Application of microemulsions for the extraction, pre-concentration of PAHs as a tool for fast screening of perspective oil chemical markers

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Abstract: A simple method for the determination of 16 priority polycyclic aromatic hydrocarbons (PAHs) from geological cores as oil markers using microemulsion extraction, pre-concentration with following fluorometric detection was developed. Parameters, such as composition of microemulsion (ME), temperature, pH, which affect the intensity of fluorescence were investigated and optimized. The potential of the developed technique has been demonstrated by the determination of these PAHs in oil and oil cores. The calculated pre-concentration factor using microemulsion (3.3% CTAB, 0.8% heptane, 8% n-butanol and 87.9% water) varies from 5 to 10. The main parameters that influence the intensity of fluorescence are the charge of a surfactant and the nature of the oil. The limits of detection ranged between 10-50 μg/kg.

Keywords: polycyclic aromatic hydrocarbons, microemulsion extraction, oil chemical markers.

1. Introduction

In modern analytical chemistry development of the rapid and simultaneous methods for the determination of substances, significantly differing in polarity and hydrophobicity is very important. Another relevant issue is the determination of trace amounts of various compounds in the objects with complex multicomponent matrix (such as oil and oil cores) and their quantitative extraction from the matrix [1, 2].

Elicitation of chemical markers is the main aim of the identification of hydrocarbon deposits and the assessment of their catagenetic maturity. Although in most cases, it was only possible to state group analysis without description of specific chemical structures [1, 3-5]. Moreover, signals from mixture of various compounds, which belong to different classes, sometimes are considered as individual compounds. It may distort and depreciate the interpretation of the results of chemical analysis. In addition, it means that numerous markers remain unexplored and those compounds or derived indices, which were considered as markers, may actually be false.

Individual oil components, such as PAHs, can serve as chemical markers (the content of PAHs in crude oil can reach up to 4%) [5-7]. Various methods of extraction and subsequent analysis are used for the determination of PAHs in oil and its products: liquid-liquid extraction with following one- and two-dimensional liquid chromatography analysis [8], 4-stage liquid-liquid extraction with following HPLC-FLD analysis [9], GC-MS in selected ion monitoring mode [7], multistage extraction with dimethyl sulfoxide and dichloromethane with following two-dimensional gas chromatography mass spectrometry.

Generally most of approaches to the analysis of oil and its products require long-term sample preparation: in the first stage, separation of resinous-asphaltene compounds takes place followed by further fractionation. It is performed by fractional precipitation or fractional extraction, preparative chromatography, distillation in deep vacuum, thermal diffusion, etc. These methods are characterized by multistage, large consumption of reagents and complexity of implementation.

The application of nanostructured systems, so-called “microemulsions” (MEs) in the extraction of PAHs from oil and oil cores is of current interest. ME is a homogeneous mixture of water and oil, stabilized by the introduction of a surfactant, often in combination with an accompanying surfactant (co-surfactant) [10-15]. Any organic matter, sparingly soluble in water (most of them are aliphatic hydrocarbons), can play the role of oil. Alcohol with a medium hydrophobic radical or ether act as a co-surfactant [16].

ME’s unique properties such as ultralow interfacial tension, large interfacial area, thermodynamic stability are mainly provided by the diphilic structure of the surfactant [10]. The surfactant molecules combine the characteristics of hydrophobic and hydrophilic compounds and show the ability to solubilize and stabilize organic compounds of different nature. Surfactants contribute to the formation of hard structures of organic compounds molecules. In this case, the intensity of fluorescence increases and the consumption of excitation energy on nonradiative transitions significantly decreases [17-20]. The main factors that influence the intensity of fluorescence are the charge of a surfactant and the nature of the oil [17-19].

Due to these specific characteristics MEs can be used as extractants in fluorescence spectroscopy and high-performance liquid chromatography with fluorometric detection (HPLC-FLD) for the development of the technique for the determination of trace amounts of organic compounds, what was the purpose of the study.

2. Materials and methods

Chemicals

Sodium dodecyl sulfate (SDS), n-heptane, 1-butanol, acetonitrile (AcN) were obtained from Panreac (Barcelona, Spain), benzene was obtained from Component-Reaktiv (Moscow, Russia), β-cyclodextrin – from Chemical Line (Saint-Petersburg, Russia), cetyl trimethylammonium bromide (CTAB) - from Sigma-Aldrich (Saint Louis, MO, USA), sodium sulfate was obtained from Baum-Lux (Moscow, Russia). Standart mixture of 16 PAHs and standard solutions of 16 PAHs (200 μg/ml and 100 μg/ml) were obtained from Ecroshin (Saint-Petersburg, Russia). All

the chemicals were of analytical grade and all solutions were prepared using ultra-pure water (>18.2 MΩ/cm) obtained from Millipore Milli-Q system (Belford, USA).

Instrumentation

Measurements were performed on FluoroLog-3 (Horiba Jobin Yvon) in the wavelength range 270-600 nm with a step of 1 nm and an optical gap width of 2 nm. Xenon lamp was used as an excitation source. The excitation of the system was carried out at λ_{ex} = 254 nm. Experiments were carried out on a chromatographic system Agilent 1200 equipped with quaternary gradient pump, online eluent degasser, autosampler, column thermostat, diode array and fluorometric detectors (Agilent Technologies, USA). Chromatographic separation was achieved with an Eclipse PAH (Agilent, USA), 4.6 x 250 mm, 5 μm at 30 °C. Mobile phase - A: water, B: acetonitrile. The gradient conditions were as follows: hold at 40% (B) for 2 min and increased to 100% (B) (25 min), hold at 100% (B) for 20 min, and then equilibrated back to initial conditions in 2 min and hold for 3 min. The total run time of the method was 50 min with a flow rate of 1.0 ml/min. ChemStation (Agilent) version B.02.01 – SR2(260) was used for instrument control, data acquisition and handling. Aliquot portions were sampled with automatic dispensers with the sampled volume ranged 5–50, 20–200, 100–1000, and 1000–5000 μL with a relative measurement error of less than ±5% (LABMATE, Poland). Accurately weighed portions were measured using an ExplorerPro balance (Ohaus, United States); the accuracy of weighing was 0.0001 g. Samples were centrifuged in an SM-50 centrifuge (Elmi, Latvia). Ultrasonic liquid extraction was carried out in an UZV ultrasonic bath (Sapfir, Russia).

Preparation of microemulsions

In current work, oil-in-water MEs with following compositions were used as extractant: ME1 - 3% SDS, 0.8% benzene, 6% n-butanol and 90.2% water, ME2 - 3% SDS, 1% heptane, 6% n-butanol and 90% water, ME3 - 3.3% CTAB, 0.8% heptane, 8% n-butanol and 87.9% water. The microemulsion solution was prepared by mixing components and sonicating for 30 minutes to aid complete dissolution and form optically transparent microemulsion. Ultrasound mixing

accelerates the process of formation of ME and improves the equable distribution of dispersed phase in dispersion medium.

Preparation of oil and oil core samples

Oil and oil core samples were obtained from Department of Geology, Lomonosov Moscow State University. The accurate weigh of oil or oil core (0.1 g) was placed into a 10 ml- vial and 5 ml of ME was added. The mixture was sonicated for 30 minutes and 15-fold excess of dry sodium sulfate over the concentration of CTAB was added to the mixture for decomposition of ME and pre-concentration of PAHs in organic phase. The oil phase was collected and centrifuged at 15000 rpm for 5 min. Then, the supernatant was collected for the further analysis.

3. Results and Discussion

FLD-detection

The compositions of MEs used in current work was proposed by our research team [18, 23].

Individual spectra of 16 PAHs (Table 1) dissolved in different media were obtained for investigation of the influence of various parameters on the fluorescence intensity of each tested substances after microemulsion extraction. The obtained results are characterized by good reproducibility and stability but there are some shifts in the maximum of the spectra of each studied PAH when the solvent was changed, that may be explained by the interaction of PAH and solvent with each other.

It was found that the intensity of fluorescence was increased in the following row: anionic ME1 - acetonitrile/hexane – anionic ME2 – cationic ME3. If microemulsion surfactant was cationic (CTAB), the analytical signal magnified in 2-3 times in comparison with acetonitrile and hexane as solvents for organic substances, if anionic surfactant (SDS) was used the intensity of fluorescence increased only in 1.5-2 times. When co-surfactant was changed from benzene to heptane the total intensity of fluorescence was multiplied on the average in 50 times (Fig. 1). The

maximum fluorescence intensity was achieved using ME based on CTAB and heptane. Further experiments were conducted with ME3.

It was mentioned previously [24] that cyclodextrin can be used as an additive of ME to increase the intensity of fluorescence, however, in current work the growth of the signal was observed only for 10 of 16 PAHs and did not exceed 3.5 % (Fig. 2)

The dependence of the intensity of fluorescence from pH and temperature was studied. It was found that the maximum value of the signal is achieved at own pH of ME3 (4.2) and with cooling of the solution (however in this case the intensity of the fluorescence increased only by 2%, that was at the level of an error for the fluorimeter (Fig. 3).

Thus, it was expedient to use ME based on CTAB and heptane at room temperature and the own pH of ME3 (4.2) for the extraction of PAHs.

Decomposition of ME

Microemulsions possess high solubilization ability and can dissolve otherwise immiscible compounds (Fig. 4). Due to its hydrophobicity, PAHs migrate into the organic phase after the decomposition of ME and pre-concentrate because of the volume reduction of organic phase [3]. Salts of strong electrolytes are widely used for the decomposition of MEs.

In current work, various amounts of sodium sulfate were mixed with ME3. The degree of pre-concentration and the volume of organic phase depends on the amount of added electrolyte. The decomposition of system (Fig. 5) started from 6-fold excess of Na_2SO_4 (0.54 M) over the concentration of CTAB, however, the pre-concentration ratio of dissolved substances was not higher than 2 because of big volume of the organic phase. When the concentration of salt was 20 times higher than CTAB (2.26 M), the pre-concentration ratio was bigger in accordance with 15-fold excess, but the difference was not significant. The optimum results were obtained at 15-fold excess (1.81 M) of dry sodium sulfate (the ratio of pre-concentration of PAHs increases up to 5-10 times).

Due to high hydrophobicity (log $P \geq 3.33$, Table 1), all 16 PAHs pre-concentrated in the organic phase after the phase separation. The pre-concentration rate was calculated as the ratio of the peak area, obtained in the analysis of the organic phase formed after separation of microemulsion, to the peak area obtained without separation of microemulsion. The pre-concentration ratios are in the range of 5–10 and are independent of log *P*. The results are in good agreement with the theoretical data calculated as the ratio of the volume of microemulsion before separation to the volume of the organic layer formed after the separation.

Further the model mixture of 16 priority PAHs were analyzed by HPLC with fluorometric detection (Fig. 6, red line). The results showed that microemulsion composed of 3.3% CTAB, 0.8% heptane, 8% n-butanol and 87.9% water was a good extractant for all 16 considered PAHs (considering that acenaphthylene does not fluorescence).

The technique was applied in the study of the real objects (oil and oil cores) (Fig. 6 and Fig. 7 - blue line). The main parameters of proposed method are shown in Table 2. Oil cores used in current work were characterized by high concentration of organic matter, wide range in total organic carbon concentrations (1.8 - 21.5%) and different sampling depth. In the group composition resinous-asphaltene compounds predominate, the content of free hydrocarbons was relatively low (about 9 kg per ton of rock or 3% per organic matter).

As seen in Fig.6 and Fig.7 not all components were determined by HPLC method with fluorometric detection in real samples. Only 5 of 16 PAHs (anthracene, pyrene, chrysene, benzo(k)fluoranthene, benzo(a)pyrene) were detected by current technique (Table 3). The determination of components was performed by using standard mixture of 16 PAHs, however shift of retention time of 5 detected PAHs is observed in real samples (Fig. 6). Therefore, an additional identification was performed by standard addition method (Fig. 7, red line). Other investigated PAHs seem to be undetectable by following method due to their low concentration in oil cores or absent.

Two-dimensional spectrofluorimetry

Excitation-emission spectrofluorimetry can be an alternative method for qualification of polycyclic aromatic hydrocarbons. Obtained two-dimensional spectra (so-called contour maps of fluorescence) resemble fingerprints, these spectra are individual for each compound and can be used for the identification of organic compounds.

The characteristic correlation obtained from the priority PAHs dissolved in acetonitrile are presented in Fig. 8 in the range of excitation wavelength from 240 to 440 nm in 7 nm step and emission wavelength from 350 to 550 nm in 1 nm step. The registration of these data allowed to evaluate the presence of PAH in real oil samples.

The two-dimensional spectrum is a set of horizontal sections of the corresponding three-dimensional spectrum (Fig. 9). The region with excitation wavelength from 290 to 410 nm and emission wavelength from 380 to 460 nm corresponds to priority PAHs. In this range, 6 most intensive peaks are distinguished from 2.5×10^6 a.u. to 6.4×10^6 a.u. (Table 4).

In Fig. 10 the contour map of the maltenes obtained after the separation of the real object from asphaltenes and resins (by adding a 40-fold excess of hexane, settling in a dark place within 24 hours and filtering) is presented. The final fraction (maltenes) was dissolved in n-hexane. As a result, a broad intensive peak corresponding to the determined components and several isoenergetic curves with equal excitation and emission wavelengths which belong to Rayleigh scattering were formed on the spectrum. The coordinates of the main peak (precisely, its most intensive part - yellow and red) are located in the same range as the PAHs region.

In the spectrum of maltenes concentrated in the organic layer after the destruction of microemulsion (Fig. 11), an increase in the intensity of the peak of target components is observed by a factor of 1.5 (from 0.84×10^6 a.u. to 1.28×10^6 a.u.), while its coordinates are in the PAHs area. It proves the effectiveness of the ME application for selective magnification of the intensity of aromatic compounds in the presence of interfering components, namely saturated hydrocarbons.

4. Conclusion

A simple screening method for the elicitation of PAHs in oil and oil cores is proposed. It consists of extraction, pre-concentration of PAHs by microemulsion (3.3% CTAB, 0.8% heptane, 8% n-butanol and 87.9% water) and qualification by HPLC coupled with fluorometric detection/two-dimensional spectrofluorimetry. Following technique is characterized by high concentration factor (5-10) and can be used in quantitative determination using standard addition method, however, by virtue of nonrepeatable background of complex matrix it is recommended to conduct additional sample preparation to reduce effect of matrix. Further, oil and oil cores can be separated from asphaltenes, divided into saturated/aromatic fractions and analyzed by HPLC-FLD.

Acknowledgements: The research was funded by Russian Science Foundation (RSF) grant № 16-13-10079.

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Table 1. 16 priority PAHs used in current work

Symbol	**PAH**	**log *P*** [21, 22]	**Pre-concentration ratio**
1	Naphthalene	3.33	7
2	2-Methylnaphthalene	3.83	5
3	Acenaphthylene	3.7	-
4	Acenaphthene	3.92	5
5	Fluorene	4.18	10
6	Anthracene	4.45	5
7	Phenanthrene	4.46	5
8	Pyrene	4.88	5
9	Fluoranthene	5.16	6
10	Chrysene	5.73	5
11	Benzo(a)anthracene	5.76	5
12	Benzo(k)fluoranthene	6.11	5
13	Benzo(b)fluoranthene	5.78	5
14	Benzo(a)pyrene	6.13	5
15	Benzo(g,h,i)perylene	6.63	6
16	Dibenzo(a,h)anthracene	6.50	10

Table 2. The parameters of calibration dependence

Compound	**Linearity, µg·kg^{-1}**	**Calibration curve**	**R^2**	**LOD, µg·kg^{-1}**
Anthracene (A)	30-250	y=33.6x+3.5	0.995	12
Pyrene (B)	40-400	y=25.4x+4.6	0.996	20
Chrysene (C)	120-2500	y=6.1x+0.7	0.994	50
Benzo(k)fluoranthene (D)	30-250	y=37.6x+3.3	0.995	10
Benzo(a)pyrene (E)	100-2500	y=9.6x+0.8	0.993	35

Table 3. The content of PAHs in oil core sample

Compound	**Mean, µg·kg^{-1}**	**SD %(n=5)**
Anthracene (A)	75±5	5.2
Pyrene (B)	64±6	6.4
Chrysene (C)	130±15	13.1
Benzo(k)fluoranthene (D)	45±5	8.4
Benzo(a)pyrene (E)	105±12	9.6

Table 4. The coordinates of the characteristic peaks in Fig. 9

Excitation, nm	**Emission, nm**	**Fluorescence intensity, a.u.**
370	395	6.43×10^6
391	403	6.11×10^6
390	425	5.68×10^6
372	420	4.92×10^6
298	400	3.25×10^6
297	422	2.51×10^6

Captions to figures

Fig. 1 The comparison of the intensity of PAHs fluorescence in microemulsions of different composition .The intensity of fluorescence in benzene was accepted as 1

Fig. 2 The comparison of the intensity of PAHs fluorescence in microemulsions with and without the additive of cyclodextrin

Fig. 3 The dependence of the intensity of PAHs fluorescence from temperature

Fig. 4 The pattern of the extraction in microemulsion medium: A—the solubilization of hydrophobic compounds in a microemulsion drop and hydrophilic compound—in a water phase; B—the formation of two immiscible phases after the decomposition of ME and pre-concentration of target compounds due to the volume reduction of organic phase

Fig. 5 The decomposition of ME. Concentration of salt, M : 1 – 0.18, 2 – 0.36, 3 – 0.54, 4 – 0.72, 5 – 0.91, 6 – 1.36, 7 – 1.81, 8 – 2.26

Fig. 6 Overlay of chromatograms of oil core sample (blue) and standard 16 priority PAHs (red, c = 2 μg/ml before separation; peak numbers correspond to symbols of PAHs in Table 1) in microemulsion in organic layer (oil) formed after the decomposition of microemulsion. 6, A – anthracene; 8, B – pyrene; 10, C – chrysene; 12, D - benzo(k)fluoranthene; 14, E – benzo(a)pyrene. HPLC-FLD method. Column Eclipse PAH (Agilent, USA, 4.6 x 250 mm, 5 μm), column temperature: 30 °C, λ_{ex}=235 nm, λ_{em}=400 nm, injection solvent: organic layer of ME, injection volume: 10 μL, mobile phase: acetonitrile – water, gradient elution, flow rate 1 mL/min

Fig. 7 Overlay of chromatograms of oil core sample (blue) and oil core sample with additives of 5 PAHs (red). . 6, A – anthracene; 8, B – pyrene; 10, C – chrysene; 12, D - benzo(k)fluoranthene; 14, E – benzo(a)pyrene. HPLC-FLD method. Column Eclipse PAH (Agilent, USA, 4.6 x 250 mm, 5 μm), column temperature: 30 °C, λ_{ex}=235 nm, λ_{em}=400 nm, injection solvent: organic layer of ME, injection volume: 10 μL, mobile phase: acetonitrile – water, gradient elution, flow rate 1 mL/min

Fig. 8 The fluorescence spectrum of the standard solution of 16 PAHs in acetonitrile (contour map of excitation spectra-fluorescence, c = 2 μg/ml)

Fig. 9 The three-dimensional spectrum of a standard solution of 16 PAHs dissolved in acetonitrile (in the isometric projection)

Fig. 10 Two-dimensional fluorescence spectrum of maltenes dissolved in hexane (0.1 g of fraction in 5 mL of solvent)

Fig. 11 Two-dimensional fluorescence spectrum of maltens in the organic layer of ME (0.1 g of fraction in 5 mL of solvent)

Figures

Fig. 1

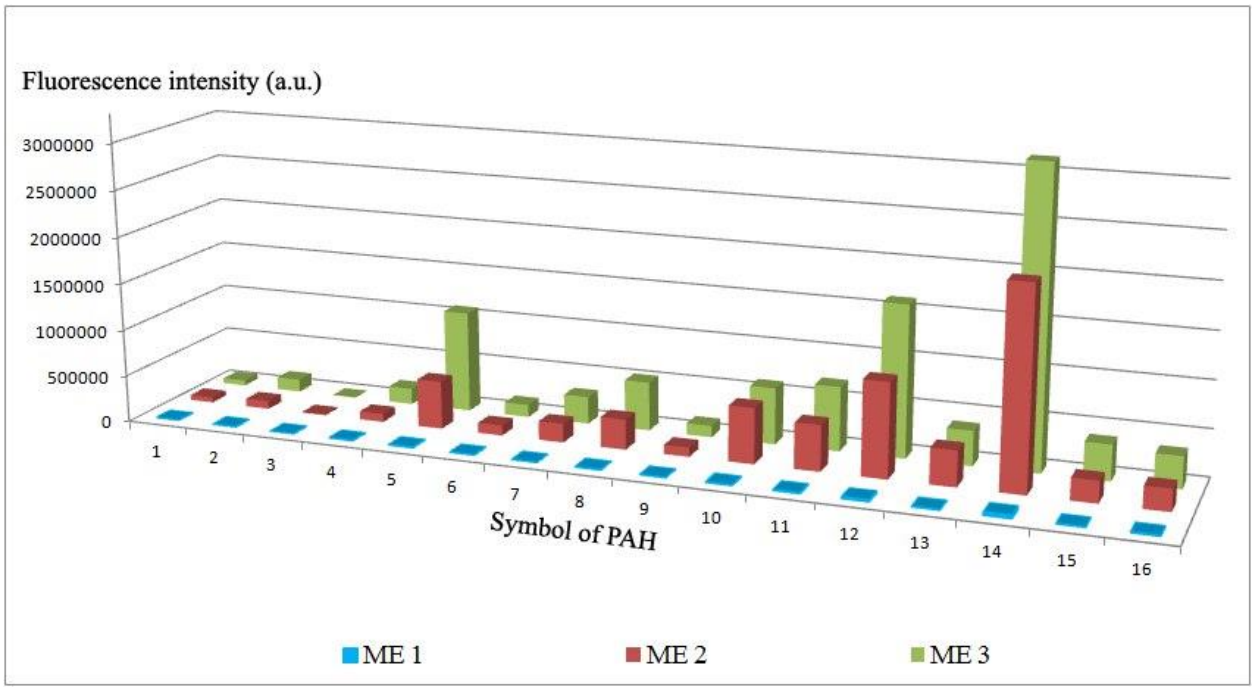

Fig. 2

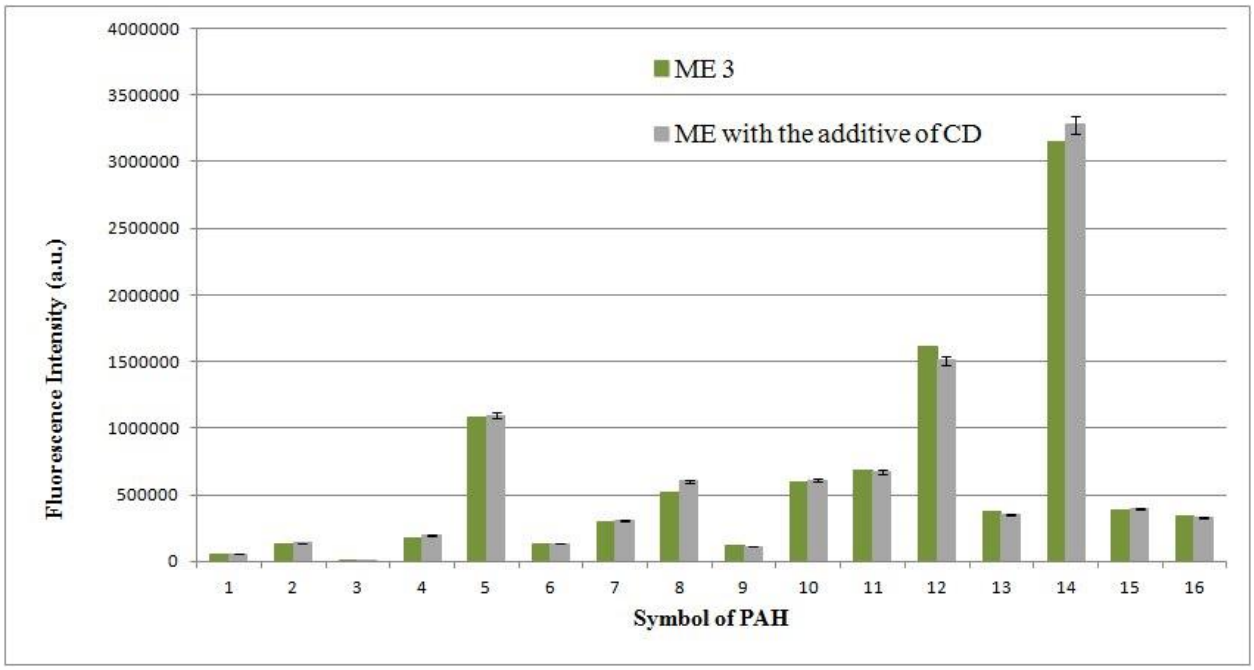

Fig. 3

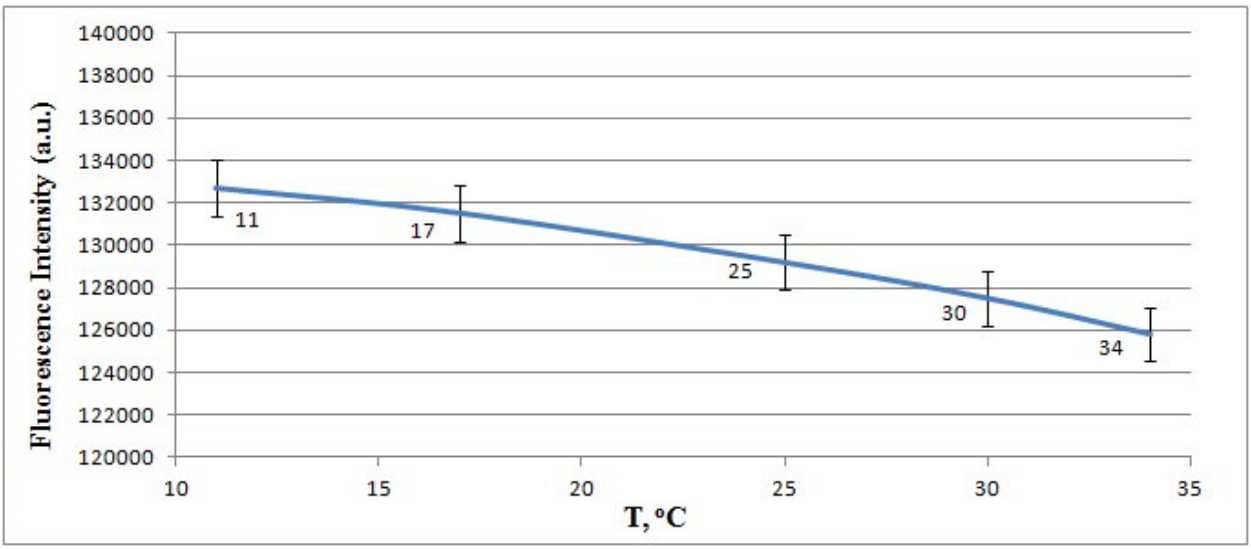

Fig. 4

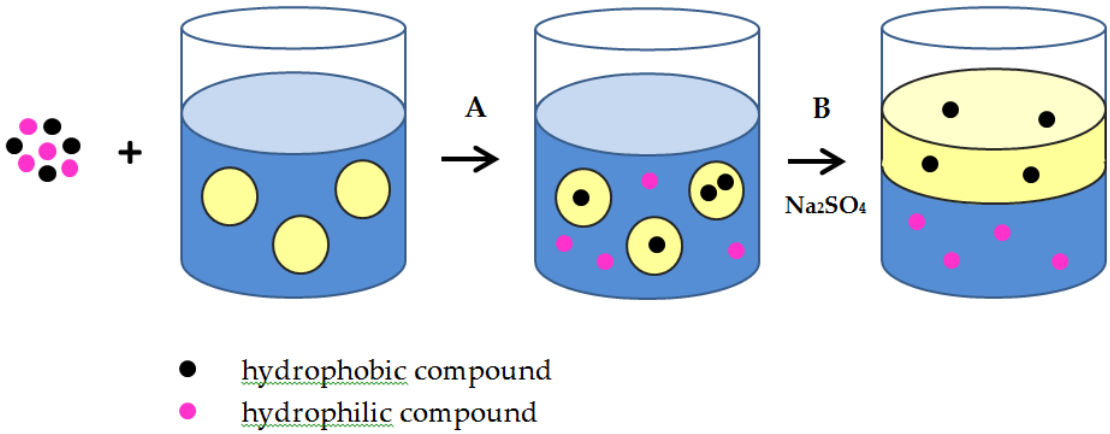

Fig. 5

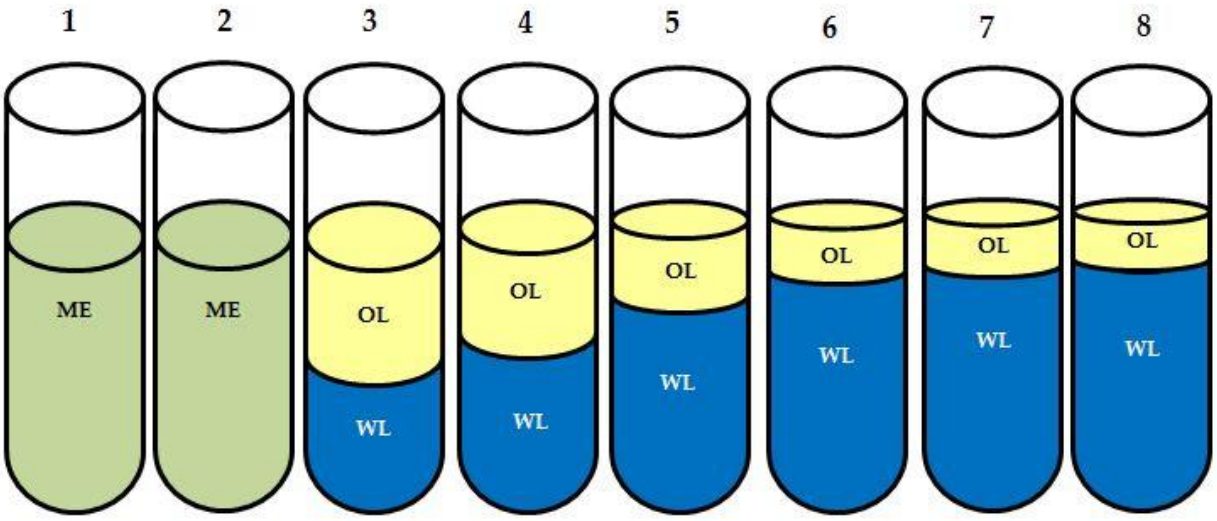

Fig. 6

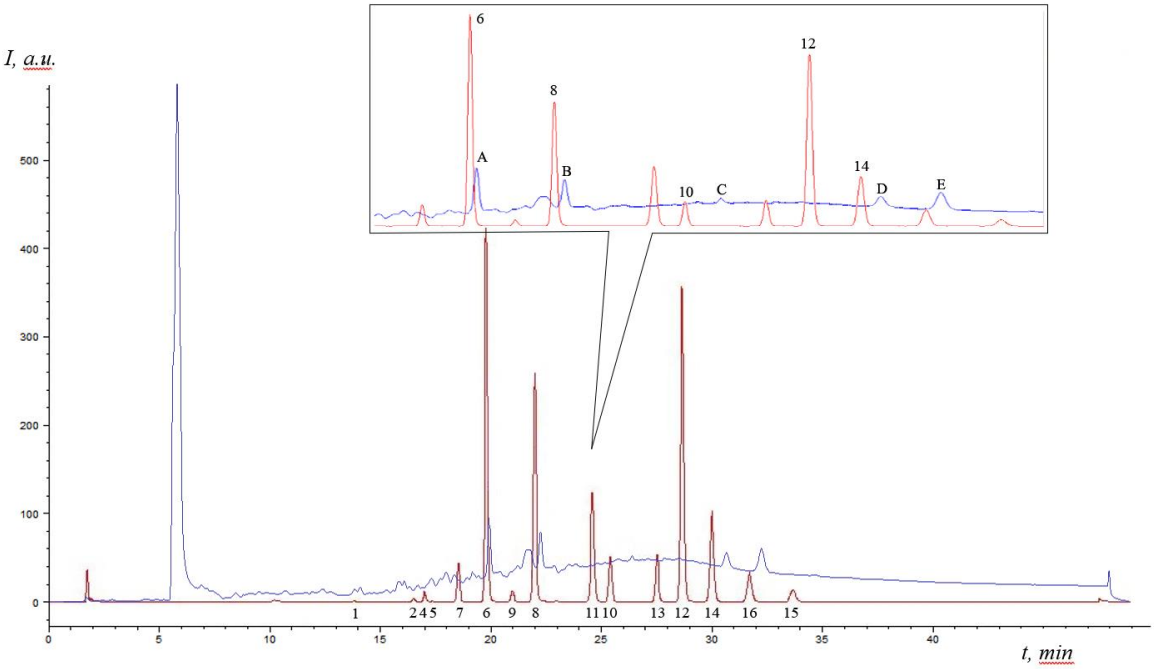
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Fig. 7

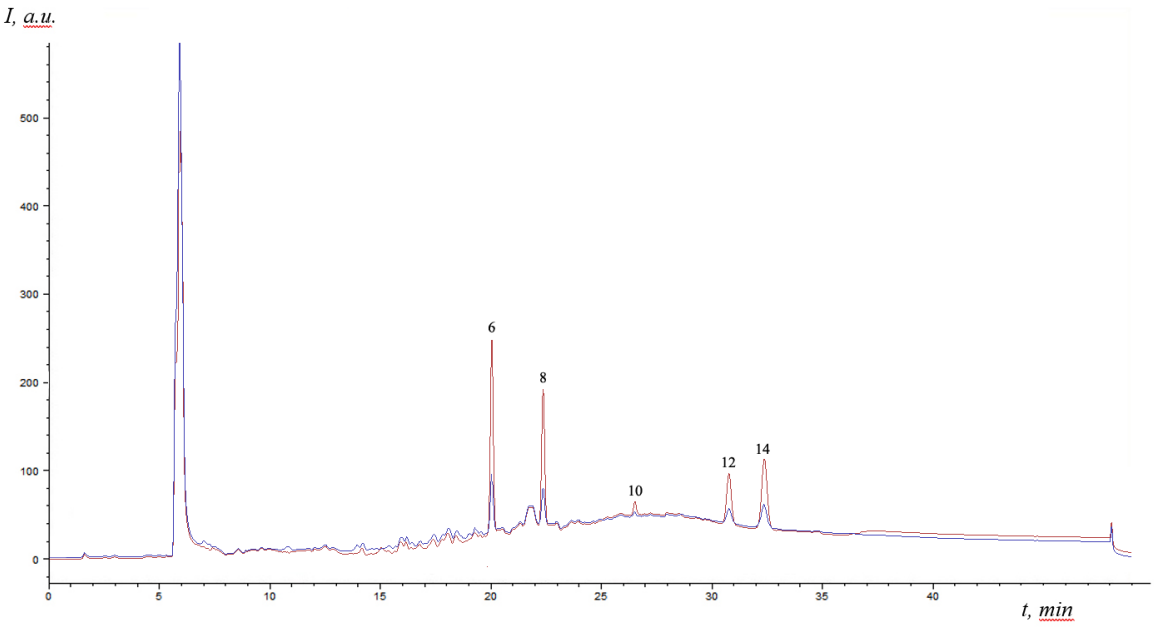

I, a.u.
t, min
6
8
10
12
14

Fig. 8

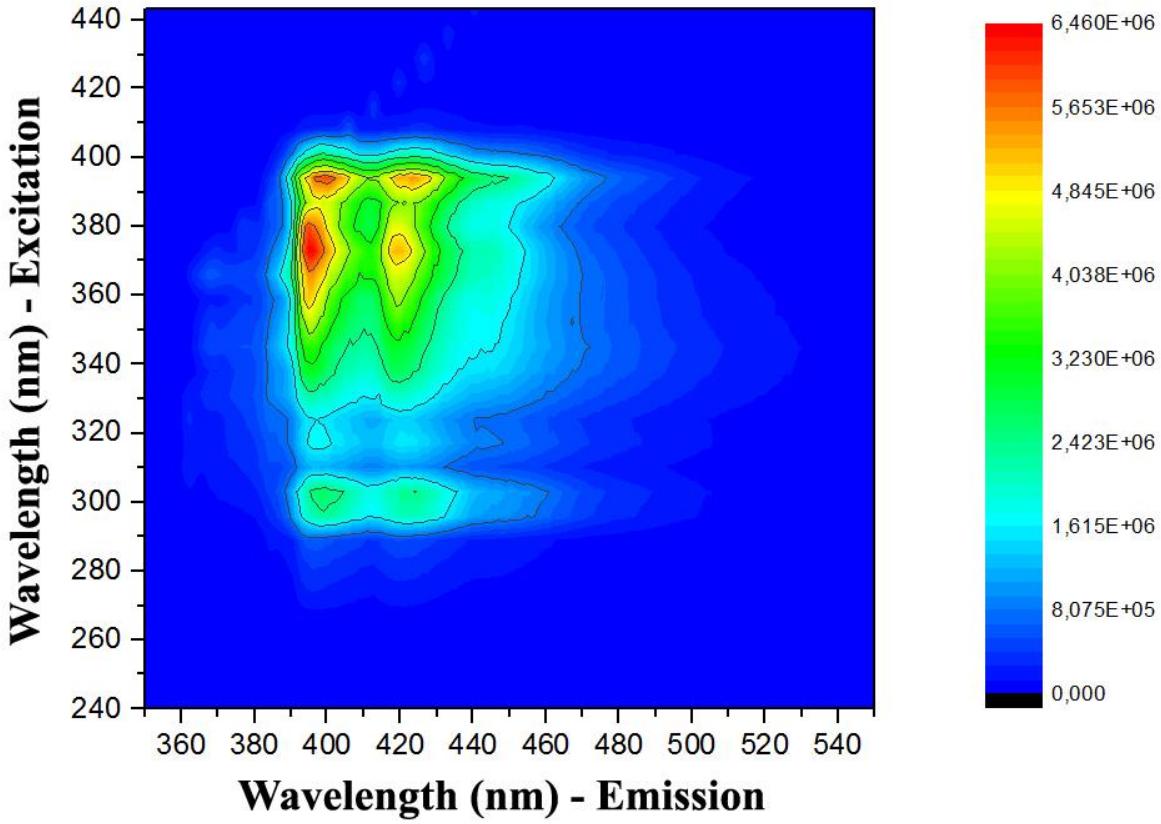

Wavelength (nm) - Excitation
440
420
400
380
360
340
320
300
280
260
240
360 380 400 420 440 460 480 500 520 540
Wavelength (nm) - Emission
6,460E+06
5,653E+06
4,845E+06
4,038E+06
3,230E+06
2,423E+06
1,615E+06
8,075E+05
0,000

Fig. 9

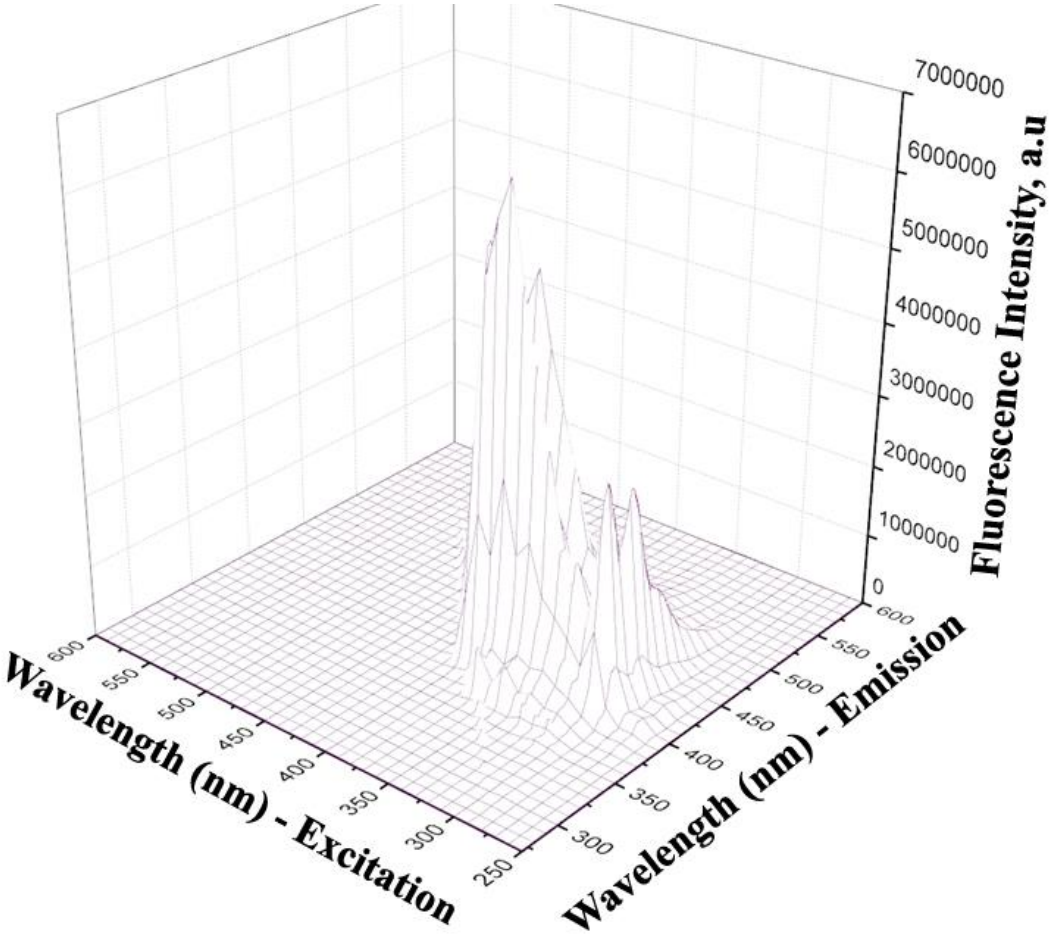

7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
Fluorescence Intensity, a.u
600
550
500
450
400
350
300
250
Wavelength (nm) - Excitation
600
550
500
450
400
350
300
Wavelength (nm) - Emission

Fig. 10

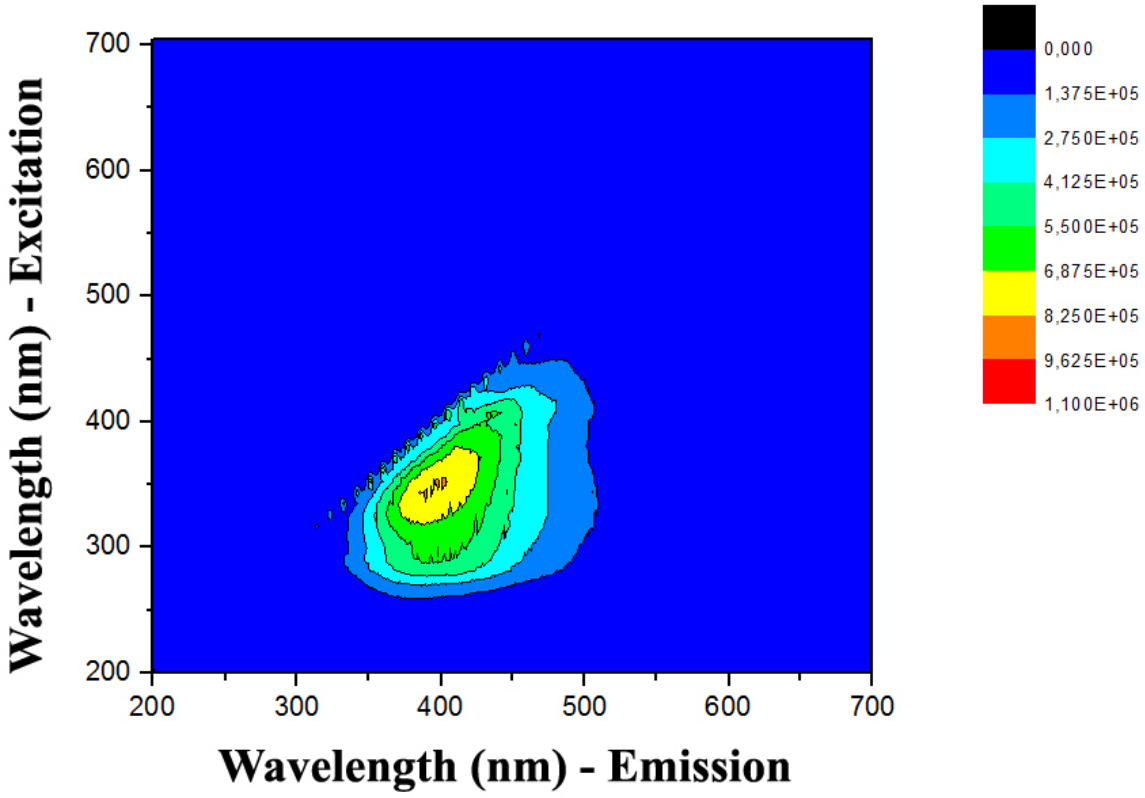
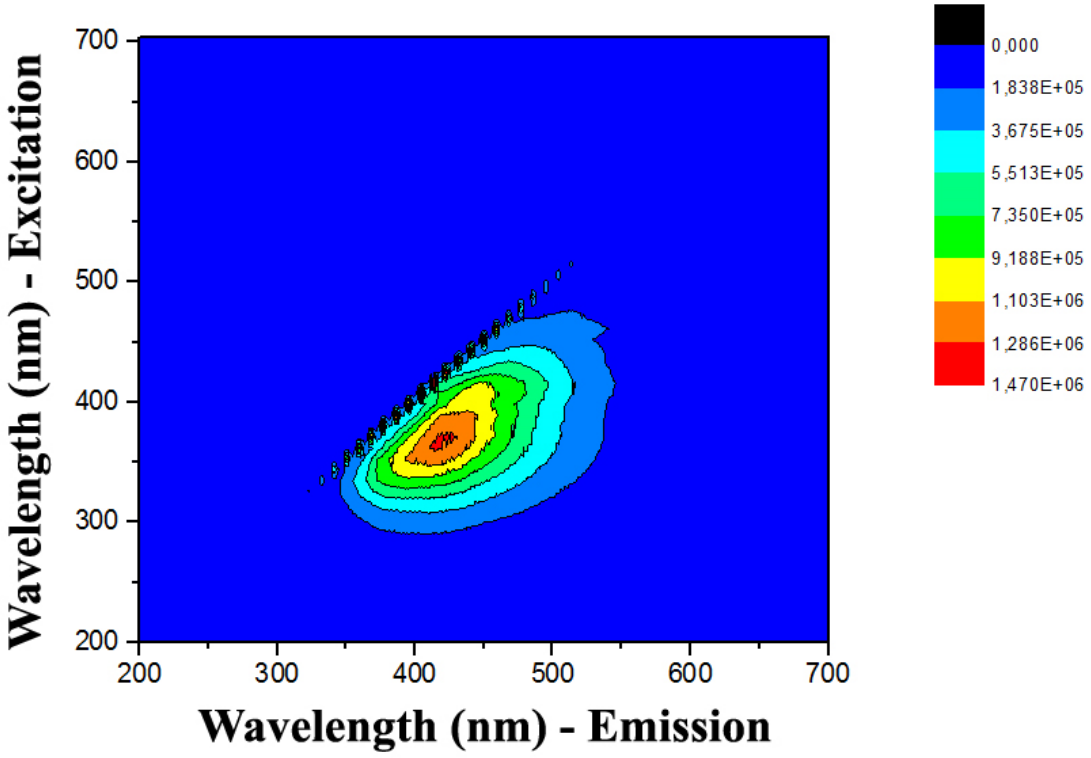

Wavelength (nm) - Excitation
700
600
500
400
300
200
200
300
400
500
600
700
Wavelength (nm) - Emission
0,000
1,375E+05
2,750E+05
4,125E+05
5,500E+05
6,875E+05
8,250E+05
9,625E+05
1,100E+06

Fig. 11


Wavelength (nm) - Excitation
700
600
500
400
300
200
200
300
400
500
600
700
Wavelength (nm) - Emission
0,000
1,838E+05
3,675E+05
5,513E+05
7,350E+05
9,188E+05
1,103E+06
1,286E+06
1,470E+06