IDENTIFICATION OF MINERAL OILS BY SYNCHRONOUS EXCITATION FLUORESCENCE SPECTROSCOPY

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Summary

Synchronous excitation fluorescence spectra allow crude oils to be characterised and identified, hence they may assist in selecting a reference oil for the identification and determination of the oil contamination of water and soil. In the synchronous excitation fluorescence spectra taken with a wavelength difference $\Delta\lambda = 20$ nm, the peaks appearing at excitation wavelengths 300 and 310 nm are characteristic of paraffinic, the one at 330 nm is characteristic of naphthenic refined oils. In the spectra of intermediate refined oils the peaks at 310 and 330 nm are of about equal intensities.

The spectra of crude oils is much broader than those of refined oils. A further peak appears at 390 nm. In the case of purely naphthenic crude oils the peak at 310 nm appears at most as a small inflection.

Introduction

Mineral oils and their derivatives are very important as pollutants of our natural water supply. The identification and determination of oil in water are, however, very difficult tasks, as neither crude oil nor fractions obtained from it are homogeneous chemically but mixtures of paraffin and naphthene hydrocarbons. The composition depends on the location, conditions of formation and on the technology of refining. Consequently, there is very little probability that an oil chosen as reference in the quantitative determination of an unknown oil pollutant of water is similar in composition to the oil to be determined. The characterization and identification of the oil pollutant may greatly enhance the accuracy of its determination.

Gravimetry, infrared and ultraviolet spectroscopy often fail to provide sufficient information on the nature of a mineral oil sample.

By using the conventional spectrophotometric method, a fairly high sensitivity can be achieved: an oil content as low as 0.01 mg/dm^3 can be detected. Furtheron, by analysing emission spectra obtained with excitation at 280 nm, the aromatic or paraffinic nature of the mineral oil pollutant can be judged. An emission peak in the interval 320–350 nm is characteristic of paraffinic whereas a peak between 370 and 400 nm is characteristic of aromatic type mineral oils [1].

Continuously excited fluorescence spectra of mineral oil samples enable further distinction to be made.

Synchronous excitation fluorescence

Synchronous excitation technique was first described by Lloyd in 1971 [2, 3]. When taking the synchronous spectrum, the excitation and emission monochromators move simultaneously with the same speed, with a constant wavelength difference of $\Delta\lambda$ previously adjusted. The spectrum is a plot of intensity of light emitted at a wavelength of $\lambda + \Delta\lambda$ against the wavelength λ of the exciting radiation. The intensity of synchronous excitation fluorescence depends on the nature of the normal excitation and emission spectra as well as on the difference $\Delta\lambda$ between the excitation and emission wavelengths.

The synchronous excitation fluorescence spectrum of a substance is of very small bandwidth. Most intense and narrowest bands can be obtained by choosing a $\Delta\lambda$ equal to the wavelength difference between the excitation and emission spectrum. Hence, the parameter $\Delta\lambda$ depends on the individual characteristics of the excitation and emission spectra of the luminescent molecules. The wavelength difference usually varies between 5 and 60 nm. The most distinctive spectra can be obtained using $\Delta\lambda$ between 15 and 30 nm.

It has been shown by Lloyd and Evett [4] as well as by Vo-Dinh [5] that the position of synchronous signals can be predicted for polynuclear aromatic compounds. The synchronous signal is shifted to longer wavelengths as the number of rings increases in polynuclear aromatic hydrocarbons.

The method provides information on most, sometimes on all the components of a multicomponent system. The spectra obtained for complex mixtures can be considered as fingerprints and are suitable for studying multicomponent fluorescent mixtures.

John and Soutar [6] have studied the applicability of synchronous excitation spectrofluorimetry for the identification of crude oils.

The first application of the technique in Hungary was reported on in 1980 [7]. In this paper the use of synchronous excitation fluorescence for studying different refined and crude oils was dealt with.

Experiments

The present study is based on the synchronous excitation fluorescence spectra of refined and crude oils available in Hungary (about 40 different oils were investigated).

The spectra were taken by a HITACHI MPF-2A type spectrofluorometer modified for the purposes of synchronous excitation. The wavelength difference $\Delta\lambda$ applied was 20 nm, the excitation and emission slitwidth was 6 nm.

n-Hexane was used as solvent throughout the work. The concentration of the oil in n-hexane was 6 mg/dm^3.

Results and discussion

In Fig. 1 the conventional fluorescence spectrum and the synchronous excitation fluorescence spectrum of a crude oil from Demjén are presented.

There is a significant difference between the two spectra. Based on the spectra, the presence of tetra- and pentanuclear polycyclic aromatic hydrocarbons can be evidenced.

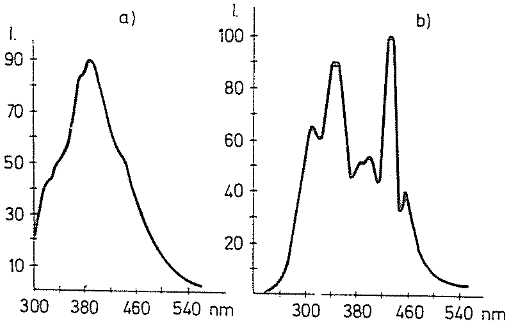

Fig. 1. Fluorescence emission spectrum of mineral oil from Demjén (Hungary): a) constant excitation; $\lambda_{ex} = 280$ nm, b) synchronous excitation; $\Delta\lambda = 15$ nm, solvent: n-hexane; concentration = 10 mg/dm^3

In Figs 2–6 the synchronous excitation fluorescence spectra of different refined oils and crude oils are shown.

In the spectra of refined oils peaks appear at 300, 310, 330, 340 and 390 nm. The small peak at 300 nm, and the more intense one at 310 nm are characteristic mainly of paraffinic products.

The peak at 330 nm can be found in the spectra of both paraffinic and intermediate oils but with paraffinic oils the peak at 310 nm is more intense. As the naphthenic character increases, the peak at 330 nm becomes more intense.

With oils freed from aromatics the peak at 330 nm is scarcely perceptible (AGIP F1). After use, however, a new, tailing maximum appears between 370 and 390 nm in the spectrum of the motor oil (Fig. 2).

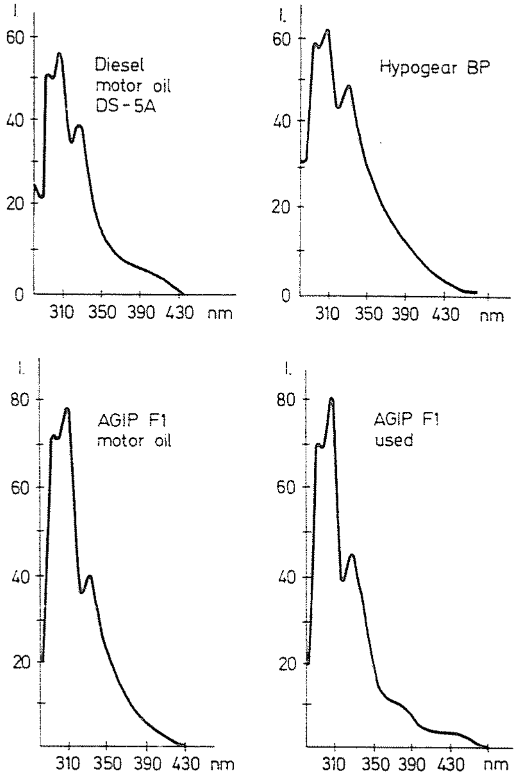

Fig. 2. Synchronous excitation fluorescence spectra of paraffin base refined oils $\Delta\lambda = 20$ nm, concentration = 6 mg/dm^3

In the spectrum of paraffin–naphthene base mineral oils the two peaks at 310 and 330 nm are of about equal intensity. In the spectrum of this type of oils a further peak of small intensity appears at 390 nm (Fig. 3). The peak between 370–390 nm is characteristic exclusively of naphthenic oils (Fig. 4).

In addition to the peaks at 300, 310, 340 and 390 nm, there appears a peak in the visible region in the spectra of crude oil samples. The peak at 390 nm is more distinct than in the case of refined oils.

The spectra of crude oil samples are broader (280–490 nm) than those of refined oils. The single peaks are broader, especially those at about 330 and 390 nm. In the spectra of naphthene base crude oils the peaks at 300 and 310 nm characteristic of the paraffinic nature appear only as inflections (Figs 5 and 6).

Based on synchronous excitation fluorescence spectra, crude oil and refined oil pollution can be distinguished with certainty, and the paraffinic, intermediate and naphthenic nature of the oil can be judged.

The spectra are very characteristic finger print spectra, depending only on the type of the oil sample. However, if different type oils are present together, only the more dominant one can be identified.

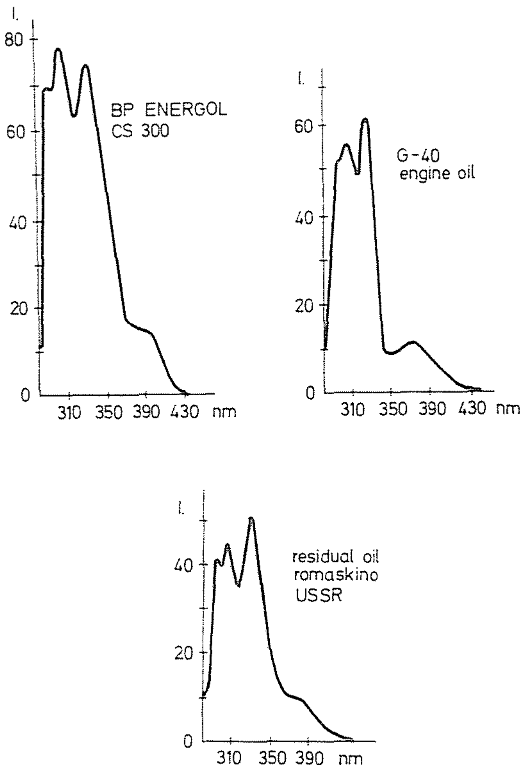

Fig. 3. Synchronous excitation fluorescence spectra of paraffin–naphthene base refined oils. $\Delta\lambda = 20$ nm; concentration = 6 mg/dm^3

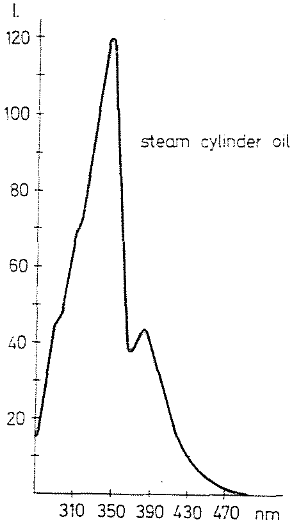

Fig. 4. Synchronous excitation fluorescence spectrum of naphthene base refined oil. $\Delta\lambda = 20$ nm; concentration = 6 mg/dm^3

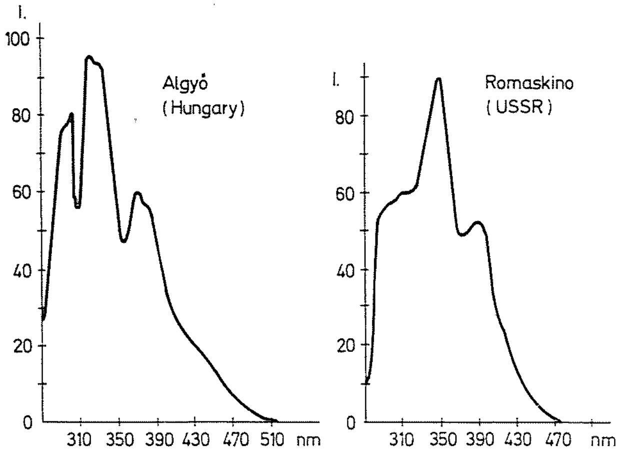

Fig. 5. Synchronous excitation fluorescence spectra of paraffin base crude oil samples. $\Delta\lambda = 20$ nm; concentration $= 6$ mg/dm^3

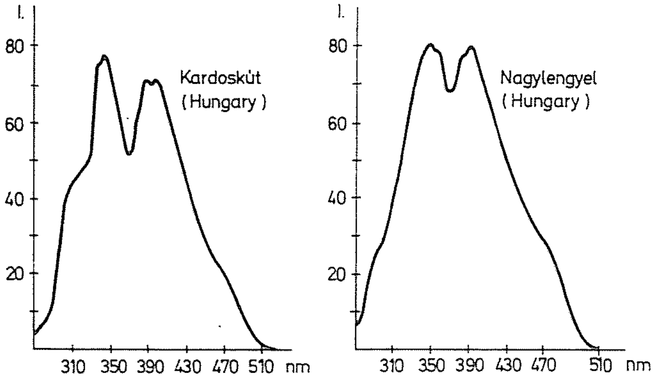

Fig. 6. Synchronous excitation fluorescence emission spectra of naphthene base crude oils. $\Delta\lambda = 20$ nm; concentration $= 6$ mg/dm^3

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