra of the mineral oil fractions

First, the spectrofluorometric investigation of the solutions of the mineral oil and the mineral oil fractions in n-heptane has been carried out at the excitation and emission wavelengths recommended in the literature. Fluorescent emission spectra recorded at various excitation wavelength (310 nm; 330 nm; 360 nm; 400 nm) are shown in Figs 1—4.

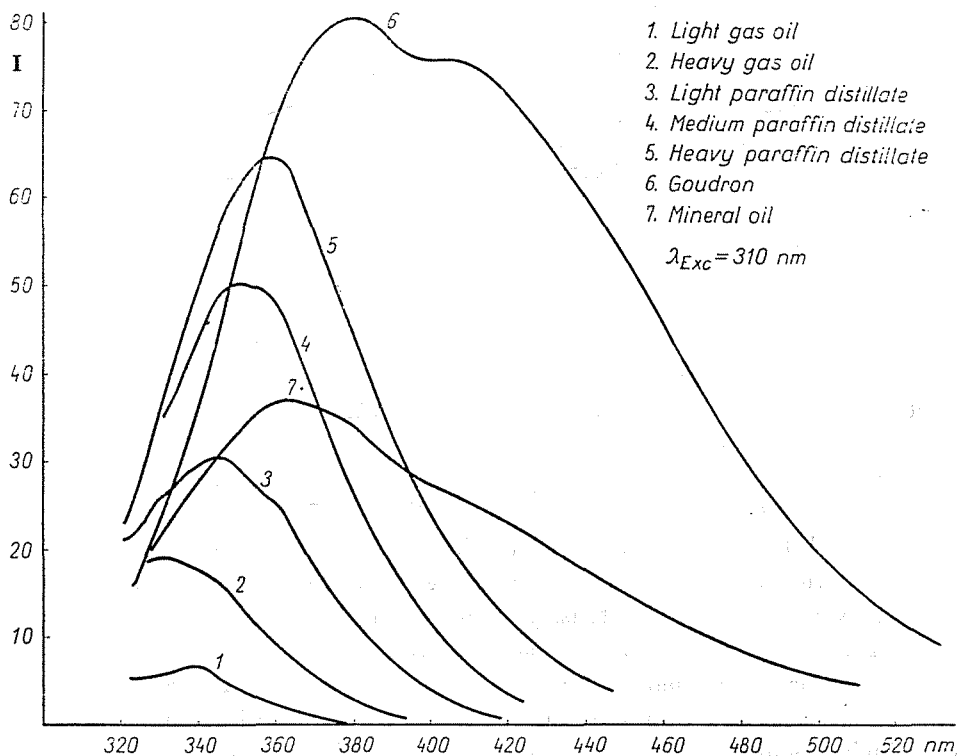


Fig. 1. Emission spectra of mineral oil and mineral oil fractions.
Excitation wavelength: 310 nm

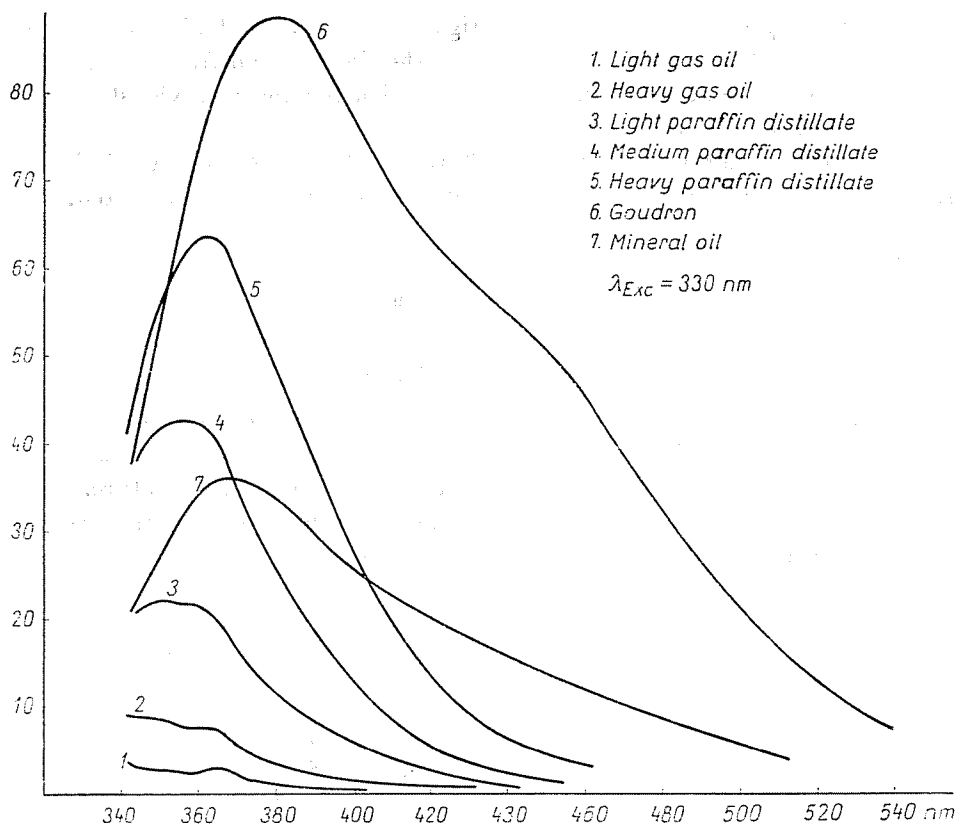


Fig. 2. Emission spectra of mineral oil and mineral oil fractions.
 Excitation wavelength: 330 nm

It can be established on the basis of the emission spectra that the intensity of fluorescent light differs greatly for the solutions of various mineral oil fractions of identical concentration. On increasing the excitation wavelength, differences in intensity further increase.

Next, fluorescent emission spectra, recorded at excitation wavelengths shorter than 310 nm, have been studied. (Figs 5–7)

Though the absolute value of the intensity of fluorescent light, emitted by the fractions, decreased with decreasing excitation wavelength, at certain emission wavelengths the intensity values of different fractions of identical concentration lie rather close to each other.

It can be established from data in Table I and from the fluorescent spectra that in the case of a common contamination of the fractions, only fractions with higher boiling point than light gas oil can be measured.

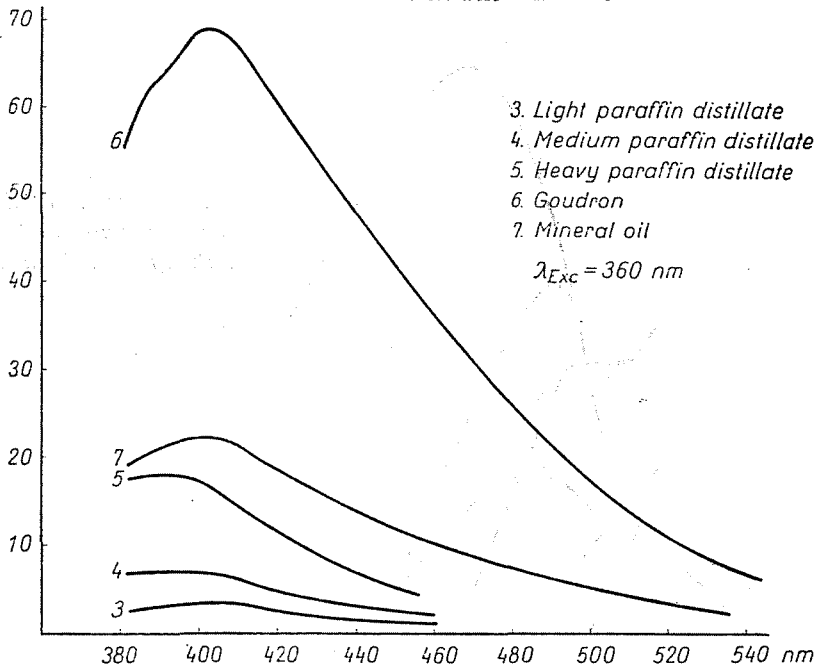


Fig. 3. Emission spectra of mineral oil and mineral oil fractions.
 Excitation wavelength: 360 nm

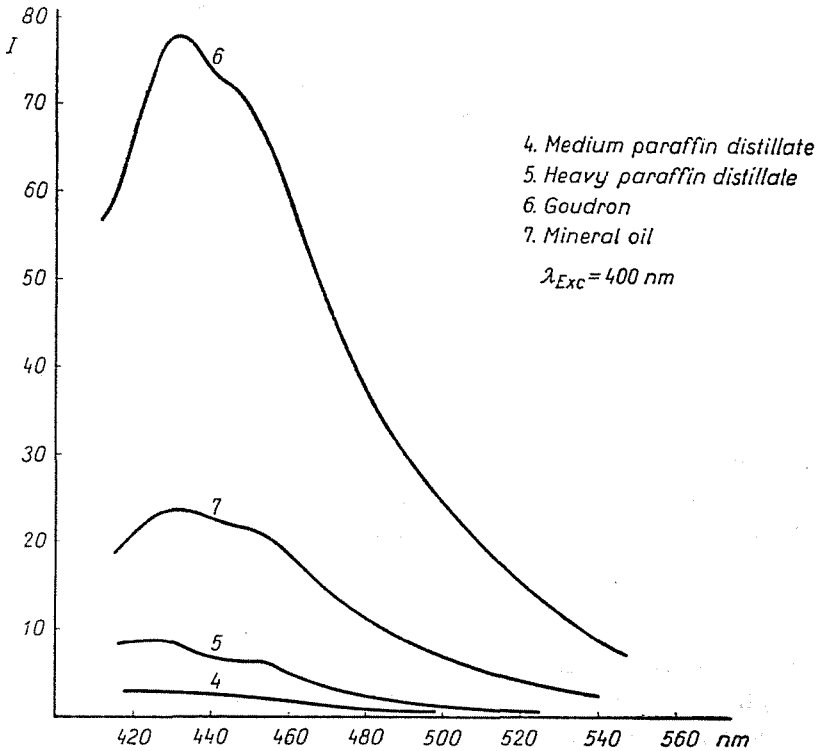


Fig. 4. Emission spectra of mineral oil and mineral oil fractions.
 Excitation wavelength: 400 nm

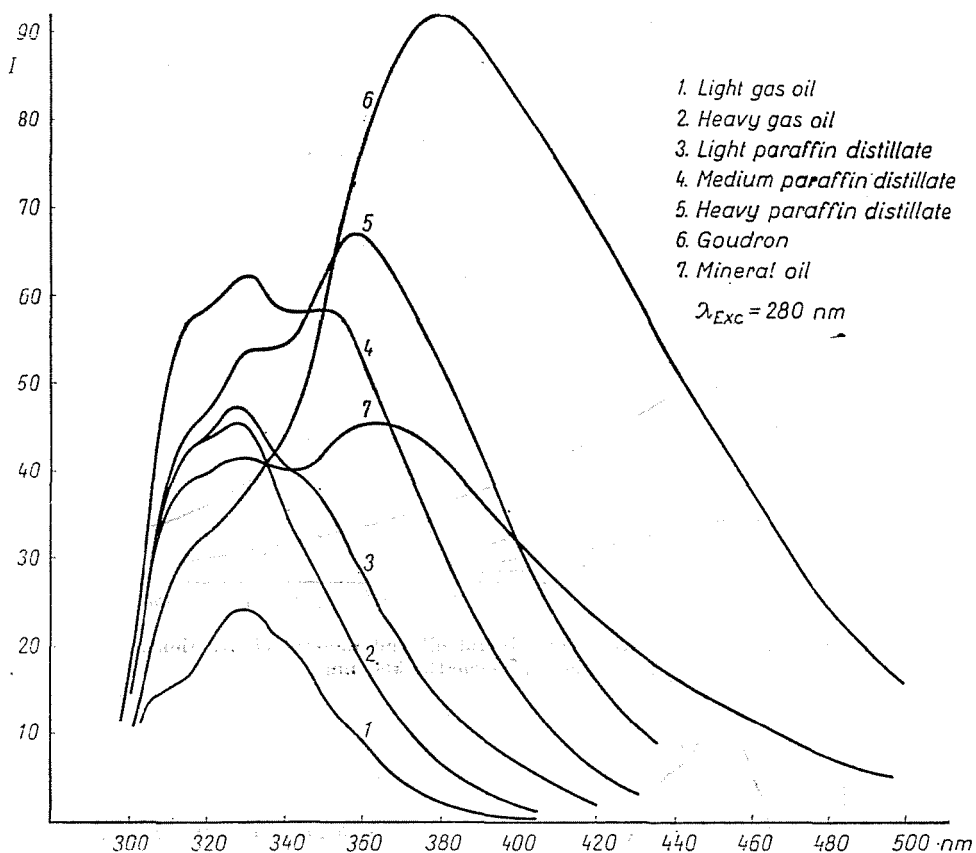


Fig. 5. Emission spectra of mineral oil and mineral oil fractions.
 Excitation wavelength: 280 nm

2. Procedure

According to the prescriptions of sampling, a 50 ml oil-containing waste water sample is prepared for extraction. Waste water to be investigated should be processed as soon as possible.

The course of determination is as follows:

Extraction: In a 100 ml separating funnel, 50 ml of waste water is shaken for 1 minute with 3×5 ml portions of n-heptane of grade "alt", further purified by distillation. To further the separation of the extract, in the first step 4 ml of 2 n sulfuric acid is poured into the separating funnel, and cautiously admixed. In the second extraction step, no further sulfuric acid is needed.

The extract is collected in a 25 ml normal flask, and the flask is filled up with n-heptane to the mark. If the solution cannot be immediately measured, it should be kept in a dark, cool place.

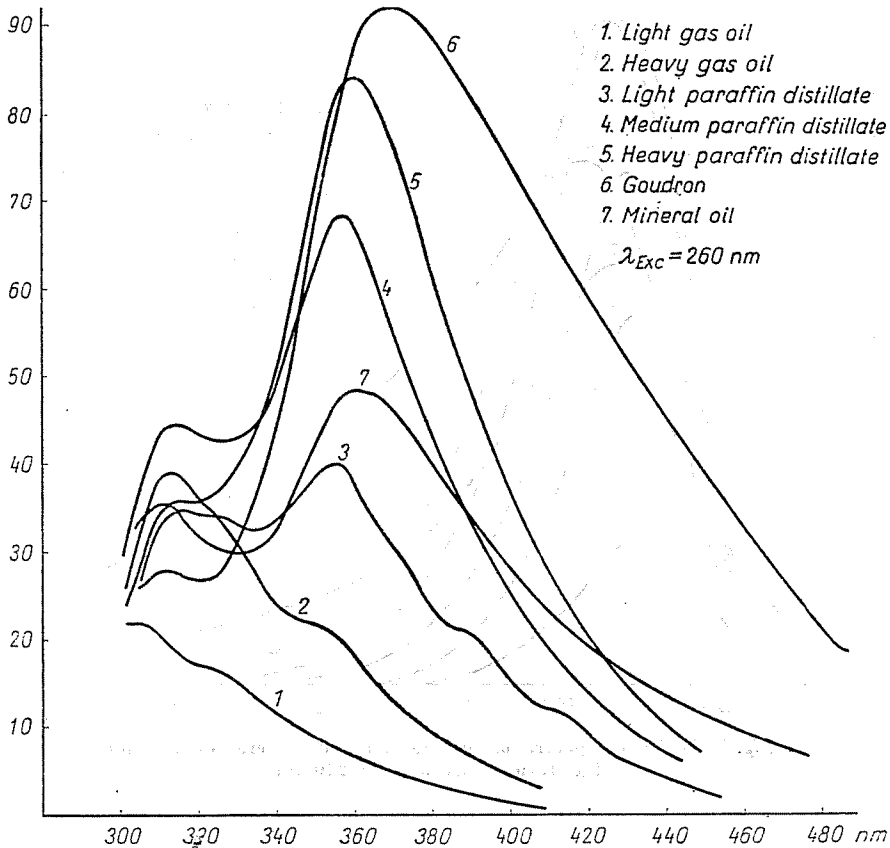


Fig. 6. Emission spectra of mineral oil and mineral oil fractions.
 Excitation wavelength: 260 nm

Fluorescent light intensity is measured at an excitation wavelength of 260 nm or 280 nm, and at an emission wavelength of 330—335 nm.

Mineral oil can be used as standard comparing solution. If the oil content of the waste water investigated is higher than 5 ppm, the extract in n-heptane must be diluted.

Oil concentration can be calculated with formula (1), if the fluorescent light intensity of the n-heptane solution of 10 $\mu\text{g/ml}$ mineral oil concentration is adjusted to 100% on the instrument.

$$c = 1.07 \cdot \frac{I \cdot E}{10 \cdot V} \text{ ppm} \quad (1)$$

c is the oil concentration of the waste water in ppm,

I is the fluorescent light intensity,

E is the volume of the extract in ml,

V is the volume of the waste water in ml.

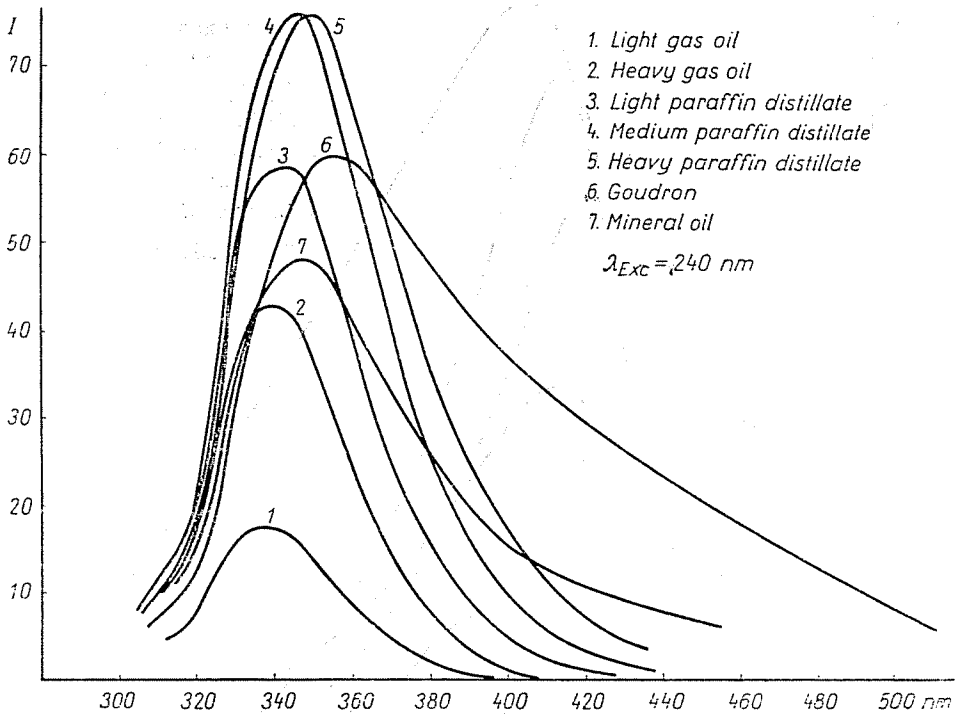


Fig. 7. Emission spectra of mineral oil and mineral oil fractions.
 Excitation wavelength: 240 nm

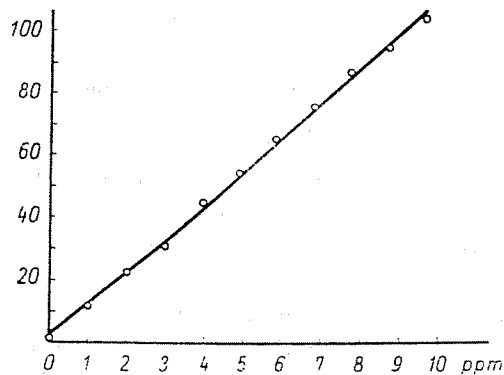


Fig. 8. Calibration curve for the quantitative determination of mineral oil. $\lambda_{Em} = 280 \text{ nm}$;
 $\lambda_{Ex} = 335 \text{ nm}$

With the empirical factor 1.07, extraction losses are taken into consideration.

At the given parameters, linearity in the organic solvent between concentration and light intensity is valid in the 1–10 ppm oil concentration range (Fig. 8).

If the type of the oil causing the contamination is known, the standard deviation of the method is $\pm 12\%$ and the standard error of mean $\pm 4.4\%$ in the measurement of a waste water with 3 ppm oil concentration.

Summary

The mineral oil content of various industrial waste waters can be extracted easily and with good efficiency with an appropriate organic solvent, thus e. g. with n-heptane. The oil content of the organic extract can be well determined by spectrofluorometry. The fluorescent emission spectra of mineral oil fractions have been studied at various excitation wavelength with the aim to determine that pair of excitation and emission wavelengths, at which the fluorescent light intensity of the single fractions differs least from each other.

It was found that the determination can be carried out in the case of different fractions with the smallest error, when the excitation wavelength is 260–280 nm, and the emission wavelength 330–335 nm. In the organic solvent, the relationship between oil concentration and fluorescent light intensity is linear in the 1–10 ppm concentration range.

If the type of oil causing the contamination is known, and an identical type of oil can be used for the plotting of the calibration curve, the standard deviation of the method is $\pm 12\%$, and the standard error of mean $\pm 4.4\%$ in the measurement of a waste water with 3 ppm oil concentration.

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