Journal of Luminescence 185 (2017) 132–140

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Full Length Article

Determination of sertraline in pharmaceutical and biological samples using 1, 10-phenanthroline-terbium probe and silver nanoparticles enhanced fluorescence

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ARTICLE INFO

Article history:
Received 3 July 2016
Received in revised form
26 October 2016
Accepted 28 December 2016
Available online 7 January 2017

Keywords:
Sertraline
1, 10-phenanthroline
Spectrofluorimetric
Terbium
Ag nanoparticles

ABSTRACT

Sertraline is an antidepressant widely prescribed for major depressive disorders. In this contribution we report a novel, rapid and sensitive spectrofluorimetric technique, developed and validated for the determination of sertraline in pharmaceutical, human urine and human plasma samples, based on the fluorescence enhancement of the sertraline by 1, 10-phenanthroline-terbium probe with Ag nanoparticles (AgNPs). The effect of pH, buffer concentration, the order of addition of reagents, terbium and 1, 10-phenanthroline concentrations, and concentration of Ag nanoparticles (AgNPs) as well as reaction time on the fluorescence intensity were investigated and the optimum conditions were determined. The linear range for determination of sertraline was obtained as 0.001–3 mg L^{-1}. The limit of detection (b+3s) and the limit of quantification was calculated as 2.9×10^{-4} mg L^{-1} and 9.8×10^{-4} mg L^{-1}, respectively. The interference effects of common excipients found in pharmaceutical preparations were studied. The presented technique was used to determine the sertraline in pharmaceutical samples, human urine and plasma as real samples. The presented method was indicated a comparable results with the standard analytical techniques for sertraline. Good linearity, reproducibility, recovery and limit of detection have made this method suitable for determination of sertraline in various types of samples.

1. Introduction

Depression, as one of the common mental diseases which has significantly negative effects on the whole life of patient and even may end to suicide actions. In the most of cases, depression can be attributed to the neurochemistry change of neurotransmitters, such as 5-hydroxytryptamine (serotonin). Nowadays, the selective serotonin reuptake inhibitors (SSRIs) in fact have become almost the first choice drugs for depression treatment which, in addition to their favorable effects have many toxic side effects, such as gastrointestinal disturbances [1]. Hence, the design and developing of analytical techniques for monitoring and measurement of these drugs are useful from several points of view. The first review on the analytical techniques for quantitative therapeutic drug monitoring (TDM) purposes of these drugs was published in 1996 [2]. Advancements in the pharmacological management of depression during the last two decades have resulted to a sharp increase in the rate of antidepressant prescriptions. Mitchell has reviewed the TDM investigations of SSRIs [3]. Sertraline (SER) (*cis*-(1*S*, 4*S*)-4-(3, 4-dichlorophenyl)-1, 2, 3, 4-tetrahydro-1-naphthyl (methyl) amine) and fluoxetine as SSRI drugs are used in clinical treatments of depression and obsessive–compulsive behavior. The daily doses of SER is in the range of 50–200 mg, and after oral administration the drug is slowly absorbed and its steady state plasma concentrations reaches to 55–250 ng mL^{-1}. So, creation of a simple and selective procedure for measurements of sertraline to ensure its therapeutic performance and safety is of great importance.

Lanthanide salts chelated with different agents exhibit a significant luminescence, which have been utilized in a wide fields of application such as medical investigations. An exceptional decay times is among the unique properties of the luminescence of chelated lanthanides, which allow efficient discrimination between the background interferences in assays. In addition to the type of central metal ions the luminescence characteristics of chelated lanthanides depends on the structure of ligands. The chelating agents (also called as 'antennas') absorb and transfer energy to the central metal ion and hence, enhance their luminescence intensity. Because of their high ligand to metal ion energy transfer efficiency, aromatic carboxylic acids as chelating

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http://dx.doi.org/10.1016/j.jlumin.2016.12.053
0022-2313/

agent and heteroaromatic compounds such as 1,10-phenanthroline (phen) results to the highest luminescence enhancement for Tb^{3+} ion, which was attributed to the better match of its energy level with the $^5D_4$ energy level of Tb^{3+} ions [4–6]. The 1,10-phenanthroline-Tb^{3+} complex (phen-Tb) has been already used as a fluorescence probe for the determination of the folic acid in different samples [4].

It is well known that the nanostructured metallic compounds improve the spectral characteristics of the fluorophore materials [5]. The investigations indicated that certain fluorophores have better interactions with certain metallic compounds and consequently leads to much higher luminescence intensity enhancement effects [7]. In this study, the compounds was irradiated by an external light source, and then the energy absorbed by fluorescent species from the external light source was partially transferred or coupled with the surface plasmones in the metallic nanostructure. This metal-fluorophore interactions phenomenon considerably enhances and increases intensity of the luminescence of the chelates [7–10].

Several methods have been reported for the determination of SER in various samples using LC [11–15], GC–MS [16,17], spectrofluorimetry [18–21], spectrophotometry [22–26], HPLC [27–33], capillary electrophoresis [34].

The aim of this paper is to describe the development of a new method for the measurement of SER in pharmaceutical formulations and biological samples using the luminescence intensity enhancement rational via interactions of SER with phen-Tb complex as a fluorescence probe and Ag nanoparticles.

2. Experimental

2.1. Materials and methods

All chemicals and solvents were of analytical reagent grade and were obtained from Merck, Germany. Deionized water (DI, Milli-Q) was used throughout the experiments. The terbium chloride ($TbCl_3$, 0.01 mol L^{-1}) stock solution was prepared from terbium oxide (Tb_4O_7, from Alfa (USA). 1, 10-phenanthroline was purchased from Merck, Germany.

Hydrochloric acid solution (1.0 mol L^{-1}) was added drop-wise on the Tb_4O_7 (0.1869 g) powder in 150 °C, until the dark brown solution was turned to the light yellow. Then, the addition of the HCl solution was stopped and heating was continued to dryness to obtain white terbium chloride powder (0.2654 g). Finally, the resulting white powder was dissolved in DI water and diluted to 100 ml to obtain a 0.01 mol L^{-1} terbium solution.

A proper amount of the 1, 10-phenanthroline was dissolved in 5 mL ethanol and diluted to the 100 mL with DI water to obtain 0.01 M stock solution.

Tris–HCl buffer solution (0.5 mol L^{-1}) was prepared by dissolving 3.025 g of tris (hydroxymethyl) aminomethane in 40 mL DI water and by adjusting its pH with 1.0 mol L^{-1} HCl solution. The resulting solution was diluted to 50 mL with DI water.

A 100 mg L^{-1} stock solution of SER was prepared by dissolving 50 mg of SER powder (Rooz daru Pharmaceutical Industry, Iran) in 20 ml of distilled ethanol and diluting to 500 ml with DI water. The stock solution was stable for one week at 4 °C. The working solutions were prepared daily by its dilution with DI water.

The colloidal AgNPs were prepared by using of a chemical procedure previously detailed elsewhere [8]. Typically, a 5 mL aliquot of AgNO3 solution (1×10^{-3} mol L^{-1}) was added drop-wise onto the 15 mL of fresh aqueous solution of NaBH4 (2×10^{-3} mol L^{-1}), with vigorously stirring. After 15 minutes, the formed AgNPs were stabilized by adding 1.5 ml of sodium citrate solution (1% w/w). The yellow reaction mixture was then agitated for additional 25 minutes and aged for 2 days at 4 °C before use. The concentration of the as-prepared AgNPs was 2.4×10^{-4} mol L^{-1}, based on the concentration of $AgNO_3$ solution used for their preparation. These can be used for at least one month after preparation.

2.2. Apparatus

Fluorescence spectra and intensities were recorded by RF-5301-PC Spectrofluoro-photometer from Shimadzu (Japan). A 1 cm × 1 cm quartz cell was used to measure fluorescence in all experiments. The bandwidths of the excitation and emission monochromator were 5 nm. Absorption spectra were measured by UV-1800 Spectrophotometer (Shimadzu- Japan). TEM images of the AgNPs were recorded by using a Transmission Electron Microscope from Zeiss (Germany) model EM-10C operating at 100 kV accelerating voltage, on the carbon coated copper grids. A pH meter (Hanna-211, Germany) was utilized for the measurement and adjustment of pH values.

2.3. Real sample preparation

Tablet formulations: Number of ten sertraline tablets (products of Rooz Daru, Iran or Dr. Abidi Pharmaceutical Laboratory Company, Iran), each of them containing 50 mg of SER, were weighed (to 0.01 mg) and mortared to get a fine homogeneous powder. An amount of 100 mg of powder (approximately the mean weight of one tablet) was added into 20 mL of ethanol in a beaker and was shaken until complete dissolution. The solution was then filtered through a No. 41 Whatman filter paper to remove non-soluble excipient particles. The filtrate was transferred into a 1000 mL measuring flask and brought to the volume by DI water to get the stock solution. The solution was stored in refrigerator at 4 °C and the working solutions were then prepared on daily base by further dilution with DI water, and proper aliquots were taken from the stock solution for measurement of SER employing of the developed procedure.

Human blood sample: The blood samples were taken from 4 depressed patients (2 males and 2 females) aged between 18–68 years old in Razi Hospital (Tabriz-Iran), who were receiving one 50 mg SER tablets each day. Each blood sample was taken 12 h after the administration of the last SER tablet and poured in the glass test tubes containing EDTA as anticoagulant. Within the not more than 2 h after sampling, The samples were then centrifuged for 25 min in a rate of 3000 rpm (EBA-20, Germany) and the blood plasma was separated as supernatant and transferred into the sample vessels and stored in a freezer at −20 °C until analysis was done [24]. Before the analysis step, the proteins present in the plasma was precipitated by treatment of the samples using a 1:1 mixture of $HClO_3$ (5%) and trichloroacetic acid (1%). The resulting mixture was then vortexed and centrifuged (4000 rpm for 10 min). Also, the blood samples from two healthy people were taken as control and spiked to validate the analytical results.

Human urine sample: The same 4 patients who were under treatment with SER, were asked to give urine samples 12 h after the last SER tablet consumption. The dark brown glass vessels were used to store the samples, which were diluted three-fold with DI water as the only pretreatment before analysis. Also, the spiking and validation of the results were made on the urine samples taken from two healthy people as control.

2.4. General procedure

An adequate volume of SER stock solution or 1 mL of real samples were added into a series of 10 mL volumetric flasks, which were already contained 1.0 mL of 10^{-3} mol L^{-1} Tb^{3+}