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Determination of dopamine in pharmaceutical formulation using enhanced luminescence from europium complex

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ABSTRACT

Biologically important compound dopamine plays an important role in the central and peripheral nervous systems. Insufficient dopamine level due to the loss of dopamine producing cells may lead to disease called Schizophrenia and Parkinson's disease. Hence, a simple and fast detection of dopamine is necessary to study in the fields of neurophysiology and clinical medicine. An enhanced fluorimetric determination of dopamine in the presence of ascorbic acid is achieved using photoluminescence of europium complex, Eu(III)–dipicolinic acid. In order to obtain better responses, several operational parameters have been investigated. Under the optimum conditions, the method showed good stability and reproducibility. The application of this method for the determination of dopamine neurotransmitters was satisfactory. Linear response was found down to 3.0×10^{-7} M with limit of detection 1.0×10^{-8} M. The relative standard deviation was found to be 3.33% from 20 independent measurements for 1.0×10^{-5} M of dopamine.

1. Introduction

Dopamine (4-(2-aminoethyl) benzene-1, 2-diol) (DA) is a biogenic catecholamine formed by decarboxylation of 3,4-dihydroxyphenylalanine. The chemical structure of DA has shown in Fig. 1(a). It is a precursor to epinephrine and nor-epinephrine in a biosynthetic pathway [1]. One of the most important functions of DA is as a neurotransmitter in the central and peripheral nervous systems. It also functions as a biological messenger. Insufficient DA level due to the loss of DA-producing cells may lead to disease called Parkinson's disease [2], in which a person loses the ability to execute smooth and controlled movements [3–5]. DA can be supplied as a medication that acts on the sympathetic nervous system, producing effects such as increased heart rate and blood pressure. Therefore, it is important to determine DA using a reliable method with good sensitivity and selectivity.

Several methodologies have been applied to develop a sensitive and selective way of determining DA level in biological samples. The chromatography methods combined with spectrometry as a detection method have been developed, such as, mass spectrometry combined with GC [6], HPLC [7,8], and capillary electrophoresis [9]. Though these methods are highly specific and sensitive, they require sophisticated and costly instrumentation, and are time consuming.

With the development of nanotechnology, many procedures have been used to detect DA by using nanomaterials such as carbon nanotubes [10,11] and gold nanoparticles [12,13]. Rather than mass spectrometry, electrochemical detection methods have also been introduced since these are the best way to directly determine DA without any separation steps of samples. In biological samples, DA often occurs with ascorbic acid (AA) in relatively high concentrations. The existence of AA is the main obstacle in electrochemical detection system since AA is oxidized at similar potentials to DA at conventional electrodes and has much larger signals in the brain than DA [14]. Therefore, to overcome the effect of AA and other interfering species in DA analysis, modified electrodes have been used to simultaneously detect both DA and AA at different potentials. Such as, electrode surface modification by surfactants [15], self-assembled monolayers [16,17] and polymers [2,18–20]. Other methods such as enzyme-based techniques [21], electrochemical pretreatment [22] were also reported. But these methods are difficult to handling and depend on various experimental parameters.

The fluorescence methods [23–25] have attracted many attentions because of its high sensitivity and, to a lesser extent, its selectivity. Ethylene diamine [26], *N*-hydroxysuccinimidyl-3-indolylacetate [27] and 1,2-bis (3-chlorophenyl) ethylenediamine [28] have been used as fluorescence derivation reagents for determining DA. Terbium ion used as fluorescence probe for the detection of DA has also been developed [29].

Under the scope of this view, the aim of our research work was to develop a more precise, accurate and reliable method for the determination of DA in pharmaceutical formulations.

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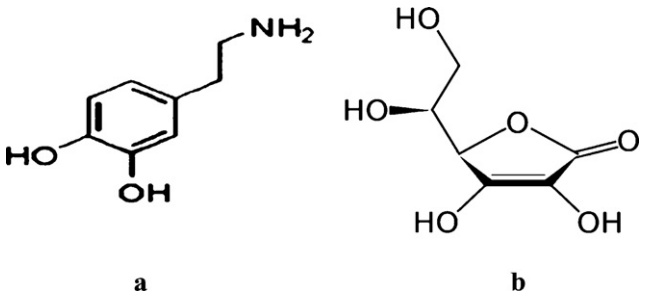

Fig. 1. Chemical structures of (I) dopamine and (II) ascorbic acid.

In our detection technique we have selected dipicolinic acid (DPA) as a ligand for binding Eu^{3+} ion, and investigated possibility of the enhancement of the Eu^{3+} ion sensitized fluorescence by DA. Experimental results show that the characteristic peak of Eu^{3+} ion at 596 nm was greatly enhanced in DPA-Eu^{3+} system by DA and the enhancement comes from the intra-molecular energy transfer in DA-DPA-Eu^{3+} ion ternary complex in close proximity. According to this, a new fluorescence method with high sensitivity and selectivity has been established for the determination of DA using DPA-Eu^{3+} as a fluorescent probe. To the best of our knowledge, there are no methods have been published using this fluorescence system. The sensitivity of this technique does not affected by coexisting AA (Fig. 1(b)). On the other hand, this method is easily performed and affords good precision and accuracy and has been successfully applied to the determination of DA in pharmaceutical injection in presence of excess amount of ascorbic acid.

2. Material and methods

2.1. Apparatus

Fluorescence intensity measurements were carried out with a Spectrofluorometer (Model FL111, Spex, Edison, NJ, USA). Xe Lamp (450 W) was used as light source while silicon diode (voltage 400 V) as reference detector. Emission signal was measured and transduced to an electric signal by a photomultiplier tube (voltage 950 V, Model R928, Hamamatsu, USA). The excitation and emission wavelengths were 596 and 626 nm respectively. Excitation and emission monochromator slit, increment, and integration time were set at 1.25 mm, 1 nm and 1 s, respectively. The angle of the quartz cell was 90°. All spectral data were obtained by SPEX DM 3000F spectroscopy computer.

2.2. Reagents

Europium complex, Eu(III)-DPA was synthesized according to the reported method [30] by dissolving $Eu(NO_3)_3$ into dipicolinic acid ($C_7H_5NO_4$, DPA) solution with a molar ratio of DPA/Eu^{3+} = 1:1. A transparent and colorless solution with 3×10^{-5} M was prepared for the experiments. Dopamine, ascorbic acid were purchased from Fluka (USA) and used without further purification. Dopamine solutions were prepared by dissolving required amount in ethanol to prevent oxidation of dopamine. All other reagents used were of analytical grade. Distilled ionized water obtained from Elga Purification system was used for the preparation of all solutions.

2.3. Experimental procedure

Appropriated amounts of dopamine and Eu^{3+}–DPA complex solutions were added to a fluorescence cell (1 cm quartz cell) and the mixtures were stirred for 1 min and kept for few minutes before fluorescence measurement. The fluorescence intensity was measured at $\lambda_{ex}/\lambda_{em}$ = 372/596 nm. The enhanced fluorescence intensity of DPA–Eu^{3+} caused by DA was represented as $\Delta F = F - F_0$. Here F and F_0 are the fluorescence intensities of the systems with and without DA, respectively. The standard curve method was used in the quantitative determination of DA in real samples. All fluorescence measurements were made using 1 nm increment, 1 s integration time, S acquisition mode and YES auto zero.

Table 1
Interferences of some foreign substances for 1×10^{-5} M DA.

Foreign substances	Tolerance level ($\times 10^{-4}$)/M
Starch	4
K^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Cl^-	2
Caffeine	3
Ascorbic acid	10
Citric acid	1
Cysteine, lysine, glucose	0.5

3. Result and discussions

3.1. Optimization of reaction time

Under the optimal experimental conditions, the value of fluorescence intensity reached stable within four minutes and remained constant in half past an hour but was started to decrease as time processed after. So we were chosen eight minutes as optimal in the following experiment.

3.2. Fluorescence kinetic curves of the systems

The fluorescence spectra of DPA-Eu^{3+}-DA and DPA–Eu^{3+} are shown in Fig. 2. It is obvious that the characteristic peak of DPA–Eu^{3+} at 596 nm (λ_{ex} = 372 nm) increases several folds after the addition of DA which indicates that the formation of the DPA–Eu^{3+}–DA ternary complex. The intra-molecular energy transfer from DA to DPA–Eu^{3+} complex was formed during the measurements were might be responsible for the increments of fluorescence intensity.

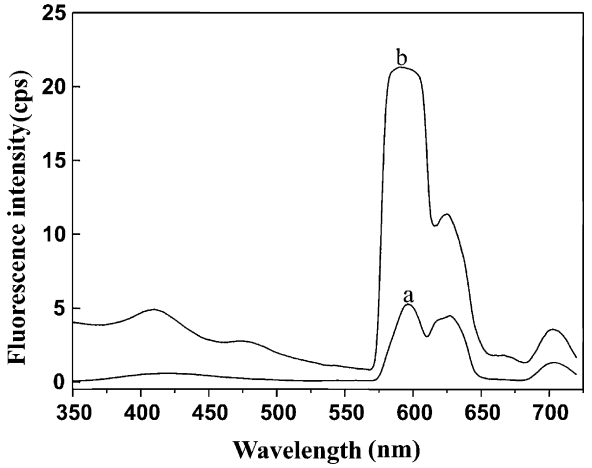

Fig. 2. Emission spectra (λ_{em} = 596 nm) of (a) Eu^{3+}–DPA complex and (b) Eu^{3+}-DPA-DA system. Conditions: Eu^{3+}–DPA complex 1×10^{-2} M, dopamine 4.8×10^{-5} M and λ_{ex} = 372 nm.