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Trace Determination of Rhodamine and Eosine in Oil-water Reservoir Using Solid-phase Extraction

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Abstract. A method for the trace analysis of rhodamine and eosine with colorimetric measurements based on solid-phase extraction (SPE) by transparent polymethacrylate matrix (PMM) is described. Solid-phase extraction on PMM allowed a 380-fold enrichment of the dyes if 10 mL sample volume is used with extraction efficiencies 98%. The method enables the determination of rhodamine to 0.06 mg/L and eosine to 1.2 mg/L combined with a fast and easy sample-preparation (pH-adjusting prior to SPE). Simultaneous extraction and determination of rhodamine and eosine in reservoir samples with high salinity confirmed the applicability and reproducibility of the method. Batch adsorption results indicated that Langmuir isotherm described the adsorption isotherms better.

Introduction

Rhodamine and eosine are suitable water tracers in oil reservoirs, ground and soil water studies [1-3]. Currently this dyes are tested as indicators in leaching studies for carbon sequestration techniques. The main advantage of xanthene dyes are due to their similar chemical and physical behavior and their large number the possibility of conducting several simultaneous studies at the same reservoir or location without interference. Because of high dilution in large reservoirs and high cost for most of the tracers, enhancing their detection limits is still of great importance. Previously rhodamine and eosine have been analyzed using spectrophotometry [4, 5], HPLC-MS [6] and capillary electrophoresis [7]. Because of the high salinity and organic compounds in samples of oil reservoir studies, capillary electrophoresis and HPLC-UV are less suitable techniques for determination at trace level due to unwanted interferences in detection or separation [8]. Therefore not applicable for a selective solid phase extraction of xanthene dyes from highly saline reservoir samples. The detection limits of the method described in this paper enables the simultaneous detection of rhodamine and eosine used as water or water-oil tracers in large reservoirs.

Water-soluble dyes are characterized by their poor biodegradability, conventional treatment techniques such as flocculation, chemical oxidation, and membrane separation are not suitable. Nevertheless, adsorption is shown to be potentially powerful because of its imaginable opportunity to design the chemical composition of the adsorbent surface [9, 10]. In comparison with classical adsorbents such as activated carbon and silica, PMM is more attractive because of its favorable physicochemical stability, selectivity, and structural diversity [11, 12].

With regard to the adsorption of adsorbates on synthetic polymeric adsorbent PMM in water and water-oil solution, hydrophobic interaction is usually considered to be a dominant driving force. When the adsorbates are not easily water-soluble, the adsorption will be significantly reduced because of the polarity mismatching between the adsorbates and the polymeric matrix.

Experimental

Materials

The PMM is a specially created material containing functional groups which provide ability to extract both the reagent and determined substance. PMM in the form of transparent plate with surface 0.5 cm^2, thickness of (0.06÷0.08) cm and mass of 0.05 g was synthesized under laboratory conditions by radical block polymerization [13].

All reagents were of analytical grade and used as purchased without further purification. Deionized and distilled water was used in all experiments. The required pH was adjusted using acid (sulfuric acid, nitric acid, phosphoric acid) and sodium hydroxide. Colorimetric scale obtained using rhodamine and eosine certified reference material (Ecoanalitika Ltd.).

Procedure

Immobilization of analytical reagents into a polymeric matrix has been carried out in a static mode. PMM soaked in water or water-organic solutions of reagents. The quantity of sorbed PMM reagent is proportional to intensity of its painting and it depends on conditions of modification: pH, concentration of the reagent in solution and durations of processing.

The interactions of the immobilized in PMM reagents were studied by solid-phase spectrophotometry under batch conditions. For this purpose, reagent was put into 50.0 mL of an analyte solution of different concentrations and pH and stirred with PMM for 5–30 min. After that absorption spectra or absorbance of PMM was measured. Besides, visible color changes of PMM were estimated with digital imaging by means of a scanner. The PMM image was captured and transferred to a computer and the color was interpreted using imaging software where the colorimetric data in RGB format were related to the concentration of the dyes.

Equipment

The working curve of the spectra absorbency of the standard rhodamine and eosine solution with different known concentrations was firstly measured, and two well fitted regression equations, $A = 0.23C+0.04$ (for rhodamine) and $A = 0.07376C$ (for eosine), were achieved with the correlation coefficient R higher than 0.999 in diapason 0.05-50 mg/L . The absorbency of the rhodamine and eosine solution adsorbed by PMM was measured and the equilibrium concentration was calculated based on the working curves.

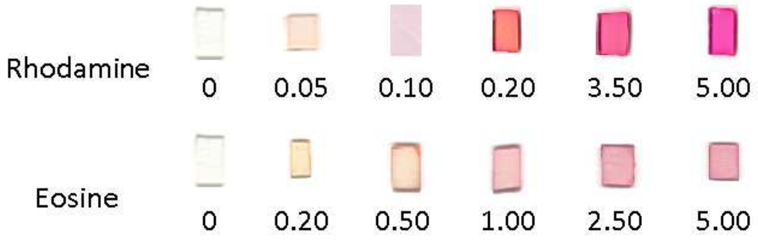

Fig. 1. Colorimertic scales, mg/L

Absorption spectra and absorbance of PMM matrix were recorded on Evolution 600 spectrophotometer (Thermo Fisher Scientific Inc., USA) against a polymer plate prepared under the same conditions, without reagents. Rhodamine or eosine concentration in aqueous solution was analyzed with the wavelength at 540 and 530 nm, respectively. The pH values were measured by I-160 ion meter (NPO "Izmeritelnaya tekhnika", Russia) with a glass pH-selective electrode.

Adsorption isotherms

The transparent plate 0.050 g of PMM were accurately weighed and introduced into a 20 mL of rhodamine and eosine aqueous solution with different initial concentrations. The initial concentration of rhodamine and eosine in aqueous solution was set to be about 0.05, 0.1, 0.5, 1.0, 2.0, 5.0, 10.0 and 50.0 mg/L. At first the pH of the sample was adjusted to 6.0 (in case of eosine to pH 1.5), then the flasks were shaken at a room temperature for about 30 min to ensure the adsorption to be in equilibrium. The equilibrium parameters were determined subsequently, and the equilibrium adsorption capacity.

Results and discussion

For separating analytes from interfering sample matrices and for simultaneous preconcentrating, solid-phase extraction is a well suited technique, especially when the analytes are contained in complex environments. For a successful enrichment of the rhodamine and eosine with a simultaneous separation from the sample matrix, choosing the right sorbent material is a very important step. The PMM is organic polymer, theoretically the protonated and the deprotonated molecules can be used for extraction. Nevertheless, the high content of inorganic ions in aqueous reservoir samples will overload any sorbent. However, the solid-phase extraction material shown by Gavrilenko [13] in 2004 will resist the high organic load solved in aqueous samples and still enrich the different adsorbates.

The microphotograph of PMM shown in Fig. 2. The BET specific surface area of PMM determined to be 8 m^2/g. Its average pore diameter was calculated to be 3-5 nm, revealing that the chemical modification induces a number of micropores and a decrease of the average pore diameter. Fig. 3, 4 shows the adsorption spectra and isotherm of dyes on PMM in aqueous solution at 293 K.

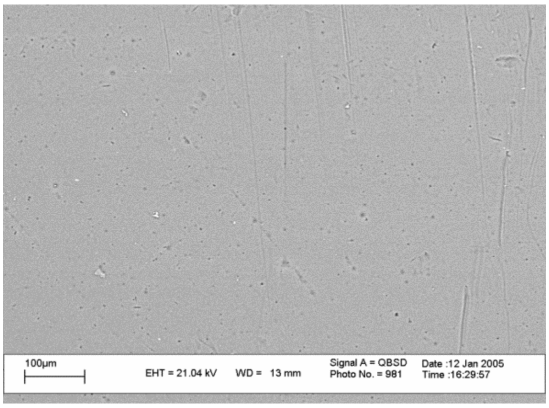

Fig. 2. The microphotograph of PMM surface

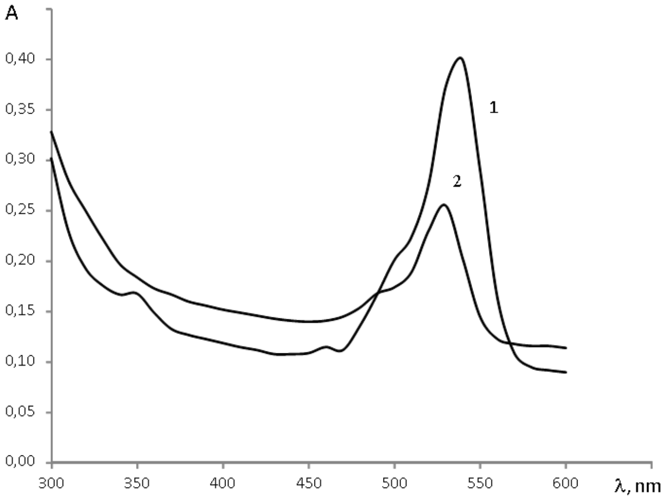

Fig. 3. The spectra of rhodamine and eosine adsorbed into PMM

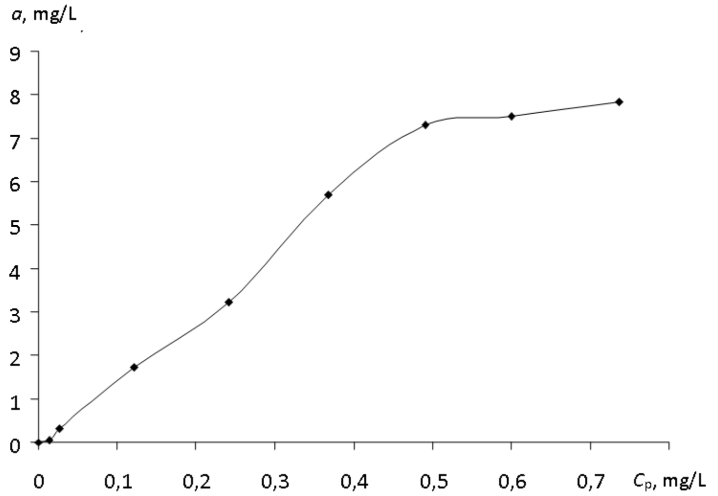

Fig. 4. Adsorption isotherms of eosine adsorbed into PMM

Comparing the adsorption capacity of rhodamine and eosine at the equilibrium concentration, it is understood that the adsorption capacity of rhodamine is a larger than that of eosine. Langmuir and semi-empirical Freundlich isotherms were adopted to describe the adsorption process [14].

The signal-to-noise ratio is the most frequent parameter used to report the diapason concentration (RDC) and the limit of detection (LOD). In this study, the LOD was defined as the real concentration required to produce a signal-to-noise ratio of three. The medial for the rhodamine was found to be approximately 0.06 mg/L and 1.2 mg/L in case of eosine. The LOD discounts the solid-phase extraction step. Including the enrichment, the detection limits lower down by factor 380. To proof the capability of the SPE, the extraction efficiency (EE) was determined. Since the SPE is followed by esterification the extraction efficiency instead of the recovery rate is obtained.

The ratio between sample volume before and after solid-phase extraction equals to the enrichment factor. The concentration of the rhodamin or eosin before SPE is known. The concentration after SPE is the product of the concentration prior to SPE multiplied with the enrichment factor.

Dyes were enriched out of 50 mL sample and extracted with 1 plate of PMM. The volume ratio results into an enrichment factor 380. Extraction efficiencies of dyes were determined by comparing after SPE of water and oil-water samples containing 2 mg/L of each. For each studied dye we selected color scale and color channel which was chosen as the analytical signal and should be used for plotting the calibration curve [15, 16]. As expected, for the red colored samples of colorimetric scales for the determination of rhodamine and eosine having absorption maxima 530-540 nm in the green region (Table), the work channel is green (G). The LOD were calculated according to the 3*s*-test also.

We compared the digital color analysis (DCA) and the solid phase spectrophotometry for determined rhodamine and eosine (Table 1). A comparison of the metrological parameters of the procedures for the determination of dyes shows that the selected components can be determinated with the use of image-processing software with practically the same sensitivity as with the use solid phase spectrophotometry.

Table 1. Comparison of RDC and LOD for solid phase spectrophotometry and DCA (work channel)

Analyte	Solid phase spectrophotometry		Digital color analysis	
	RDC, mg/L	LOD, mg/L	RDC, mg/L	LOD, mg/L
Rhodamine	0.07 - 50.00	0.06	0.02 - 0.30	0.6
Eosine	1.25 - 50.00	1.20	0.02 - 0.80	1.32

The accuracy and precision of the results of the determination of the test components were verified by the standard addition method. A comparison of the determination methods shows a good accuracy and precision of the determination of xanthene dyes in water or oil-water emulsion using a scanner and image-processing software.

Conclusions

In this work, a sensitive and rapid SPE-DCA method for simultaneous determination and quantification of rhodamine and eosine in water samples was developed. The sorbent material PMM was found to be best suited, to provide high recovery rates in combination with very good reproducibility even at amounts <0.1 mg/L for rhodamine. Parameters such as sample matrix, SPE material, and conditioning steps optimized.

Solid phase extraction behaviors for rhodamine and eosine indicated that Langmuir isotherm can characterize the adsorption more efficiently. The proposed PMM can be used for determination of xanthene dyes by both solid-phase spectrophotometry and digital color analysis. The DCA can provide a metrological performance not worse than that of spectrophotometry.

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