

SPECTROFLUORIMETRY OF CHOSEN DISTILLATES OF OIL AFTER PYROLYSIS OF SCRAP TIRES

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Abstract

One of way to obtain liquid hydrocarbons can be pyrolysis of scrap tires. The hydrocarbon substances produced by this method may be an addition to traditional fuels, i.e. gasolines or fuels for diesel engines. In laboratory conditions at Department of Mechatronics of University of Warmia and Mazury there were obtained pyrolytic products and prepared three distillates related to temperatures 160, 204 and 350°C. Analyses of shapes of fluorescence spectra were carried out in Department of Physics of Gdynia Maritime University. Spectra of fluorescence were prepared applying the spectrofluorimeter Hitachi F-7000 FL, which allows applying of excitation wavelength from 200 nm until 600 nm, whereas analysing of emitted, can be performed until 750 nm. In here reported study excitation and emission range for the most intense fluorescence are presented. There were prepared four solutions of pyrolytic products in the n-hexane: 4 ppm, 20 ppm, 100 ppm and 500 ppm. In order to show dependence of intensity fluorescence and shapes of excitation-emission spectra on type of distillate and concentration both kind of visualization – three-dimensional and as contour maps – are shown in this article. In analysed range of wavelengths, intensity of fluorescence grows with concentration of oil, whereas structure of the shape of spectra simplify when concentration increases. The presented effects associated with the fluorescence of pyrolysis products allow to predict the possibility of developing a method for determining the content of these substances in mixtures with petroleum refining products and other liquid hydrocarbons.

Keywords: *fuels, used car tires, pyrolysis, fluorescence, excitation-emission spectra*

1. Introduction

Used tires, like every waste, are an environmental problem. They are very poorly biodegradable. The most effective way to remove non-degradable waste from the environment is to convert it into a financial income (of course, provided that these are fairways). The term “utilization” applies to all issues of disposal of waste from the environment, connected with production useful products not related to their transformation into harmful substances dispersed into the environment, thus invisible (until their concentration becomes cumbersome). As far as tires are concerned, various methods of utilization or transformation into useful substances have been considered for several decades [3-5, 7, 9]. A group of pyrolytic methods is considered as one of suitable method of used tires utilization. There were analysed pyrolytic products of various type of tires [6] and produced in various physical conditions [1, 8].

This article analyses the properties of an exemplary substance obtained from laboratory pyrolysis of tires in the field of their fluorescent properties. Initial analysis of the fluorescence spectra of this substance was carried out in an earlier work [2]. It describes the characteristics of the fluorescence spectra of the three distillates of the pyrolytic product. In contrast, this article presents extended analysis of fluorescence spectrum shapes of distillate solutions at various concentrations. In addition, methodological remarks are provided here as to how to identify the pyrolytic substance by analysing the shape of the fluorescence spectrum.

2. Material and method

Pyrolysis was performed in temperature 500°C for 8 h without oxygen [2]. The distillation of the pyrolytic product was then carried out at three temperatures (Tab. 1).

Tab. 1. Types of samples tested

probe	distillate temperature [°C]
pyrolytic product (PP)	-
D1	160
D2	204
D3	350

Each sample was diluted in n-hexane to concentration 4 ppm, 20 ppm, 100 ppm and 500 ppm (by weight).

Excitation-emission spectra (EEMs) were determined using spectrofluorimeter *Hitachi F-7000 FL*. Fluorescence measurements were performed in the excitation wavelength range from 200 to 480 nm and emission wavelengths in the range from 260 to 700 nm.

3. Results

Spectrofluorimeter creates a digital array of intensities of fluorescence, which in order to visualize, is converted into charts that are presented in Fig. 1. It presents both graphs showing absolute fluorescence intensity as well as intensity normalized to the highest value. The first method was used to illustrate changes in fluorescence intensity depending on the type of distillate and its concentration in the solution in n-hexane. In turn, the second way is to show the shape of the spectrum and the location of spectral peaks. By far the strongest fluorescence is observed for the raw pyrolytic product. The weakest fluorescence is shown by the substance obtained from the distillation of the pyrolytic substance at a temperature of 160°C. The fluorescence of this distillate, shown in the same scale as that used for crude pyrolysis product, is almost invisible (Fig. 1b). A characteristic feature of the spectra of all studied hydrocarbons is the narrowing of the area of fluorescence occurrence as the concentration of the solution in n-hexane increases. A characteristic feature of the spectra of all studied hydrocarbons is the narrowing of the area of fluorescence occurrence as the concentration of the solution in n-hexane increases. In the case of a pyrolytic substance, three maxima appear on the spectrum for the lowest concentration, including two very high. In the case of a pyrolytic substance in the spectrum, the lowest concentration in the spectrum shows three maxima, including two very high, while for the highest concentration only one maximum. A similar effect is visible in the case of other substances (distillates).

The spectrum of fluorescence observed in spectra is the widest in the case of the raw substance obtained in the pyrolysis process of tires. The phenomenon of fluorescence occurs when it is excited by light in the wavelength range from 200 to 360 nm.

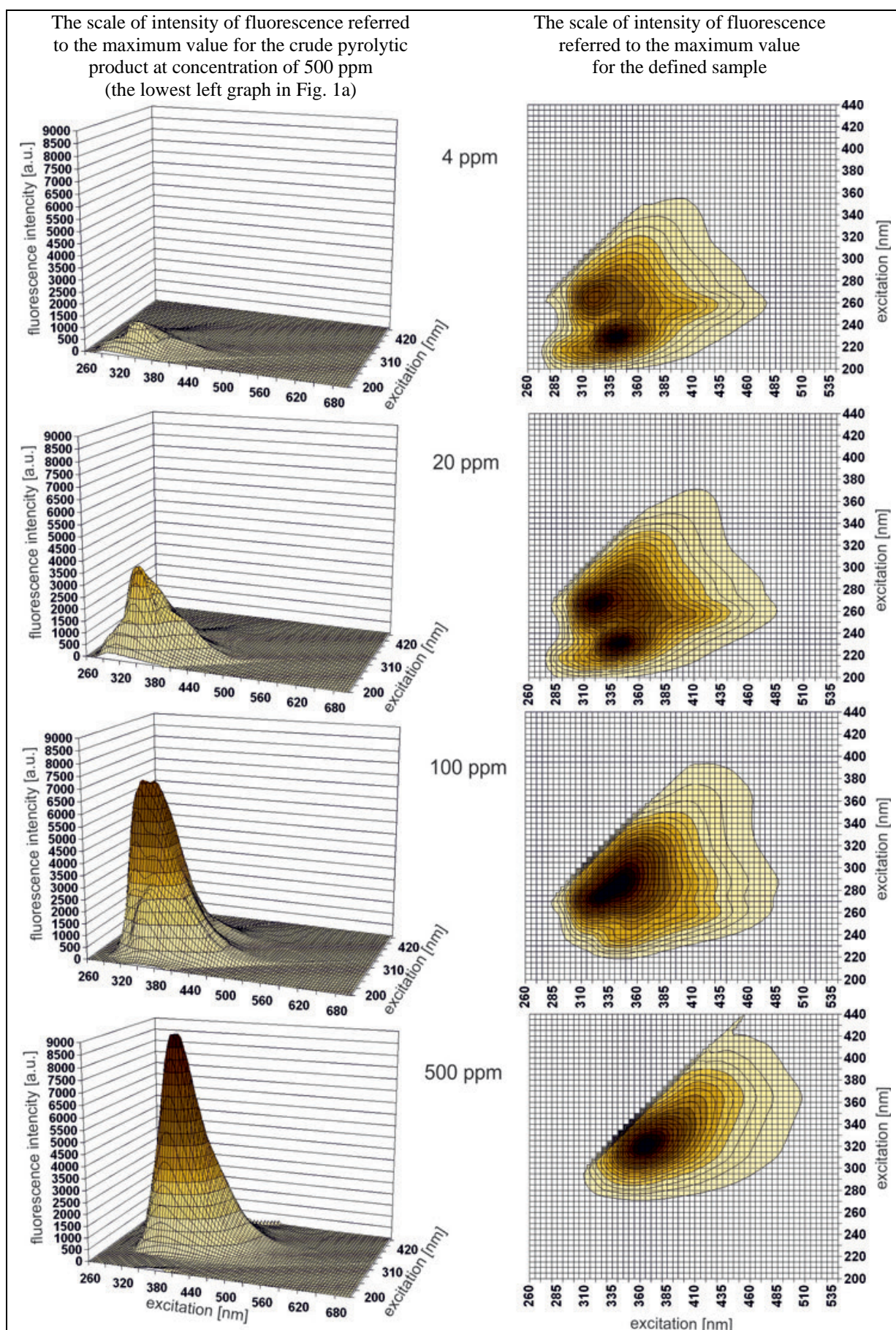


Fig. 1a. Fluorescence of pyrolytic product

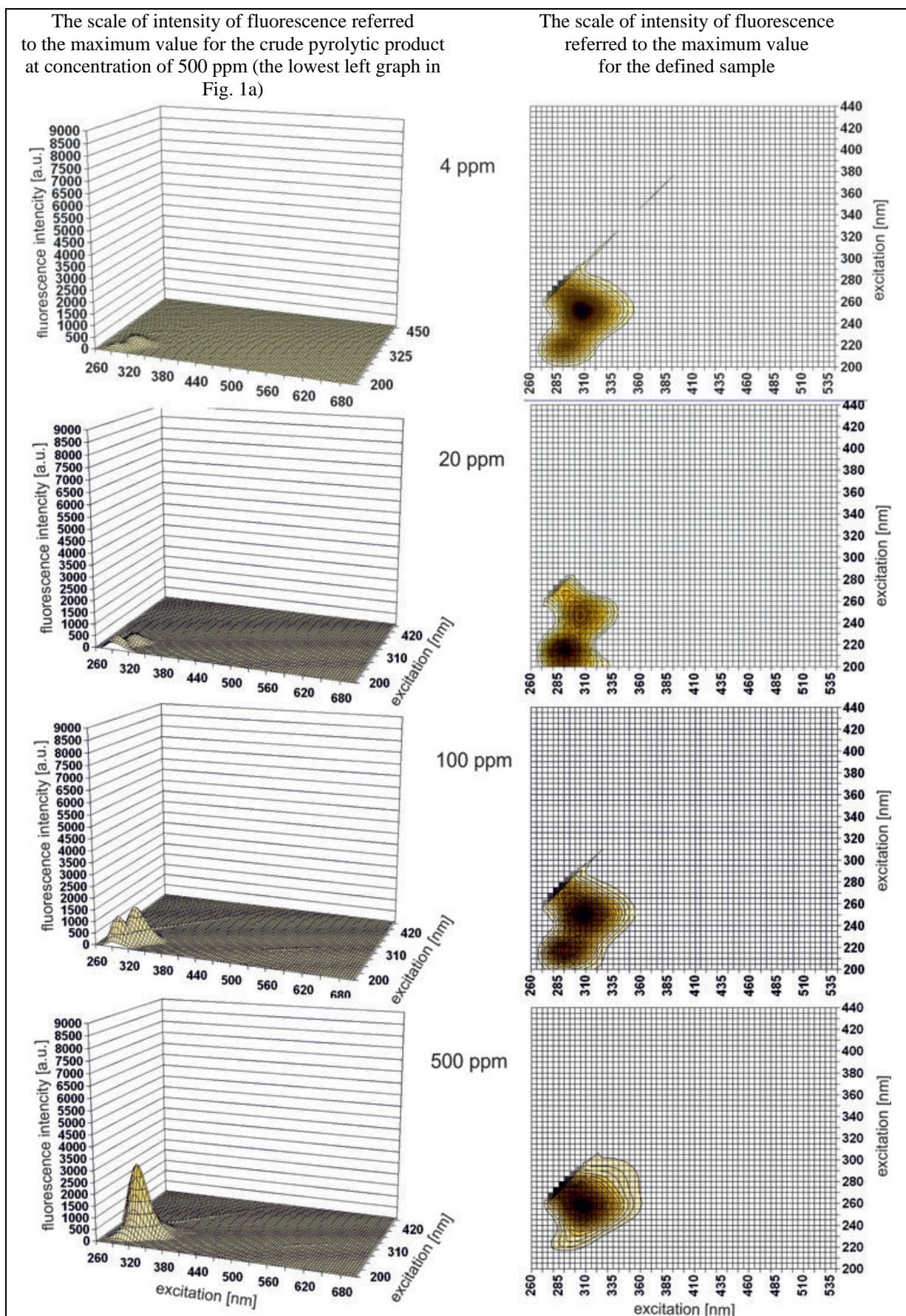


Fig. 1b. Fluorescence of distillate from pyrolytic product performed at 160°C

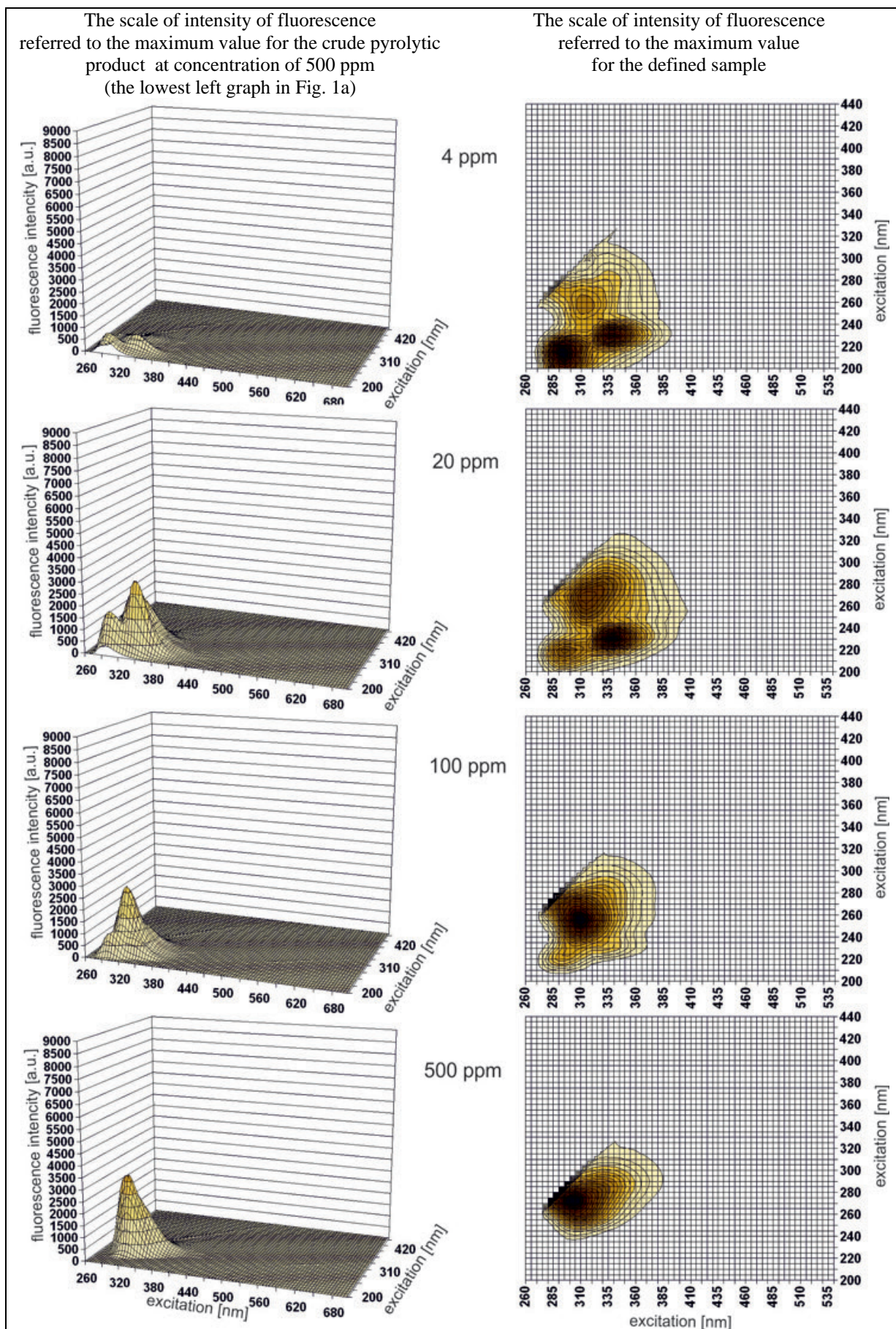


Fig. 1c. Fluorescence of distillate from pyrolytic product performed at 204°C

4. Discussion

In order to obtain a spectrum with an individualized structure for a given type of sample, it would be necessary to carry out measurements with the greatest possible dilution. Of course, at low concentrations, the fluorescence signal weakens, and therefore the precision of the measurement decreases. It seems, however, that when analysing the above-mentioned test results, it can be concluded that a concentration reaching several dozen ppm would be appropriate.

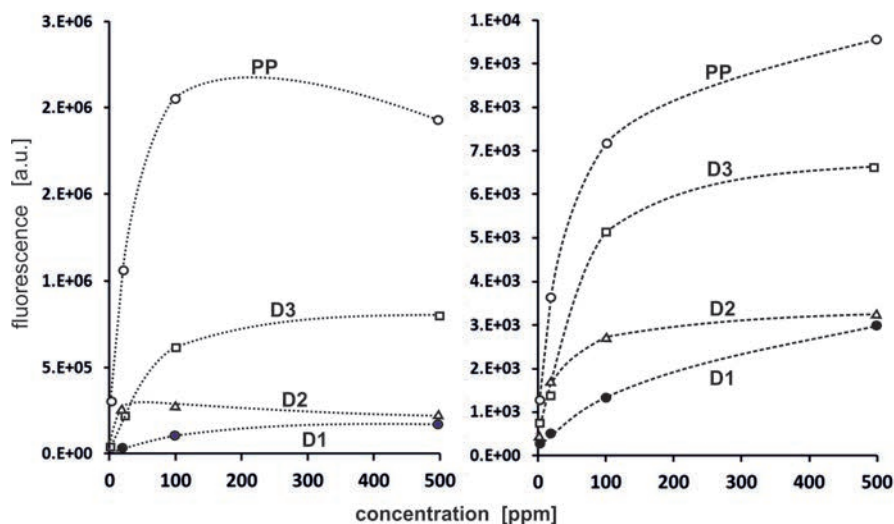


Fig. 2. Dependence of intensity of fluorescence on oil concentration in *n*-hexane solution for total (left) and maximum (right) fluorescence for pyrolytic product (PP) and three distillates: at 160°C (D1), 204°C (D2) and 350°C (D3)

In principle, concentrations should be avoided for which the linear relationship disappears between fluorescence intensity and concentration. In the analysed case, as shown in Fig. 2, it is below 20 ppm.

Author contribution: M. A-W carried out laboratory preparing pyrolytic product and distillates, Z. O. performed fluorescence measurements and wrote the manuscript with support from M. A-W.

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