SPECTROFLUOROMETRIC STUDY OF PETROLEUM FRACTIONS AND CRUDES OF DIFFERENT ORIGIN

A METHOD FOR THE DETERMINATION OF PETROLEUM IN SURFACE WATERS

By

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Received October 4, 1976
Presented by Prof. Dr. L. Gy. NAGY

Continuous and reliable control of the petroleum content in natural waters and in industrial effluents is of high importance from the aspect of environment protection.

Many analytical methods have been proposed for the quantitative determination of petroleum in water. For concentrations exceeding 10 p.p.m. a standard method based on gravimetry is known [1, 2]. The results obtained with this method largely depend on the nature and boiling point of the solvent and on the conditions of solvent removal [3—5].

For concentrations below 10 p.p.m., primarily instrumental analytical procedures have been considered, e.g. spectrophotometry [6, 7], IR spectrometry [8, 9], gas chromatography [10, 11] and spectrofluorometry [12—17].

Spectrofluorometry, in addition to its high (1 $\mu g/dm^3$) sensitivity, yields a system of informations, namely excitation and emission spectra, that allows certain qualitative identifications too.

Due to these advantages, the analytical significance of the spectrofluorometric method is steadily increasing.

The method is based on the finding that one can conclude to the petroleum content from the intensity of the fluorescent light emitted by the luminescent compounds present in the studied petroleum product. The luminescent compounds present in most petroleum products present highest fluorescent light emission, when the wave-length of the exciting light is 310—365 nm. Therefore all spectrofluorometric analytical procedures reported until the present apply excitation within this wave-length range.

However, the spectral composition and intensity of the emitted light varies with crudes and particularly with petroleum fractions of different origin. This fact may cause significant errors. It is therefore very important to choose an appropriate reference standard in order to reduce this error.

Our objective was to study the fluorescent properties of petroleum fractions and of crudes of different origin and type, and to develop a spectrofluorometric analytical method for the determination of petroleum in surface waters.

Experimental

The studied petroleum fractions were based on Romashkino crude from the Soviet Union.

Distillation parameters of the fractions are listed in Table 1.

Solutions with concentrations of 1—10 p.p.m. were prepared from the individual fractions. The solvent was analytical grade 1,2-dichloroethane further purified by repeated distillation.

The studied crudes were partly Hungarian and partly foreign. Their characteristics are summarized in Table 2.

Table 1

Distillation parameters of petroleum fractions

Fraction	Distillation temperature, °C	Distillation pressure, torr
Gasolene	60—170	760
Kerosene	140—240	760
Light gas oil	170—300	760
Heavy gas oil	220—370	760
Light paraffinic fraction	180—280	10
Medium paraffinic fraction	210—310	10
Heavy paraffinic fraction	280—350	10
Goudron	<350	10

Table 2

Characteristics of the crudes of different origin

Source	Density at 20 °C	Viscosity at 50 °C °E	Solidification point °C	Yield analysis (wt.-%)			
				Gasolene	Kerosene	Gas oil	Residue
Algyő	0.810	1,17	+13	34.45	17.75	8.94	38.74
Nagylengyel	0.959	64.7	+ 1	2.66	10.12	—	87.10
Kardoskút	0.870	2.2	+33	6.52	11.83	9.84	71.69
Lispe	0.828	1.12	— 1	25.36	29.61	11.63	33.28
Demjén	0.844	1.28	+12	22.35	16.30	9.69	51.54
Romashkino*	0.863	1.48	—11	18.78	17.39	6.08	56.63
Iraq	0.845	1.34	+ 8	24.64	17.80	4.96	52.48
Albania	0.961	39.5	—10	11.84	8.71	—	79.33
Egypt**	—	—	—	—	—	—	—

* U.S.S.R.

** Um El Yeusr

From these crudes, solutions in dichloroethane were prepared with concentrations of 8 p.p.m. each.

A HITACHI MPF-2A type Japanese spectrofluorometer was used for measurements.

Results and discussion

Fluorescent properties of petroleum fractions

Among petroleum fractions, only the heavy gas oil fraction obtained in atmospheric distillation above 300 °C and the high-boiling products obtained in vacuum distillation are comparable with the fluorescence of the initial crude. Atmospheric fractions with boiling points below 300 °C did not show visually observable fluorescence even in concentrations as high as 1000 p.p.m.

Many authors have suggested the use of 330 nm exciting wave-length. Emission spectra obtained with such light are presented in Fig. 1.

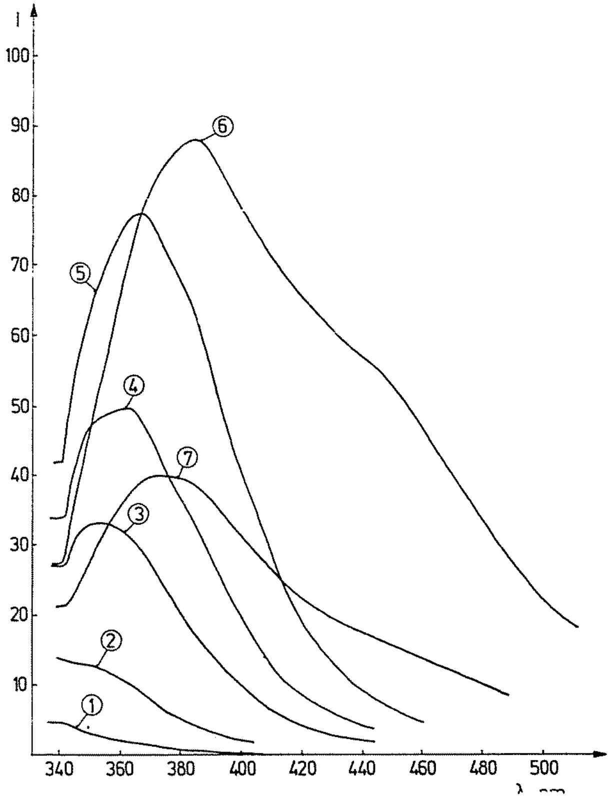

Fig. 1. Fluorescent emission spectra of petroleum fractions. $\lambda_{ex} = 330$ nm; c = 8 p.p.m.; Solvent: 1,2-dichloroethane. 1 — Light gas oil; 2 — Heavy gas oil; 3 — Light paraffinic fraction; 4 — Medium paraffinic fraction; 5 — Heavy paraffinic fraction; 6 — Petroleum tar; 7 — Crude oil

The higher the boiling point of the fraction, the higher the intensity of the fluorescent light. Hence, the error of the determination may be significant, if the contaminant petroleum's type differs from the type of the reference standard.

Intensity differences between individual fractions are still greater, if wave-lengths exceeding 330 nm are used (Fig. 2).

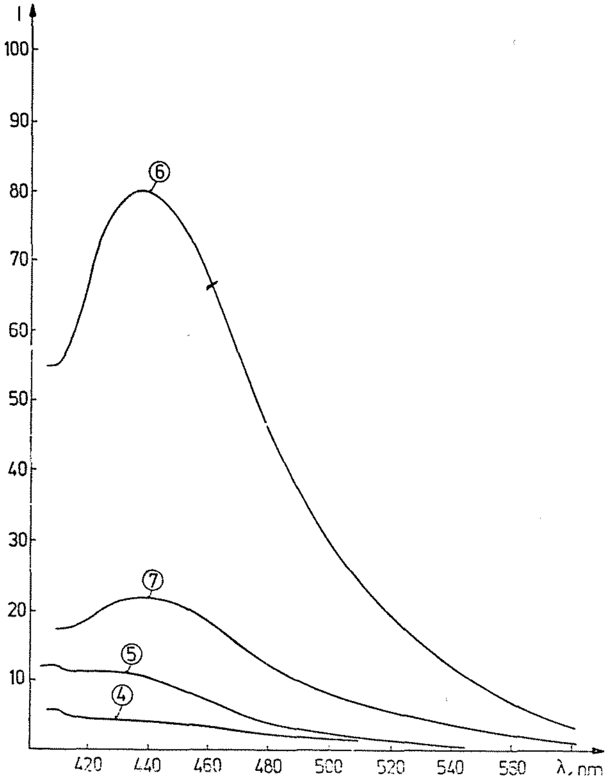

Fig. 2. Fluorescent emission spectra of petroleum fractions. $\lambda_{ex} = 400$ nm; c = 8 p.p.m.; Solvent: 1,2-dichloroethane. 1 — Light gas oil; 2 — Heavy gas oil; 3 — Light paraffinic fraction; 4 — Medium paraffinic fraction; 5 — Heavy paraffinic fraction; 6 — Petroleum tar; 7 — Crude oil

At an exciting wave-length of 400 nm, fluorescent light intensities are comparable only in the case of the fractions obtained by vacuum distillation above 280 °C (for a given sensitivity of the measuring instrument).

Our measurements indicated that the most intensive fluorescent emission is obtained with exciting wave-lengths in the range of 310 to 360 nm. However, in this case the differences between intensities are also greatest.

With decreasing wave-lengths, fluorescent light intensities also decrease, but so do differences between intensities (Fig. 3.).

In emission spectra obtained with 240 nm exciting light, emission wavelengths can be found where the fluorescent intensities of the individual samples are much closer to each other than in the previous case where the exciting wave-length was longer.

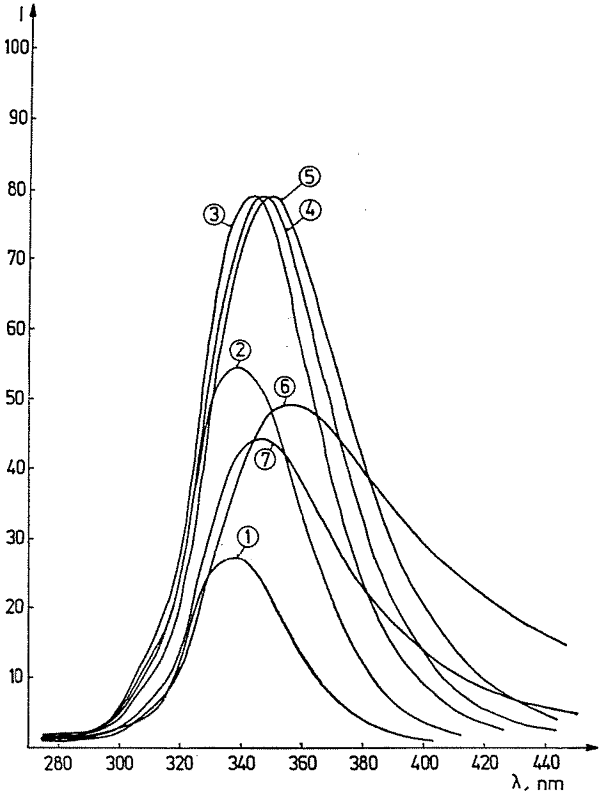

Fig. 3. Fluorescent emission spectra of petroleum fractions. $\lambda_{ex} = 240$ nm; c = 8 p.p.m.; Solvent: 1,2-dichloroethane 1 — Light gas oil; 2 — Heavy gas oil; 3 — Light paraffinic fraction; 4 — Medium paraffinic fraction; 5 — Heavy paraffinic fraction; 6 — Petroleum tar; 7 — Crude oil

The fluorescent light intensities of the fractions (the concentration of all solutions being identical) are plotted against the exciting wave-length in Fig. 4.

The exciting wave-length is plotted on the abscissa axis, the measured intensity of the fluorescent light, at the emission wave-length found the most favourable from the point of view of measurement, on the ordinate axis.

The results demonstrate that exciting wave-lengths in the range of 240 to 280 nm are very suitable for determining petroleum concentrations, since in this case the smallest differences arise between the fluorescent light intensities.

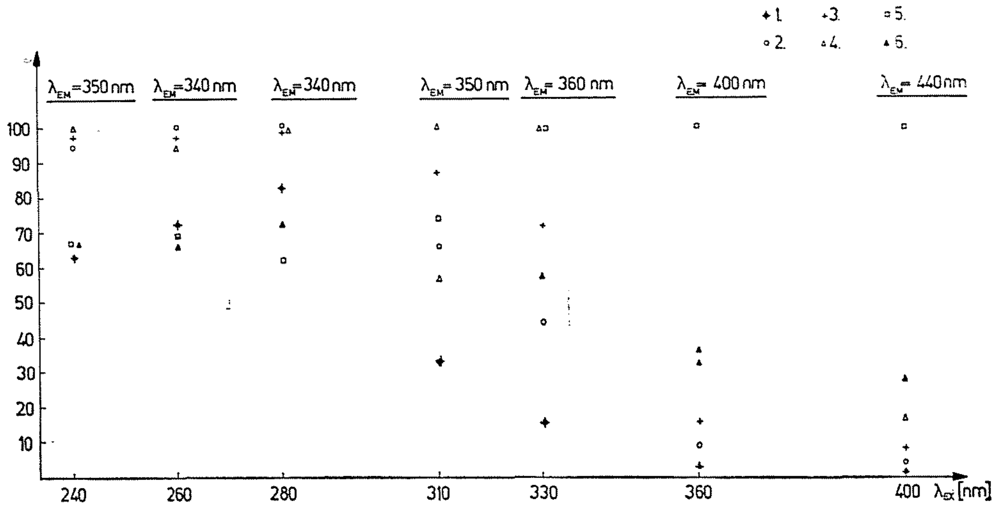

Fig. 4. Intensities of fluorescent light at different wave-lengths *vs.* wave-length of exciting light for petroleum fractions. c = 10 p.p.m.; Solvent: 1,2-dichloroethane; * = Heavy gas oil; o = Light paraffinic fraction; + = Medium paraffinic fraction; Δ = Heavy paraffinic fraction; □ = Petroleum tar; ▲ = Crude oil

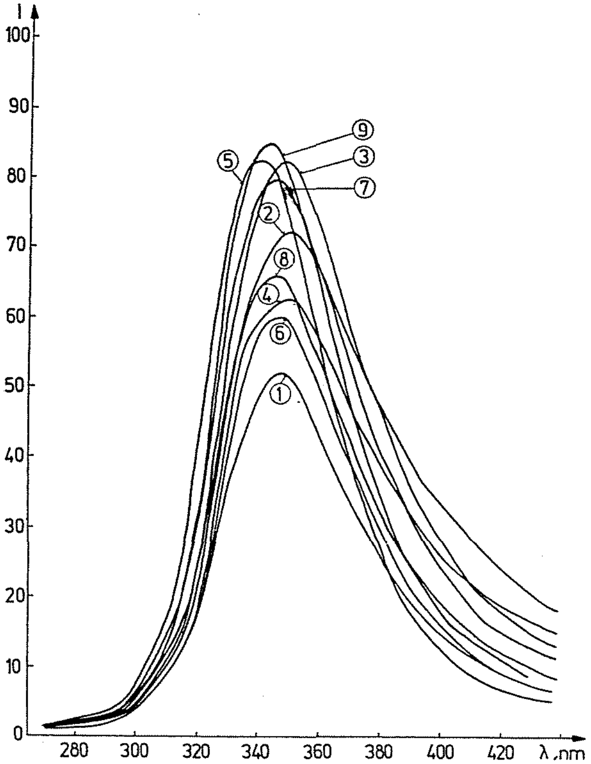

Fig. 5. Fluorescent emission spectra of crudes of different origin. λ_{ex} = 240 nm; c = 8 p.p.m.; Solvent: 1,2-dichloroethane. 1 — Romashkino; 2 — Nagylengyel; 3 — Egypt; 4 — Albania; 5 — Lispe; 6 — Algyő; 7 — Kardoskút; 8 — Iraq; 9 — Demjén

Fluorescent properties of crudes of different origin and type

Emission spectra obtained with our crude samples, using exciting wave-lengths of 240 nm and 260 nm, resp., are shown in Figs 5 and 6.

At exciting wave-lengths exceeding 240 nm, under equal conditions, the fluorescent light emission intensities of paraffinic crudes are substantially lower than those of naphthenic crudes. Emission spectra of the two types can readily be distinguished when 280 nm exciting wave-length is used (Fig. 7).

Hence, emission spectra obtained with 280 nm exciting wave-length yield some information as to the nature of the petroleum contamination, thereby opening up the possibility to choose the reference standard appropriately.

With increasing exciting wave-lengths the intensity differences in the fluorescence of individual crudes steadily increase. Naphthenic crudes have a significantly more intensive fluorescent emission in all cases.

A summarizing diagram, similar to Fig. 4, for comparing the intensity differences measured at different exciting wave-lengths, is presented in Fig. 8.

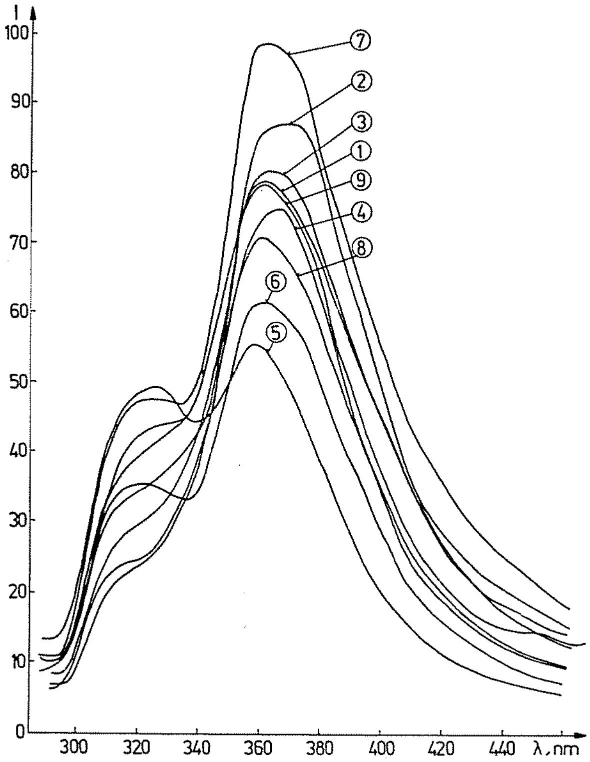

Fig. 6. Fluorescent emission spectra of crudes of different origin. $\lambda_{ex} = 260$ nm; c = 8 p.p.m.; Solvent: 1,2-dichloroethane. 1 — Romashkino; 2 — Nagylengyel; 3 — Egypt; 4 — Albania; 5 — Lispe; 6 — Algyő; 7 — Kardoskút; 8 — Iraq; 9 — Demjén

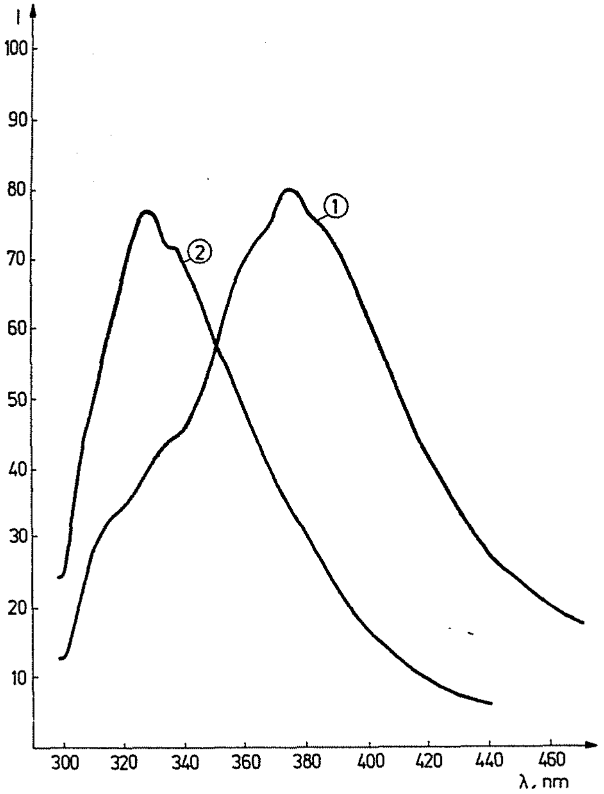

Fig. 7. Fluorescent emission spectra of naphthenic and paraffinic crudes. $\lambda_{ex} = 280$ nm; c = 8 p.p.m.; Solvent: 1,2-dichloroethane

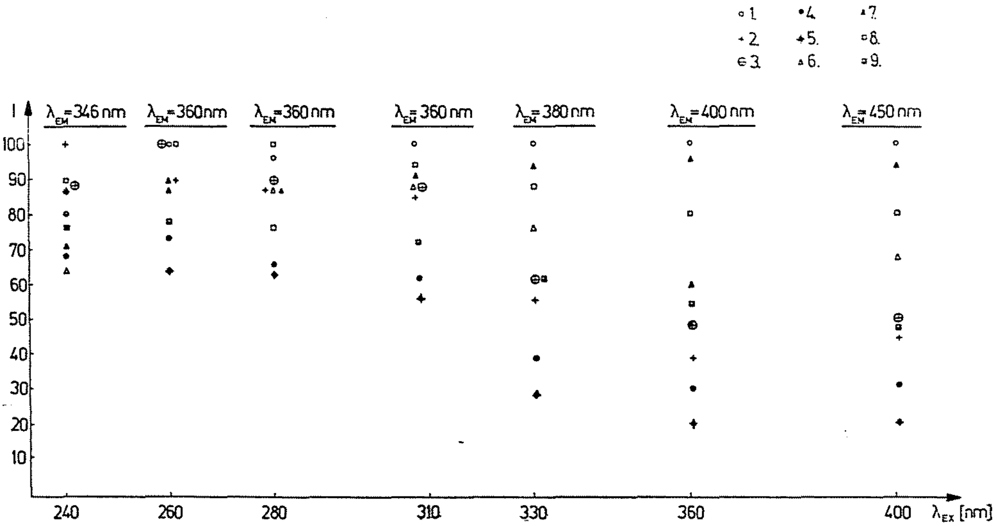

Fig. 8. Intensities of fluorescent light at different wave-lengths *vs.* wave-length of exciting light, for crudes of different origin. c = 8 p.p.m.; Solvent: 1,2-dichloroethane. 1. o = Nagylengyel; 2. + = Demjén; 3. ⊕ = Kardoskút; 4. ● = Algyő; 5. * = Lispe; 6. △ = Romashkino; 7. ▲ = Albania; 8. □ = Egypt; 9. ◪ = Iraq

From the experimental results the same conclusion can be drawn for the different crudes as for the different petroleum fractions, namely that the use of exciting wave-lengths below 310 nm substantially reduces the intensity differences between individual types of crudes, this being of great importance from the view of accuracy of quantitative determinations.

Determination of petroleum content

Two routes for determinations of petroleum in natural waters and effluents are feasible. In the simpler case, fluorescent emission of petroleum is directly measured [16]. In this case, the intensity of fluorescent light will depend not only on petroleum content, but also on its form (extent of emulsification, dissolution, adsorption etc.). Besides, background emission due to the presence of non-petroleum contaminations, e.g. decay products of biological origin may also interfere.

A substantially more accurate results is obtained by extracting the petroleum content of the water with an organic solvent. Suitable solvents are e.g. gasolene, *n*-heptane, cyclohexane. However, these solvents — being lighter than water — form the upper phase after extraction, this being inconvenient in the technique of multiple extraction. In an earlier paper [17] we reported a spectrofluorometric method utilizing extraction with *n*-heptane.

Chlorinated hydrocarbons heavier than water, namely carbon tetrachloride, chloroform and trichloroethylene are excellent solvents for petroleum, but cannot be used at low exciting wave-lengths, since they completely absorb the exciting light.

After testing numerous solvents, we found that 1,2-dichloroethane was preferable from the view of both extraction and spectrofluorometric measurement. Its density is 1.256, its boiling point 83.7 °C, and at a wave-length of 240 nm it still transmits 40% of the incident light.

The technique of the determination

50 cm^3 of petroleum-contaminated water or effluent are prepared for extraction in conformity with sampling regulations. The sample is transferred into a 100 cm^3 extraction funnel and shaken with 3 times 5 cm^3 of dichloroethane for 1—2 minutes. To accelerate separation and to improve extraction efficiency, 2 cm^3 of 4 N sulphuric acid are added to the emulsion formed in the first extraction. The extract is collected in a 25 cm^3 volumetric flask and made up to the mark with dichloroethane. If necessary, an aliquot of the solution is further diluted so as to have a final petroleum concentration in the range of 1 to 8 p.p.m.

The intensity of the fluorescent light is measured at 340 nm emitted wave-length, using 260 nm wave-length light for excitation. Under such conditions, the relationship between petroleum concentration within the 1 to 8 p.p.m. range and intensity of fluorescent light is linear (Fig. 9).

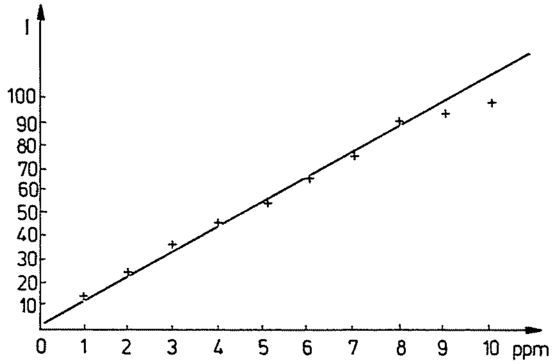

Fig. 9. Calibration curve. $\lambda_{ex} = 260$ nm; $\lambda_{em} = 340$ nm; Solvent: 1,2-dichloroethane

Petroleum concentration is calculated using Formula 1, if the fluorescent light intensity of the reference standard used in a concentration of 8 $\mu g/cm^3$ corresponds to 100% by setting the instrument accordingly.

$$c = \frac{I \cdot E \cdot H}{10 \cdot V} \quad [\text{p.p.m.}] \tag{1}$$

where c is the petroleum content of the water in p.p.m., I the measured intensity of the fluorescent light, E the volume of the extract [cm^3], V the volume of the water sample [cm^3] and H the dilution.

If the contaminating petroleum is similar in nature to the reference standard, standard deviation of results measured at 3 p.p.m. is ±12%, the standard deviation of the mean value is ±4.4%.

If the nature of the contaminant and the reference standard is not similar, the error is, of course, substantially higher, and may reach 30—40% even when using short exciting wave-lengths. At low concentrations, in the p.p.m. to p.p.b. range, however, such errors are acceptable for practical purposes.

Summary

Fluorescent properties of petroleum fractions and of crudes of different origin have been studied. Atmospheric distillation fractions below 300°C show no visible fluorescence even in concentrations as high as 1000 p.p.m. Differences in fluorescence intensities between fractions with higher boiling points are minimum if exciting wave-lengths of 240 to 280 nm

and emitted wave-lengths of 340 to 360 nm are chosen for measurement. Similar results were obtained when studying crudes of various origins. Significant differences were also found between the emission spectra of paraffinic and naphthenic crudes, yielding some information regarding the nature of the petroleum contaminant.

A spectrofluorometric method introducing 1,2-dichloroethane as extracting agent was developed for the determination of petroleum in surface waters and effluents. The intensity of the fluorescent light is linearly related to petroleum concentration within the range of 1 to 8 p.p.m., if the wave-length of the exciting light is 240—280 nm and emission is measured at 340—360 nm.

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