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ARTICLES

Recognition and Determination of Sulfonamides by Near-IR Fluorimetry Using Their Effect on the Rate of the Catalytic Oxidation of a Carbocyanine Dye by Hydrogen Peroxide

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Abstract—The work aims at developing fluorimetric methods used for bioassay to expand the range of the determined low-molecular-weight organic analytes and cut down sample preparation operations using available fluorophores, reagents, and identical fluorimetric systems for qualitative and quantitative analysis. We proposed using the reaction of carbocyanine fluorophore oxidation by hydrogen peroxide, catalyzed by copper(II), changing fluorescence intensity in the near-IR region (700 nm). Several organic compounds of different nature accelerate or slow down the indicator reaction, to varying degrees, and at different times of the process. The model analytes were eight sulfonamides, which can be distinguished qualitatively using the kinetic factor in data processing by principal component analysis. We demonstrated on an example of phthalylsulfathiazole that the signal could be obtained not only in an aqueous solution but also in the presence of a turkey muscle homogenate at a level of 0.08–0.5 mM (RSD = 9%) without separation. The prospects for the development of such fluorescence platforms are discussed.

Keywords: NIR fluorimetry, carbocyanines, catalysis, sulfonamides, phthalylsulfathiazole, fingerprint method

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Fluorimetric methods for the determination of low-molecular-weight organic compounds are developing in the field of the direct determination of analytes and the minimization of sample preparation operations [1]. Such methods are simple, rapid, and relatively accessible in terms of instrumentation. However, the development and broader use of fluorimetry of organic analytes are hindered by several circumstances. In the majority of cases, selective probes should be presynthesized. Synthetic difficulties and low availability of the reagents limit the practical use of the probes, and the probe response to a single analyte impedes the determination of others using the same platform. The fluorimetric determination of typical quenchers, compounds capable of energy or electron transfer or covalently binding to a fluorophore [1–4] is rather simple; for other analytes, fluorimetric analysis is carried out indirectly or using derivatization [5]. To determine low-molecular-weight organic analytes, fluorimetry in the near-IR spectral region is not widely used. In the so-called first transparency window of biological tissues (NIR-I, from 650 to 1000 nm [6, 7]), the intrinsic fluorescence of biological samples and the absorption of the exciting and emitted light are minimal. Spectrofluorimeters and, less often, photocameras [8], particularly cameras of smartphones, are most often used to record fluorescence signals in the visible region [9]. Photography is also advisable to record emission in the near-IR (NIR) spectral region [10].

Thus, developing new fluorescent sensor platforms, which would make it possible to obtain a response of organic compounds of different nature (including those non-fluorescent and not interacting with fluorophores), is rather urgent. A possibility of measuring signals in biomatrix using the NIR spectrum region can contribute to creating a series of various sensors on a united platform. It is advisable to use a combination of two signals: fluorimetric and photometric [11]. It is also desirable that the platforms being developed do not require the synthesis of reagents.

We have proposed an approach to solving the above problems using oxidation reactions of dyes emitting in the near-IR region. If a transition metal ion catalyzes such a reaction, then ligand compounds can be determined by the effect on the reaction parameters. That strategy will expand the range of analytes determined by fluorimetric methods. Varying the nature of the metal catalyst can lead to an expansion of the range of analytes. Many catalytic redox systems are used in chemical analysis [12–14]; however, NIR fluorophores were not used as reductants. However, the selection of such oxidation conditions should not cause difficulties.

In this work we have studied the oxidation of commercially available carbocyanine dye I with hydrogen peroxide, catalyzed by copper(II) (Scheme 1). Hydroquinone is one of the conventional reducing agents in this catalytic reaction [14], and amino compounds serve as activators [14, 15]. The studied effect of low-molecular-