

SPECTROFLUOROMETRIC DETERMINATION OF PETROLEUM IN DRINKING WATER

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Besides of polluting the environment, materials of petroleum origin getting into the rivers and soil may also impair the quality of drinking water.

The drinking water supply of cities is usually provided either from wells in direct contact with rivers or by surface draw-off. Even after thorough filtering and cleaning it can happen that petroleum remains in the drinking water. Although the exact, biological effect of drinking water containing petroleum in some tenth or hundredth mg/l concentration is not known, but it is certainly harmful, furthermore the deliciousness of the drinking water decreases to a great extent with the increase of petroleum content [1], [2]. Consequently, the regular control of petroleum content of drinking water is a more and more important requirement.

The quantitative determination of petroleum content is restricted by the fact that the petroleum and its products are not the same structure materials, but mixtures of paraffin and various aromatic hydrocarbons and their composition depends on their site and conditions of refining.

Several analytical methods are known for the determination of oil content in water, but because of the above mentioned reasons the oil content can only approximately be determined. In most cases this is satisfactory, especially for drinking water, namely the majority of methods is unsuitable for the determination of low oil contents (in the concentration range of 10^{-2} ppm or below).

Table I shows the volume of water samples necessary for the well-known oil determination methods in the case of an assumed 0.01 ppm oil concentration.

Based on data in Table I, the gravimetric methods, can be stated to be practically inconvenient because of the big water sample required.

IR-spectrophotometry can only be used after previous adsorption of the oil contaminants. Passing the water of 50 l volume through the adsorption column, dissolution of the bound oil from the adsorbent and concentration are rather work- and time-consuming processes.

To extract 10 l drinking water necessary for the measurement, by UV-spectrophotometry at least 300 cm³ from the solvent are required and this

Table I

Water sample volumes necessary in different oil determination methods for the analysis of water containing petroleum in the 0.01 ppm range (informative data)

Measuring method	Minimum oil quantity in 10 cm ³ extract [μg]	Volume of the necessary water sample [dm ³]
Gravimetry	10	1000
IR-spectrophotometry	0.5	50
UV-spectrophotometry	0.1	10
Spectrofluorometry	0.1	1

quantity is to be concentrated to a volume as little as 10 cm³. The rapid evaporation of the solvent at the boiling point can result in oil loss [3, 4].

The advantage of the spectrofluorometric method appears, first of all, in the low concentration range. A water sample of only 1 l is needed and if working with 50 cm³ extract, it should be concentrated only if the drinking water has an oil concentration lower than 0.05 ppm.

Experimental

Materials and instruments

The *n*-heptane as well as the sulphuric acid used to the extractions were of analytical purity.

Water samples were taken from the drinking water supply of the Technical University, Budapest.

A Japanese spectrofluorometer Type Hitachi MPF-2A was used to the spectrofluorometric measurements. Spectra presented are uncorrected.

Course of measurement

1 l water sample is acidified with 10 cm³ sulphuric acid at 50% by wt, then extracted with 3 × 10 cm³ *n*-heptane, applying a motor mixer. The extract collected is made up to a known volume. The oil content in the extract should be at least of 1 ppm concentration, in the opposite case it must be concentrated. The most expedient way of concentration was found to be pumping filtered air at room temperature to the surface of the extract. In the spectrofluorometric measurement of the *n*-heptane solution the excitation wavelength was $\lambda_{\text{EX}} = 280 \text{ nm}$ and the emission wavelength $\lambda_{\text{EM}} = 340 \text{ nm}$ [5, 6].

Results and discussion

The fluorescent emission spectra of the *n*-heptane extract as well as of the reference *n*-heptane solution of turbine oil are seen in Fig. 1.

That *n*-heptane extracts of water samples containing fact petroleum was proved by thin-layer chromatography as suggested by SEMENOV [7].

In the 1–10 ppm concentration range, the fluorescent light intensity and the reference oil concentration used to the calibration are in linear relation. The oil content of the samples was usually between 0.09 and 0.02 ppm. Although the error of the determination is quite great, an interesting correlation was found between the Danube water level and the oil concentration in drinking water. Namely, the oil concentration in drinking water is inversely proportional to the Danube water level. A more detailed analysis would, however, require a very great number of data.

In the quantitative determination of petroleum the greatest difficulty is to choose a reference petroleum in all but the gravimetric methods. The proper or improper selection of the reference considerably influences the accuracy of the measurement. In general, the origin, quality and composition of oils extracted from a river or sea water are unknown. The fluorescent spectra of the pollutant give approximate information regarding the quality of the oil [6, 8].

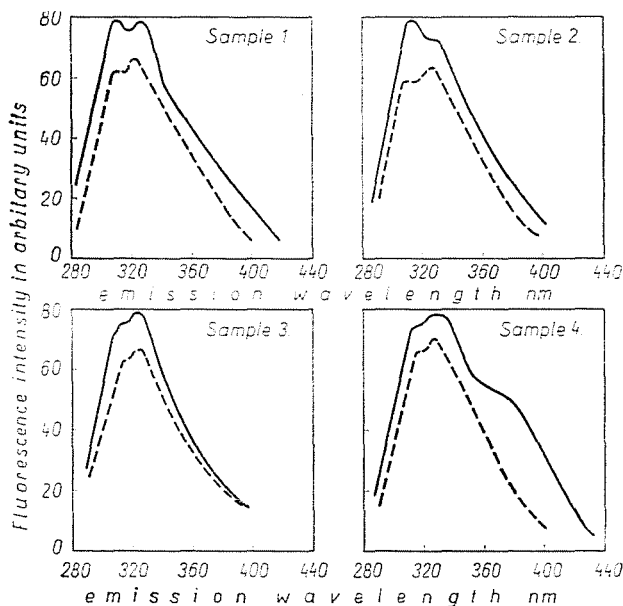


Fig. 1. Fluorescent emission spectra of petroleum extracted from drinking water. — — — Fluorescent spectra of water samples, — — — Fluorescent emission spectra of the reference, excitation wavelength: 280 nm, emission wavelength: 340 nm, solvent: *n*-heptane

Each laboratory uses different oils as reference as a rule. For the sake of comparison and the reproducibility of reference later or in another laboratory, it is expedient to compare the fluorescent light emission of the reference oil with that of another reproducible fluorescent solution. Ratio of fluorescent light emissions of *n*-heptane solutions of turbine oil of 8 ppm concentration used by us and of naphthalene of 200 ppm concentration was found to be 2.6 (excitation wavelength: 280 nm, emission wavelength: 330 nm).

For the approximate estimation of the error due to the different qualities reference oil and the extracted oil, the fluorescent light intensities of *n*-heptane solutions of 4 ppm concentration prepared from petroleums listed in Table II were measured. Values of fluorescent light intensities of various petroleum and their derivatives were referred to the light intensity of the Romaskino crude oil sample and the deviation percentages are summarized also in Table II.

The data of Table II are, of course, only of informative character, since the Table contains only a part of petroleums used in Hungary. On the basis of

Table II

Deviations of fluorescence intensities of petroleums from those of the Romaskino petroleum chosen as reference. Conc: 4 ppm, excitation wavelength: 280 nm, emission wavelength: 340 nm

Fractions*	%	Refined oils	%
heavy petrol	non measurable	motor oil MMA-60	-45
petroleum	non measurable	motor oil MSE-10	-85
light gas oil	-50	motor oil Shell-10 w	-82
heavy gas oil	+12	motor oil Agip F-1	-69
waxy lighs oil	+49	Diesel oil	-41
mean waxy oil	+49	turbine oil	-64
heavy waxy oil	+49	machine oil	+21
residual asphalt	+12	spindle oil	-3
		transformator oil	-3
Crude oils**			
Nagylyngyel (H)	-16	Demjén (H)	-20
Kardoskut (H)	-12	Albania	-4
Lispe (H)	-42	Iraq	-24
Algyó (H)	-32	Egypt	+2

* Distillates from Romaskino crude oil

** Hungarian (H) and imported crude oils

the measured data it can, however, be stated that the quantitative determinations of an oil pollutant of unknown quality in the sample is quite uncertain even when using a reference oil having average fluorescent characteristics.

The relative error of spectrofluorometric results may often reach 100%. This is why in this low concentration range the determination of petroleum content gives only an estimation to the order of magnitude of the pollution. This information is, however, very useful in environmental engineering, especially, because (ppm-ppb) in the low concentration ranges spectrofluorometry is one of the simplest and fastest methods.

Summary

The petroleum content of drinking water can only be determined by highly sensitive analytical methods. Spectrofluorometric method is suitable to analyse 1 l drinking water containing petroleum even in 0.01 ppm concentration. The extracting agent is n-heptane, the lowest oil concentration in the extract should reach 1 ppm. Excitation wavelength: $\lambda = 280$ nm, emission wavelength: $\lambda_{Em} = 340$ nm.

The error of determination highly depends on choosing the standard reference oil. In the case of contamination by an unknown oil, the relative error of the determination can reach 50–100%. In most cases, however, this accuracy can be accepted in such low concentration ranges (ppm-ppb), the method being fast and simple, and at present no similar fast and simple method is available.

References

1. BLUMER, M.: Colloquium on the pollution of the sea by oil spills. NAO Bruxelles (1970)
2. GAUFIN, A. R., TORZWELL, C. M.: Public Health Repts. U. S. **67**, 57 (1952)
3. KAIZER, P. P., GORDON, JR. D. C.: J. Fish. Res. Board. **30**, 1039–1046 (1973)
4. KONDO GORO SATTO TOSHIHIDA, OZASA YOSHIO: Osaka, Kogyo Gijutsu Shikensho Kiho **22**, 18–23 (1971) C. A. **75**, 91149 t.
5. KÁSA, I., BAJNÓCZY, G.: Periodica Polytechnica Chem. Eng. **20**, 169–177 (1976)
6. KÁSA, I., BAJNÓCZY, G.: Periodica Polytechnica Chem. Eng. **21**, 199–209 (1977)
7. SEMENOV, A. D., STRADOMSKAYA, A. G., ZURINA, L. F.: Gig. Samit. **35**, 45 (1970)
8. LLOYD, G. B. F.: Analyst **99**, 729–738 (1974)

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