

# Luminescence of Quantum Dots and their Use as an Optical Sensor for the Determination of Sulfur-Containing Impurities in Hydrocarbon Mixtures and Oils

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## Abstract

The study examines the possibility of developing an optic luminescence sensor with a transducer based on semiconducting colloidal material CdSe/CdS/ZnS (quantum dots) for operational analysis of several sulfur-containing impurities in hydrocarbon mixtures that are products of refining sulfur-containing oil samples. The effect of a strong drop in the intensity of quantum dot emission by sulfur-containing impurities in oil samples is established. Possible causes of this phenomenon are discussed. Quantum dots with a semiconductor (and dielectric) shell with luminescence in the 580-650 nm range are synthesized. Their surface is modified with organosilanes and fluorine-containing polymers, providing high photostability, high colloidal compatibility with mixtures of hydrocarbons of different natures, and a quantum yield of 80-90%. To construct the sensor sensing element, semiconductor colloidal material is embedded in a porous matrix of fluorine-containing F-42 copolymer. The paper reports the results of examining the effects of quenching and flare-up of luminescence in the process of interaction with sulfur-containing impurities in mixtures of hydrocarbons and oil samples. The sensitivity of the method is estimated and found to amount to  $10^{-3}$ - $10^{-5}$  mg/kg.

## Keywords:

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## 1. Introduction

The presence of sulfur-containing compounds is one of the basic factors determining the quality of extracted oil raw materials. Such impurities include elemental sulfur, hydrogen sulfide (H<sub>2</sub>S), thiols (R-SH), sulfides (R'-S-R), disulfides (R'-S-S-R), thiophene derivatives (C<sub>4</sub>H<sub>4</sub>S), acids, sulfuric acid esters, sulfonic acids, high-molecular sulfur compounds, as well as complex sulfur compounds containing oxygen, nitrogen, etc. By now, several analytical methods to determine such impurities in hydrocarbon mixtures and oil samples have been developed. In this respect, these methods require complex and expensive equipment and labor-intensive techniques. The preparation of samples is long and laborious and uses large amounts of reagents, glassware, and sophisticated analytical instruments. The most common methods as of now are those relying on gas chromatography [1] and infrared spectrometry [2], oxidative combustion and electrochemical detection, methods based on X-ray fluorescence spectroscopy [3, 4], ionometric methods [5] atomic emission methods [6], and some other methods.

Importantly, from the point of modern trends in the development of organic chemistry, these methods have several principal flaws. They require rather long and labor-intensive preparation of samples and large amounts of reagents, glassware, and sophisticated analytical instruments, which is only possible in laboratory conditions. Thus, preparation of the required solutions and other analytical procedures take a long time, making these methods unsuitable for real-time monitoring.

A promising method for detecting small amounts of sulfur compounds in the systems of interest to us is laser-induced fluorescence. In the considered system, luminescence turns out to be sensitive to interfacial processes on the surface of quantum dots, associated with the adsorption of an entire range of compounds [7-11]. Furthermore, the efficiency of luminescence quenching by sulfur-containing compounds is rather high and can serve as a basis for the transducer action of sensor devices.

## 2. Methods

In this study, we used semiconductor phosphors based on CdSe/CdS/ZnS type compounds (quantum dots) specially obtained by colloidal synthesis. Quantum dot nuclei were synthesized by hot injection of organometallic precursors in alkylphosphine (particularly trioctylphosphine) medium. Dimethyl or cadmium stearate in octadecene solution were used as precursors. To increase the quantum yield of luminescence, we employed the method of epitaxial deposition of CdSe/ZnS semiconductor shell after isolation of CdSe nuclei. The separation of nuclei was carried out by precipitation with methanol followed by centrifugation and dispersion in hexane. Exciton absorption peak maximum [12]. To increase the stability of quantum dots and quantum yield, CdSe nuclei are covered with a ZnS shell. The build-up of the semiconductor shell was accomplished by the following technique. The container with trioctylphosphine oxide (TOPO) and hexylphosphonic acid was degassed at 180°C. Next, a dispersion of the nuclei synthesized in octadecene was added and then converted to hexane, after which the hexane was vaporized at 80°C. The vessel was then placed in an argon atmosphere at 80°C and stirred for two hours after the addition of decylamine. The vessel was heated to 160°C and solutions of diethylzinc and dimethylcadmium in trioctylphosphine (TOR) and hexamethyldisilyl were added by injection at a low rate of 2 mL/hour for 2 hours. The vessel was then cooled to 80°C and stirred overnight for surface annealing. CdSe/ZnS quantum dots were deposited twice as described above, redispersed in toluene or hexane, and filtered through a 0.2 µm microfilter. Thus, quantum dots with an emission maximum at 635 nm and a quantum yield of 85% measured from rhodamine (610 nm) in methanol were obtained.

Further, to make the sensing element, the synthesized quantum dots were embedded in a porous film based on a fluorine-containing copolymer of ethylene with tetrafluoroethylene (F-42). F-42 is a statistical copolymer (60:40) of tetrafluoroethylene and vinylidene fluoride. First, a 5% solution of the copolymer in tetrahydrofuran was prepared. Then quantum dots were introduced into the solution at the rate of 3 mg/L. After that, isopropanol (as a precipitant) was added to the solution until the onset of precipitation, and then film casting by evaporation on the glass surface was carried out. The obtained 1 mm thick microporous films were subsequently used as a sensitive element of the sensor. The nature of the porosity of the sensing layer was not studied. Preliminary studies demonstrated high stability, both colloidal and photostability, of quantum dots in the matrix of the above fluorine-containing copolymer. It can be assumed that the modification leads to effective passivation of surface electronic states, while neither water nor other polar solvents have a noticeable effect on the character of luminescence. Mercaptopropionic acid was also used to stabilize the surface. Measurements were carried out in a specially designed box allowing measurements in both gas and liquid hydrocarbon media containing sulfur impurities. The design of the box (in the laboratory version) is provided in Fig. 1. The box contains a chamber for the introduction of analyte vapors (1), a cuvette for placing the sensing element (2), and valves for vapor injection (3). An LED with a wavelength of 395 nm was used as a source of excitation radiation. The receiver of the emitted radiation was the entrance face of the light guide [6] connected to a computer-controlled FLAME-S-UV-VIS

spectrometer unit [7]. Measurements were performed in the "0/45" geometry, in which the effective axis of irradiation does not exceed the angle of 10° relative to the normal to the sample surface [13]. The luminescence spectrum of the described sensing element is given in Fig. 2. Here, peak [1] represents the diffusely scattered flux of excitation radiation with a wavelength of 395 nm. Peak [2] with a maximum of 633 nm represents the emission of quantum dots. The observed kinetics of change in sensing element luminescence intensity are shown in Fig. 3. The box shown in Fig. 1 was used for measurements in the liquid phase. In this case, a layer of the investigated solution was applied to the sensing element placed in a special cuvette.

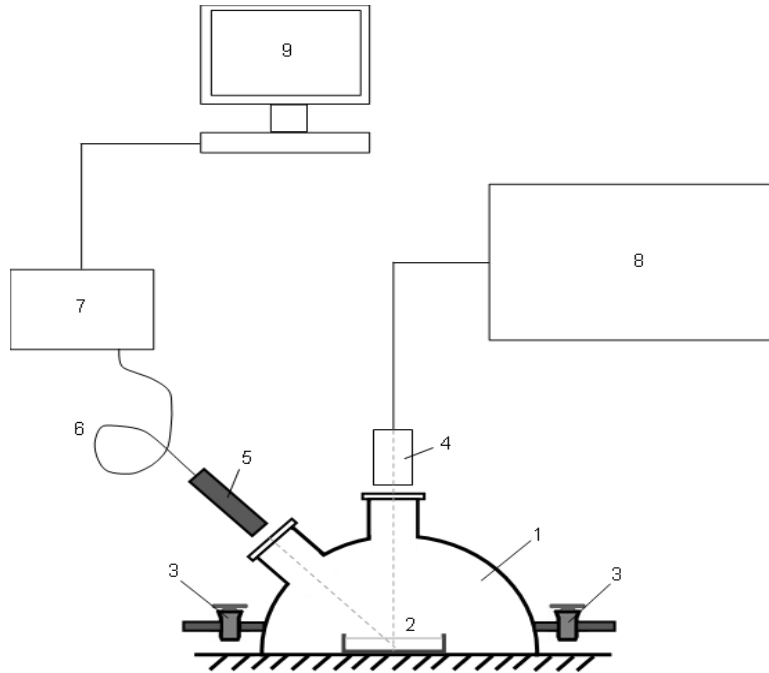
## 3. Results and discussion

The literature analysis and the studies carried out in the present work show that sulfur-containing impurities in liquid hydrocarbons are effective quenchers of luminescence of CdSe/CdS/ZnS-based quantum dots. The mechanism of this effect is rather complicated, but it can be assumed to be static in nature and not related to the common mechanisms of electronic excitation energy transfer such as Förster resonance energy transfer (FRET) or similar. FRET is a process that involves two fluorophores, a donor (D), and an acceptor (A) of transfer. In the process of this resonant energy transfer, the transfer occurs from one fluorophore to the other. The use of the Stern-Volmer representation for interpreting the experimental data on quenching made it possible to conclude that quenching by sulfur-containing impurities occurs by different mechanisms. If the effect of sulfur compounds is dynamic (collision), the quenching of the used nanocrystals is static. The most probable process here appears to be the adsorption of sulfur compounds on the surface of nanocrystals with the formation of non-luminescent complexes in the spectral range of 350-800 nm. Importantly, this circumstance is also associated with the fact that the change in the luminescence intensity of quantum dots is not accompanied by a change in the position of the luminescence peak maximum. This was observed in the work of Krause et al. [14], as well as in our studies. The desorption of sulfur-containing molecules from the surface of nanocrystals naturally leads to the restoration of emission intensity. The curves of luminescence intensity changes upon change of the concentration of some sulfur-containing impurities in samples of high-boiling hydrocarbon mixtures were approximated in the coordinates of the Stern-Volmer equation [15],

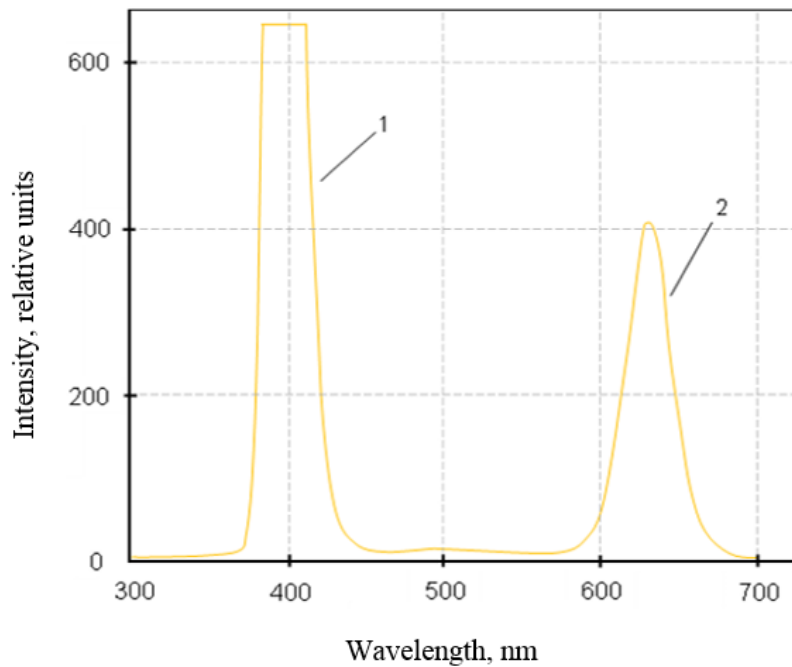
$$\frac{A}{A_0} = 1 + k_s [Q]$$

Herein, A – luminescence intensity in the absence of the component to be determined, A0 – in its presence, ks – quenching constant, Q – quencher concentration. The approximation results shown in Fig. 5 allowed us to estimate the detection limit of the studied impurities, which amounted to about 3·10<sup>-4</sup> mg/kg, as well as the root-mean-square error, which reached 10<sup>-4</sup> mg/kg. The dynamic range of measurement in the area of impurity concentrations from 30 µg/L to 40 mg/L is at least 70 dB. These values are on the order of magnitude corresponding to expensive instrumental methods of determination, in particular, spectral and X-ray fluorescence methods.

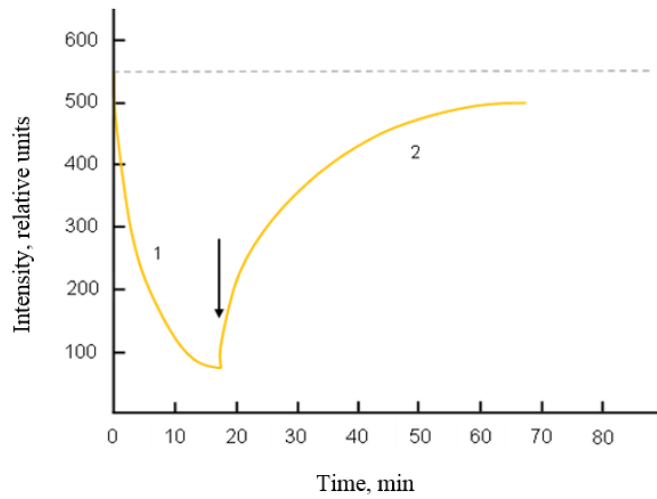
**Table 1:** Sports infrastructure statistics for the Rabat-Salé-Kénitra Region [9]



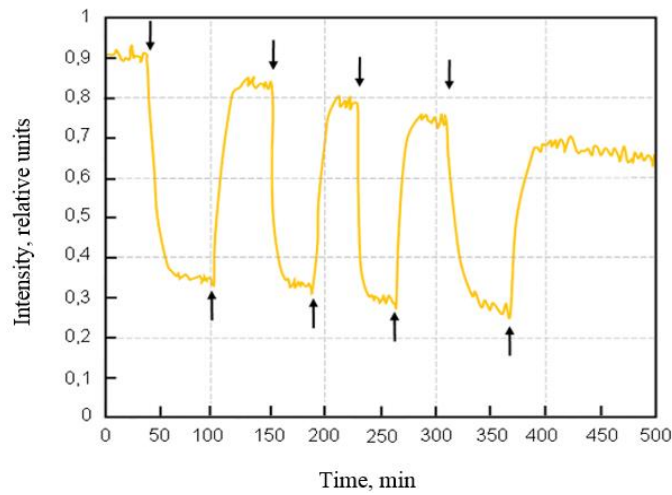
**Figure 1.** Box of the device for testing the sensor with a quantum dot-based sensing element. 1 – vessel for creating a gaseous medium, 2 – cuvette for placing the sensing element in the liquid sample, 3 – vapor injection valves, 4 – excitation radiation source, 5 – luminescence receiver, 6 – light guide, 7 – FLAME-S-UV-VIS spectrometer unit, 8 – radiation source power supply unit, 9 – computer



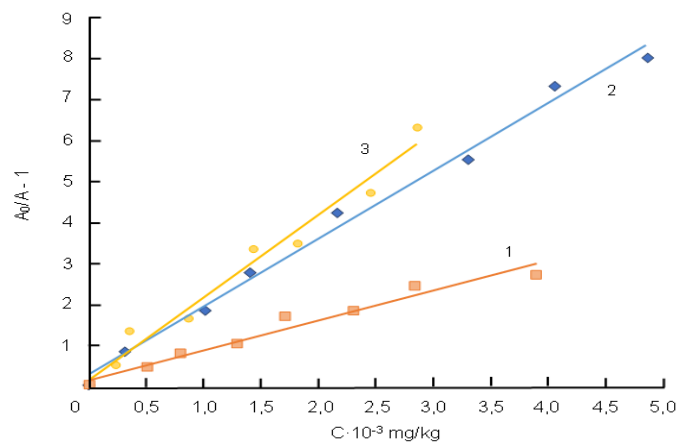
**Figure 2.** Excitation light spectrum (1) and radiation of the sensitive element (2) containing used synthesized CdSe/CdS/ZnS quantum dots in a porous matrix of fluorine-containing polymer



**Figure 3.** Kinetics of luminescence quenching of the sensing element (section 1) when the sample is introduced into the box and its ignition upon removal



**Figure 4.** Kinetics of change in the intensity of the sensitive layer luminescence at the periodic introduction of the sample into the box. The arrow pointing downwards marks the moment of injection, upwards – removal of the sample from the cell and its replacement with pure solvent. The concentration of sulfur-containing impurities is  $10^{-4}$  mg/kg



**Figure 5.** Light intensity dependences in coordinates of the Stern-Volmer equation for ethylmercaptan (1), disulfide (2), and thiophane (3) samples in a mixture of high-boiling hydrocarbons

#### 4. Conclusions

The present study is the first to propose a method of detecting sulfur-containing compounds in hydrocarbon mixtures and in oils based on changes in the intensity of quantum dot emission. At its rather high sensitivity, in comparison with existing methods, this method is much simpler in terms of instrumentation and measurement control and allows to effectively carry out measurements in real time.

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