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An eosin Y-based "turn-on" fluorescent sensor for detection of perfluorooctane sulfonate

Jiaman Liang, Xiaoyan Deng, Kejun Tan *

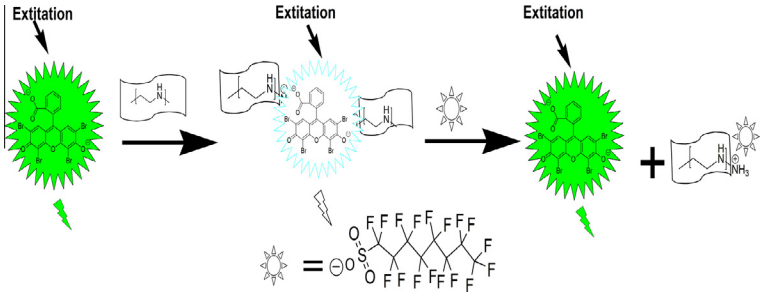
Key Laboratory of Luminescent and Real-Time Analytical Chemistry, Ministry of Education, College of Chemical and Chemistry Engineering, Southwest University, Chongqing 400715, PR China

HIGHLIGHTS

- A novel fluorospectrophotometry for the detecting of PFOS has been developed.
- The proposed method is capable of differentiating PFOA and PFOS.
- The method is simple, fast and cheap.
- The method successfully eliminated the interference of SDS by added Ba^{2+} cation.

GRAPHICAL ABSTRACT

A novel fluorospectrophotometry with a higher sensitivity of perfluorooctane sulfonate (PFOS) than perfluorooctanoic acid (PFOA) has been proposed detection of PFOS in aqueous solution replying on the "off–on" switch of eosin Y/polyethyleneimine (PEI)/PFOS fluorescence system.



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ABSTRACT

In this paper, a novel sensing method with a higher sensitivity of perfluorooctane sulfonate (PFOS) than perfluorooctanoic acid (PFOA) has been proposed detection of PFOS in aqueous solution replying on the "off–on" switch of eosin Y/polyethyleneimine (PEI)/PFOS fluorescence system due to the higher affinity of PEI to PFOS than eosin Y. In pH 7.0 Britton–Robinson buffer solution, eosin Y reacts with protonated PEI to form complex by electrostatic attraction, which leads to a strong fluorescence quenching of the eosin Y. When PFOS presents, the fluorescence of eosin Y is recover due to the electrostatic and hydrophobic interactions between PFOS and PEI. The recovered fluorescence intensity is proportional to the concentration of PFOS in the ranging from 0 to 2.0×10^{-6} mol/L with the limit of detection (LOD, 3σ) being 1.5×10^{-8} mol/L without preconcentration. In this study, the optimum reaction conditions and the interferences of foreign substances were investigated. In addition, the effects of PFOA, the analog of PFOS, on the fluorescence recovery of the system were also studied. The presented approach has been successfully used to detect PFOS in real samples with RSD $\leqslant$2.9%.

Introduction

Perfluorinated compounds (PFCs), as synthetic fluorinated organic compounds, are characterized by a fluorinated alkyl chain and a terminal functional group and applied in a broad spectrum of industrial, commercial and consumer sectors, such as surfactants, aerosol propellants, insecticide, refrigerants, anesthetics, plastics, particular fire-fighting foams, and these compounds have been detected in the environment all around the world since manufactured by 3M company in 1951 [1,2]. On account of its wide application and harmfulness, PFCs have aroused extensive studies. As

* Corresponding author. Tel./fax: +86 23 68367257.
E-mail address: tankj@swu.edu.cn (K. Tan).

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we all know, the eight-carbon-chain perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are typical and predominant PFCs, which have been widely detected both in environmental media such as activated sludge, waters, atmosphere and in a variety of living organisms including fishes, birds, and humans [3–9]. What is more remarkable is that PFOS even has already been found in living Polar bears from the Arctic on the highest level [10]. PFOS, as the end product of the degradation of many sulfonated fluorochemicals, has been listed as one of the new persistent organic pollutants (POPs) in the Stockholm Convention in 2009 due to its persistence, bio-accumulation and long range transportation [1,11]. Furthermore, PFOS is prone to accumulate in the trophic chain and the half-life of PFOS in humans is 5.4 years, which results in biomagnification in living organisms [12–15]. A number of studies in vitro and vivo experiments demonstrated that PFOS would cause toxicity of human and animals, including reproductive toxicity, neurotoxicity, and hepatotoxicity [16–18]. Thus, the wide application and potential health risks of PFOS lead to an increasing focus on exploring the fate, distribution and levels in the environment. In recent years, considerable efforts of environmentalists were dedicated to developing appropriate methods for qualitative analysis of it.

Currently, a large number of analytical methods based on different principles of the determination of PFOS in environmental matrixes have been reported, such as liquid chromatography–mass spectrometric (LC–MS) [19–22], capillary zone electrophoresis (CZE) [23], gas chromatography–mass spectrometry (GC–MS) [24–26], and liquid chromatography–tandem mass spectrometry (LC–MS–MS) [27,28]. Among above methods, the sensitivity of CZE is lower. Although the GC–MS, LC–MS and LC–MS–MS have higher selectivity, all of them require extensive sample preparation during the process, including derivatization, purification and preconcentration. Moreover, the relatively long analysis time and expensive instruments of these methods make the widespread application restrained. Therefore, it is highly desirable to develop a simpler method to detect PFOS.

Fluorospectrophotometry, which exhibits fascinating features, including its accuracy, simplicity, high sensitivity and inexpensive instrumentation, has attracted great attention. Thus, it has been applied in many fields for sensing target analytes. Previous studies indicated that the eosin Y can reacts with protonated polyethyleneimine (PEI) by electrostatic attraction, resulting in a strong fluorescence quenching of the eosin Y [29]. In this work, we established a fluorescence spectrophotometric method to determine the PFOS in aqueous solution based on the off–on fluorescence signal of eosin Y. In our research, we mainly investigated the spectral characteristics, the effect factors, and the optimum conditions of reaction. PFOA, the analog of PFOS, on the fluorescence recovery of eosin Y was studied as well. The experimental results further demonstrated that such methodology can be used for distinguishing PFOA and PFOS.

Experimental

Apparatus

All absorption spectra were recorded on a Hitachi U-3010 spectrophotometer (Tokyo, Japan). The fluorescence spectra were obtained by a Hitachi F-2700 spectrofluorometer (Tokyo, Japan). And a MVS-1 vortex mixer which was purchased from Beide Scientific Instrumental Ltd. (Beijing, China) was used for mixing the solutions.

Reagents

PFOS and PFOA were purchased from TCI Development Co., Ltd. (Shanghai, China). Eosin Y and Ethylene imine polymer (PEI, purity 98%, MW = 1800) were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). All other reagents used in the experiment were analytical grade, and the double distilled water (18.2 MΩ cm^{-1}) was used throughout. Britton–Robinson buffer solution (BR, PH 7.0) was used to control the acidity of the aqueous solutions.

Procedures

20.0 μL eosin Y solution of 1.0×10^{-7} mol/L and 200 μL BR buffer solution (pH 7.0) were added into a 2.0 mL microtube. Next, 100 μL PEI of 1.0×10^{-7} mol/L was added to the mixture. Then an appropriate volume of PFOS or PFOA working solution or sample solution was added. The mixture was vortex after each addition of the interacting additives, and then diluted to 2.0 mL with super-purified water. After having been mixed thoroughly, the mixture was equilibrated in 30°C water for 10 min and then transferred for fluorescence and absorbance measurements.

Results and discussion

Spectral characteristics

The Spectral characteristics of eosin Y, eosin Y/PEI, and eosin Y/PEI/PFOS were evaluated. Fig. 1 shows the fluorescence emission spectra of eosin Y (cure a), eosin Y/PEI (cure j), and eosin Y/PEI/PFOS (cure b–f). As illustrated in Fig. 1, the free eosin Y has a strong fluorescence emission at 548 nm when excited at 513 nm in pH 7.0 BR buffer solution. After addition PEI into the eosin Y system, the fluorescence emission intensity of eosin Y is significantly decreased. From Fig. 2, it can be seen that there is a strong characteristic absorption peak at 514 nm of the eosin Y, which is greatly decreased in the presence of PEI. Hence, these data clearly demonstrated that the eosin Y may reacts with PEI form eosin Y–PEI complex resulting in the fluorescence quench of eosin Y. On the one hand, in pH 7.0 BR buffer solution, eosin Y is fully ionized and exists in the bivalent anion, but on the surface of PEI, the amino groups are protonated with a great deal of positive charges. Therefore, it is speculated that the electrostatic interaction plays an essential role in the complex formation between eosin Y and PEI molecules. Meanwhile, the zeta value further confirmed it. Under our experimental condition, the zeta value of eosin Y in the absence of PEI was −6.82 mv, while the zeta value increased to 10.5 mv with PEI. On the other hand, PEI has a large amount of amino groups which are strong electron donors. Whereas, eosin Y, a xanthene dye with redox capability, can act as an electron

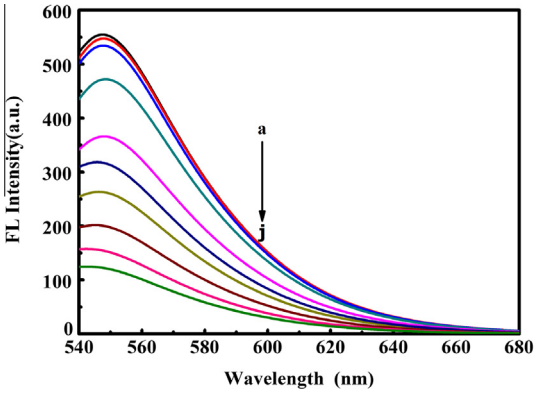

Fig. 1. Fluorescence emission spectra of eosin Y (curve a), eosin Y/PEI (curve j) and eosin Y/PEI/PFOS (curve b–i). Concentration: eosin Y (0.1×10^{-6} mol/L), PEI (0.5×10^{-6} mol/L), PFOS (i–b: 0.5, 0.8, 1.0, 1.2, 1.5, 2.0, 3.0, 5.0×10^{-6} mol/L). Britton–Robinson buffer solution, pH 7.0.