Luminescent control of polycyclic aromatic hydrocarbons content in water systems

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Abstract. To control the content of polycyclic aromatic hydrocarbons in aqueous media and to ensure effective sewage treatment of natural contaminated waters, a luminescent solid-substrate method was applied. This method permits combining the preceding sorption concentration of substances on a cellulose matrix, modified with a surfactant, and analyzing directly in the solid phase of the sorbent. Optimal characteristics of luminescent control of ecotoxicant content before and after water purification were determined.

Introduction
Providing the required quality of drinking water as well as water for residential use, and compliance with sanitary and environmental quality standards for wastewaters requires monitoring and quality control of water both in water supply sources and at wastewater treatment facilities. Increasing the monitoring quality of water bodies for maintaining proper levels of public health is facilitated by creating new effective technologies for water quality control.

The article is devoted to the problems of water purification and to development of novel technologies for water quality control. Pollution adversely affects the natural sources of fresh water, which in turn has a negative impact on human health. It is crucial to identify the composition of all pollutants in the water body, which is not possible without using innovative methods for water quality monitoring.

The choice of cleaning method and water quality control requires conducting water analyses. The required stage of water analysis includes determination concentrations of particularly dangerous highly toxic substances, which can potentially cause considerable damage to human health. PAHs occupy one of the leading positions in the list of priority pollutants. Control of PAHs content in various environmental objects is mandatory. Most PAHs are carcinogenic and mutagenic substances that can accumulate in the organisms and pose a hazard even at trace concentrations in the environment [1-2]. Standard procedures for determination of PAHs in environmental objects are based mainly on chromatographic methods with various detectors [3-4]. Although the analytical effectiveness of these methods is widely recognized, the PAHs analysis in this case is characterized as laborious, relatively expensive and time-consuming process. For these reasons, it is of great interest to develop simpler and more sensitive methods for the detection and determination of PAHs. Luminescent methods are especially prospective for these purposes [5].

The goal of this study involved development of new technologies for adsorption water treatment from complex composition based on the use of modified bentonites.
Methods for Water Quality Control

We selected the luminescent assay as priority pollution control technique for ecotoxicants in the water. Luminescent methods have a number of advantages for determining the PAHs in aqueous media. First, many of the PAHs representatives are capable of fluorescing, and therefore the use of luminescent methods allows obtaining the best results of the analysis. Secondly, it is well known that these methods are among the most sensitive methods of analysis, which is especially important for identifying trace concentrations of substances in environmental objects.

However, it should be taken into account that the luminescence specters of the solutions of most organic substances are represented by broad, blurry bands. It is possible to simplify the identification of pollutants via significant narrowing of the spectrum bands, which can be achieved either by significant decrease in temperatures [6] or by using water-micellar solutions [7].

Another effective method for improving the characteristics of radiative processes in molecules is immobilization of a luminophore on a solid substrate [8-11]. This phenomenon is based on the method of solid-substrate luminescence (SSL), which enables combining preceding sorption concentrating and analysis of substances directly in the sorbent phase. Sorption of luminophores is carried out on various luminescent matrices, the most common of which is cellulose matrix [12-13]. It is well known that signal intensity of SSL luminophores on the cellulose matrix is dependent on the presence of various substances: alkalis, salts, and surfactants. They can significantly reduce or increase the intensity of luminescence. On the basis of luminescent methods, the development of sensors and screening systems for water quality control is conducted [10, 15-16].

Hence, we used the SSL method with analytical signal registration on modified cellulose matrix as the basis for original effective and highly sensitive technique of determining the PAHs.

We took Fluka-manufactured Purum brand pyrene, the least toxic PAHs, as a model compound for our experimental study. The fluorescence spectrum of pyrene was observed in the wavelength range 360-400 nm. As the matrix modifying agent, a cationic surfactant, cetyltrimethylammonium bromide (CTAB) was used. We used cellulose matrix of Red Tape brand for sorption concentrating (solid phase extraction) and applied luminescence research. Sorption of PAHs was carried out dynamically. With this goal in mind, the solution was filtered for 30 min through a sorbent layer in a plastic cartridge. Then the sorbent was dried for 15 minutes at a temperature of 80°C. PAHs luminescence spectra were recorded on a Perkin-Elmer fluorescence spectrometer LS 55.

Results of Studies on Luminescent Method of Water Quality Control

In the course of our experimental studies on the development of an effective method of water quality control for the content of ecotoxicants, we selected optimal characteristics of the luminescent determination of PAHs on a cellulose matrix.

We established that fluorescence intensity of pyrene, the PAHs representative, on the matrix is higher than in the aqueous solution, from which its sorption was conducted. We explain this finding by mobility loss of pyrene molecules during the sorption and by increase in the probability of radiative luminescent transitions (fluorescence) from the first singlet excited state to the ground state.

However, we discovered that an efficiency of sorption by a hydrophilic matrix of hydrophobic PAHs is not high enough. It can be increased by modifying the surface of the matrix with surfactants. It is known that water-micellar solutions in luminescent assay are widely used [7]. However, there are only a few studies, in which surfactants were used to observe luminescence on solid matrices [14]. We have experimentally confirmed that pyrene sorption from water-micellar solutions of surfactants, contributed to concentrating of PAHs in the surface layer of the sorbent. Such modification of the matrix surface allows improving analytical characteristics of the method.

It is known, that the sorption of cationic surfactants on the negatively charged matrix is more effective compared with anionic surfactants. Perhaps, that is due to the fact that cationic surfactants interact better with a hydrophilic matrix, the structure of which includes a hydroxyl group, -OH. We confirmed this hypothesis experimentally. Significant increase in pyrene fluorescence intensity with increasing concentration of the cationic surfactant in the solution is observed during the pyrene
sorption from aqueous cationic surfactant on cellulose matrix. It was established experimentally, that
the sorption of luminophore on a modified cellulose matrix could significantly increase fluorescence
signal intensity.

The fluorescence spectra of pyrene on a surfactant-modified cellulose matrix were analyzed. Linear
dependences of pyrene fluorescence intensity on surfactant concentrations in the solution were
constructed. It was found that maximum fluorescence signal of pyrene on a solid matrix was observed
at concentrations of the cationic surfactant CTAB near the critical concentration of micelle formation
\((9.5 \cdot 10^{-4} \text{ M})\).

Limit of pyrene fluorescent detection on the modified cellulose matrix is \(4.9 \text{ ng/ml}\), range of
detectable contents is \(10 - 200 \text{ ng/ml}\), relative standard deviation \(Sr = 0.04\).

However, pyrene phosphorescence was observed neither by using CTAB, nor in solution, nor on
the cellulose matrix. Phosphorescence allows analysing mixtures of PAHs with higher selectivity. The
maximums of phosphorescence spectra of individual PAHs are more spaced in wavelength than in the
fluorescence spectra.

Probably, the electrostatic repulsion of like-charged cations of heavy atoms, required to observe
PAHs phosphorescence and of cationic surfactants take place.

Therefore, in the case of observing phosphorescence, it is expedient to use sodium dodecyl sulfate
as concentrating and modifying agent.

**Effectiveness of using luminescent assay for PAH content control in aqueous media**

Sorption concentrating in combination with the measurement of an analytical signal on the surface
of a sorbent allows reducing the detection limit of polluting components by several orders of
magnitude. Using the sorbent modified with the surfactant allows increasing the effectiveness of
concentrating the pollutants on the sorbent and sensitivity of the method. It has been experimentally
established that the sorption of luminophores on a cellulose matrix modified by micellar nanosystems
causes a significant increase in fluorescence signal intensity. Optimal characteristics of a luminescent
solid-substrate method for controlling PAHs content in aqueous media are optimally chosen to ensure
purification and quality control of sewage or natural waters

However, it should be noted that it is necessary to take into account possible composition of
analyzed waters while using our original highly sensitive luminescent assay, because presence of
interfering components (for example, heavy metals) may affect the results of luminescence analysis. In
some cases of analyzing highly contaminated water, it is recommended to conduct a routine stage of
sample preparation, including preliminary separation of the components and cleaning of the sample.
Our future study will be devoted to the development of a solid-substrate luminescent method for
determination of heavy metals and their concentrations in polluted aqueous media.

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