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RESEARCH ARTICLE

Surfactant Induced Modulation of Sensor Efficiency of Murexide towards Manganese

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Abstract: In this paper Murexide as a sensor for manganese in a micellar nanocage has been studied. It was found that the efficiency of the quenching-based fluorosensor increased by several orders of magnitude in the presence of commercially available anionic surfactants like SDS. The method was found to be simple, inexpensive, direct, non-extractive, highly sensitive and virtually specific for the trace and ultra-trace (5 ng mL^{-1} to 1 μg mL^{-1}) analysis of manganese.

Keywords: Murexide, Manganese, Anionic surfactant, Fluorosensor

Introduction

Manganese in trace amounts is important industrially, as a biological nutrient and genotoxicant, as an environmental pollutant and as an occupational hazard. Exposure to manganese dusts and fumes should not exceed the ceiling value of 5 mg m^{-3} even for short periods because of its toxicity level. Manganese poisoning has been linked to impaired motor skills and cognitive disorders. Only a limited amount is absorbed by the intestines, but this small amount shows severe effects on the kidneys and on the liver[1,2]. A form of neurodegeneration[3] similar to Parkinson's disease called "manganism" has been linked to manganese exposure amongst miners and smelters since the early 19th century[4]. Allegations of inhalation-induced manganism have been made regarding the welding industry. Therefore, determination of the metal at trace and ultra trace levels is important. Several spectrofluorimetric methods have been reported[5-13]. However, none of these methods deal with surfactant induced modulation of fluorescence which is a very important tool in sensor research. The present method is a simple in-expensive, non-extractive and virtually specific fluorimetric method for the determination of manganese at trace and ultra trace levels. In the present method tuning of the sensory capability of murexide in a micellar nanocage has been carried out. It has been shown that surfactant concentration dictates the sensory ability of the fluorophore towards the potent toxicant manganese(II).

Experimental

All fluorimetric measurements were performed with a Shimadzu spectrofluorophotometer (RF-5000) equipped with a 150-W xenon lamp, 12" color video display, parallel line thermo sensitive printer recorder and 1x1 cm quartz cells with a Shimadzu ASC-5 auto sample changer. Operational performance and sensitivity of the instrument were checked by running the Raman spectrum of distilled water and wavelength error was kept below ±2.0 nm. A digital pH meter (model pH 5651, Electronic Corporation of India Ltd.) was used for the measurements of the pH. A Hanovia (model 11A) 240V, 50 Hz, arc tube fluorescence UV lamp was used for preliminary qualitative investigations.

General procedure

To a 10 mL volumetric flask containing 0.4 mL of 10^{-4} (M) or 0.4 mL of 10^{-3} (M) murexide solution and 2 mL 10^{-2} (M) solution of sodium dodecyl sulfate (SDS), 0.05-1.0 µg or 1.0-10 µg of manganese(II) solution and 1 mL of 0.5 (M) H_2SO_4 were added. The fluorescence intensity was measured at 443.0 nm against a corresponding reagent blank in micellar medium, keeping the excitation wavelength at 354.0 nm under the same instrumental settings. From the difference of fluorescence intensities of the solution measured in the absence and in the presence of manganese(II), the concentration of manganese(II) was determined with the help of a standard calibration graph.

Results and Discussion

Factors affecting the fluorescence intensity

Spectral characteristics

The uncorrected excitation and emission spectra of murexide in presence and in absence of manganese(II), in acidic media were recorded with the Spectrofluorimeter. In micellar medium the wavelength maxima of excitation and emission were found to occur at 354.0 and 443.0 nm respectively (Figure 1) whereas that of murexide in absence of SDS was 353.6 and 444.8 nm.

Effect of acidity

In the present system sulfuric acid provides a wide range of acidity for the maintenance of constant maximum fluorescence intensity. The constant maximum difference in fluorescence intensity (with respect to corresponding reagent blanks) was observed in the presence of 0.8-3 mL of 0.5 (M) sulfuric acid in a total 10 mL solution. This corresponds to 0.04 (M) - 0.15 (M) acidity range in final dilution.

Effect of reagent

To study the influence of reagent concentration on the fluorescence intensity, different molar fold excess of reagent was added to a fixed metal ion concentration and the fluorescence intensities were measured according to the general procedure. The reagent: Mn(II) molar ratios between 11:1 and 220:1 produce almost constant fluorescence intensity beyond which intensities were greatly reduced.

Effect of micellisation

The efficiency with which manganese(II) quenches the fluorescence of murexide is much enhanced by altering its environment with the use of a suitable surfactant. In the present work a commercially available anionic surfactant - sodium dodecyl sulfate (SDS) has been utilized. It was found that the quenching efficiency increased many folds with the increase in concentration of SDS up to a certain level and then decreased. The effect obtained for the quenching of the fluorescence of murexide upon addition of manganese(II) in SDS medium was found to be in accordance with Stern - Volmer equation, which can be expressed as follows $F_0 / F = 1 + K_{SV} [Mn (II)]$ where F_0 and F are the fluorescence intensity of murexide in absence and in presence of manganese(II). The slope of the plot of F_0 / F against [Mn (II)] gives the Stern – Volmer quenching constant (K_{SV}) which is an indicator of the degree of sensitivity of the fluorophore towards the quencher. The variation of K_{SV} with SDS concentration has been shown in Figure 2. It was found that as SDS concentration increased up to 2 mM, value of K_{SV} also increased and then it decreased with further addition of SDS. The study showed that at SDS concentration of 2 mM the K_{SV} increased almost 1600 times its value in pure aqueous medium for manganese(II) concentration in the range 5 ng mL^{-1} - 1 μg mL^{-1}.

Effect of foreign ions

Large number of cations, anions and some complexing agents were studied individually and found to have negligible interference in the determination of 0.1 μg mL^{-1} of manganese(II), when present in relatively large to moderately large mass excess. The study revealed that, two thousand fold excesses of chloride, fluoride, bi-fluoride, sulfate, nitrate, thiosulfate, thiourea, thousand fold excesses of alkali and alkaline earth metal ions, Ag^+, PO_4^{3-}, tartrate, oxalate, citrate, acetate, EDTA, hydroxyl amine hydrochloride, HCO_3^-, CO_3^{2-}, NH_4^+, 500 fold excesses of Pb^{2+}, Tl^{3+}, Al^{3+}, I^-, ClO_4^-, DMG, HSO_4^-, $S_2O_8^{2-}$, 100 fold excesses of U^{6+}, As^{3+}, Sb^{3+}, La^{3+}, Zr^{4+}, Th^{4+}, Cu^{2+}, Co^{2+}, Hf^{4+}, Bi^{3+}, Ni^{2+}, 50 fold excesses of Fe^{3+}, Cd^{2+}, W^{6+}, Cr^{3+}, Zn^{2+} have no interference. During the interference studies, any insoluble substances that formed were simply removed by centrifugation and the fluorescence was measured with the centrifugates.

Mechanism

The acceleration of quenching occurs due to the concentration of the reagents within the micellar phase. This is because of the fact that quenching of the fluorophore takes place due to the direct collision of the reagents. Use of non-ionic surfactants could not produce such results.

Applications

The present method may be applied to determine manganese(II) contents in a series of synthetic mixtures as well as in certified reference material, environmental water, food and blood samples.

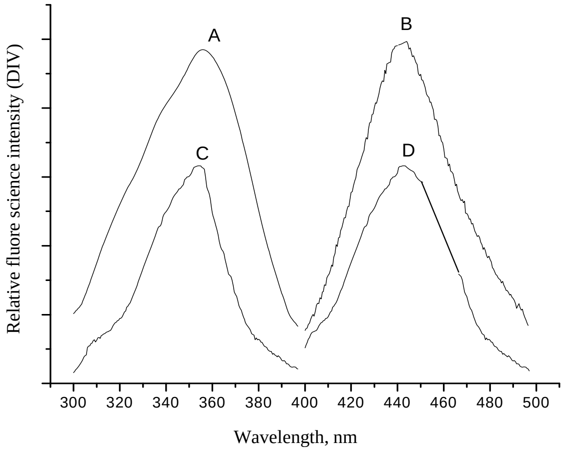

Figure 1. Fluorescence spectra for manganese(II) - murexide system in micellar solution

A & C are the uncorrected excitation spectra of the reagent (Murexide) system and (Manganese(II)–Murexide) system respectively B & D are the uncorrected emission spectra of the reagent (Murexide) system and (Manganese(II)–Murexide) system respectively.

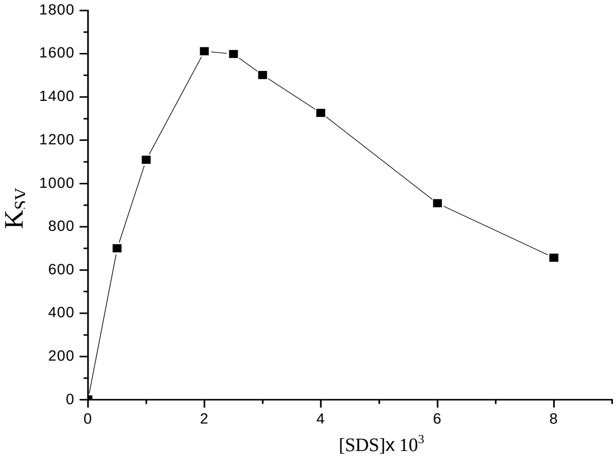

Figure 2. Variation of K_{SV} as a function of SDS concentration

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