

# Determination of sulfur contents of $\text{SO}_3^{2-}$ , $\text{S}_2\text{O}_3^{2-}$ and $\text{S}^{2-}$ based on the electrocatalytic interaction with homogeneous mediator tris(2,2'-bipyridyl)Ru(II)

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## Abstract

A sensitive voltammetric method has been developed for the determination of total or single species of sulfur anions containing sulfide, sulfite and thiosulfate. The method is based on the catalytic effect of tris(2,2'-bipyridyl)Ruthenium(II) ( $\text{Ru}(\text{bpy})_2^{+2}$ ) as a homogeneous mediator on the oxidation of those anions at the surface of a glassy carbon electrode. A reversible redox couple of  $\text{Ru}(\text{II})/\text{Ru}(\text{III})$  were observed as a solute in aqueous solution. Cyclic voltammetry study showed that the catalytic current of the system depends on the concentration of the anions. Optimum pH values for voltammetric determination of sulfite, thiosulfate and sulfide has been found to be 5.6, 10.0 and 10.0, respectively. Under the optimized conditions the calibration curves have been obtained linear in the concentration ranges of 0.8–500.0, 0.4–1000.0 and 0.5–5000.0  $\mu\text{mol L}^{-1}$  of  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{S}^{2-}$ , respectively. The detection limits have been calculated to be 0.40, 0.17 and 0.33  $\mu\text{mol L}^{-1}$  for  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{S}^{2-}$ , respectively. The diffusion coefficients of sulfite and thiosulfate have been estimated using chronoamperometry. The chronoamperometric method also has been used to determine the catalytic rate constant for catalytic reaction of the  $\text{Ru}(\text{bpy})_2^{+2}$  with sulfite and thiosulfate. Finally the proposed method has been used for the determination of total sulfur contents in real samples of water and wastewater. Moreover the sulfite content in sugar and sulfur dioxide in air has been determined with satisfactory results. © 2008 Elsevier B.V. All rights reserved.

**Keywords:**  $\text{Ru}(\text{bpy})_2^{+2}$ ; Sulfur anions; Electrocatalytic; Voltammetry

## 1. Introduction

Sulfur anions containing sulfite, sulfide and thiosulfate are important in chemical, biological, industrial and environmental protection. These anions are very reactive and unstable; and can react with each other and undergo decomposition or air oxidation. Those anions were shown to have diverse impact on plants, animals and humans [1,2]. There is a growing interest in sensitive, simple and rapid determination of sulfur species. However, the main problem in the analysis of the anions mixture usually arises from their instabilities. The determination of sulfide, sulfite and other sulfur-containing compounds in water, food and other materials is of great importance for environmental protection, food assurance and quality control

because of their potential toxicity. Since the sulfur compounds can be formed in a number of pathways and biogeochemical processes [3,4], the determination of sulfur species has been rapidly developed over the last 10 years. Several papers have been published on the determination of sulfur anions using various detection systems. Classical methods including spectrophotometry [5,6], polarography [7], fluorescence [8] and chemiluminescence [9] methods have been proposed to this purpose. These methods suffer from numerous chemical interferences and prevented from working by solution turbidity. Amperometric detection, in combination with chromatographic procedures represents a sensitive and selective scheme for monitoring sulfur-containing species [10,11].

Sulfur anions have large oxidation overpotential at ordinary carbon electrodes and one approach for minimizing overvoltage effects is through the use of electrocatalytic process at chemically modified electrode (CMEs). Electrochemically

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pretreated glassy carbon electrode with copper, palladium [12], hexacyanoferrate [13], cobalt(II) annulene [14], Prussian blue [15], and copper hexacyanoferrate modified graphite electrode prepared by mechanical immobilization method [16] have been used for electrocatalytic oxidation of sulfite, persulfate and thiosulfate. Unfortunately most modified electrodes contain certain disadvantages such as irreversible adsorption behavior, leaching of electron transfer mediator, poor long term stability, and some of them are not sensitive enough for real sample analysis. Despite the sensitivity observed with some of the chemically modified electrodes, the electrodes require regeneration to obtain a reproducible response. Therefore it is of a great importance to be able to develop a method for rapid and sensitive analysis of these species in real sample analysis. Among the proposed electrochemical techniques, the electrocatalytic techniques offer the high sensitivity and precision, and also benefit from the fast analysis in the real sample analysis.

Up to now, only a few soluble electrocatalysts have been used for a single sulfur anion determination including iron(II) complexes of 1,10-phenanthrolines for sulfide [17], iron-porphyrins for thiosulfate [18], cobalt porphyrin for tetrathionate [19] and Prussian blue for sulfite [15]. To the best of our knowledge, there is not any report for simultaneous determination of sulfur contents using soluble mediator as an electrocatalyst. That may be due to the fact that using modified electrode is simple than the other techniques. However, modified electrodes contain certain disadvantages such as irreversible adsorption behavior, leaching of electron transfer mediator, and poor long term stability and require regeneration to obtain a reproducible response.

Using linear sweep voltammetry (LSV) at fast scan rate is suitable for study of rapid electrochemical reactions. In this work we report a study of electrocatalytic application of  $\text{Ru}(\text{bpy})_2^{2+}$  on the oxidation of sulfide, sulfite and thiosulfate in aqueous media at the surface of a glassy carbon electrode. The activity of the mediator toward the electrocatalytic oxidation of  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{S}^{2-}$  at the glassy carbon electrode is described. The method offers high sensitivity, and has wide linear dynamic range, while it is independent from the interferences and allows determination of sulfur species in real sample analysis.

## 2. Experimental

### 2.1. Reagents and chemicals

All the solutions were prepared from analytical-reagent grade materials with doubly distilled water.

A  $1.0 \times 10^{-2} \text{ mol L}^{-1}$  stock solution of sulfite was prepared daily by dissolving 0.1260 g of sodium sulfite ( $\text{Na}_2\text{SO}_3$ , Merck) in water and diluting to volume with water in a 100-ml volumetric flask, and standardized by iodometric method just before uses.

A  $1.0 \times 10^{-2} \text{ mol L}^{-1}$  stock solution of sulfide was prepared daily by dissolving 0.2402 g of sodium sulfide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , Merck) in water and diluting to volume with water in a 100-ml volumetric flask, and standardized by iodometric method just before uses.

A  $1.0 \times 10^{-2} \text{ mol L}^{-1}$  stock solution of thiosulfate was prepared daily by dissolving 0.2481 g of sodium thiosulfate

( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , Merck) in water and diluting to volume with water in a 100-ml volumetric flask, and standardized by iodometric method just before uses.

$\text{Ru}(\text{bpy})_2^{2+}$  solution,  $1.0 \times 10^{-2} \text{ mol L}^{-1}$ , was prepared by dissolving 0.7482 g of tris(2,2'-bipyridyl)dichloro Ruthenium (II) hexahydrate (Aldrich) in water and diluting with water in a 100-ml volumetric flask. Universal buffer solutions (pH 2–11, 0.10 M) were prepared by dissolving and mixing of acetic acid, phosphoric acid, boric acid and treating with sodium hydroxide, using a pH-meter to control the pH.

### 2.2. Apparatus

The electrochemical experiments were performed using an AUTOLAB PGSTAT 12, potentiostat/galvanostat connected to a Metrohm three electrode cell, Model 663 VA stand, that was linked to a computer (Pentium IV, 1200 MHz) and with Autolab software. A conventional three electrode cell, containing a glassy carbon electrode as a working electrode, a carbon bar electrode as a counter and an Ag/AgCl (sat'd with  $3.0 \text{ mol L}^{-1}$  KCl) as a reference electrode, was used. A pH-meter (Corning, Model 140) with a double junction glass electrode was used to check the pH of the solutions.

### 2.3. Recommended procedure

For determination of sulfite ions, the blank solution was prepared as follows: 1.0 mL of buffer solution (boric acid, phosphoric acid, acetic acid/sodium hydroxide, pH 5.6), 1.0 mL of potassium chloride ( $1.0 \text{ mol L}^{-1}$ ) and 50.0  $\mu\text{L}$   $1.0 \times 10^{-2} \text{ mol L}^{-1}$  of  $\text{Ru}(\text{bpy})_2^{2+}$  solution were transferred into a 10-mL volumetric flask. The solution was diluted to the mark with water transferred into the three electrode electrochemical cell (glassy carbon as a working, a graphite electrode as an auxiliary and an Ag/AgCl reference electrode). The initial and final potentials were adjusted to +0.70 and +1.20 V vs. Ag/AgCl, respectively. The voltammogram was recorded to give the blank signal ( $I_b$ ) with a scan rate of  $100 \text{ mV s}^{-1}$ . The same experiment was repeated in the presence of several microliters of sulfite solution as a sample to give the analytical signal ( $I_s$ ). The difference between the blank and the analyte signal, ( $\Delta I_p = I_s - I_b$ ), was proportional to the analyte concentration. Calibration curves were constructed by plotting the net peak current ( $\Delta I_p$ ) vs. the analyte concentration.

For determination of thiosulfate and/or sulfide, the above procedure was used with a buffer solution with pH=10.0. For determination of total sulfur anions, the recommended procedure have been used except using a buffer solution pH=7.0.

### 2.4. Determination of sulfite in sugar and sulfur dioxide in air

For the analysis of sulfite species, a sample solution of sugar was prepared by dissolving 25.00 g of sugar in water and diluting to 250 ml with water. To evaluate the quantities of sulfur dioxide in air, a 15 ml volume of 10% NaOH solution was added to the flask of the air sampling apparatus and air was pumped through the flask for 5 h at  $2.01 \text{ L min}^{-1}$ . Then the solution was acidified by adding HCl ( $0.10 \text{ mol L}^{-1}$ ) to pH near 5.5 and the prepared

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