



Ultrasensitive electrochemiluminescence determination of trace Ag ions based on the signal amplification caused by its catalytic effect on Mn(II) oxidation using graphite catheter as electrode



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ABSTRACT

In this work, an ultrasensitive electrochemiluminescence (ECL) method was established for the detection of trace amount of Ag ions (Ag^+). In sulfuric acid medium, Ag(II), the electro-oxidized product of Ag(I), oxidizes manganese ions (Mn^{2+}) to produce permanganate (MnO_4^-) by using a pair of graphite catheters as electrodes. While permanganate and luminol can produce strong chemiluminescence, based on the catalytic effect of Ag(II) on Mn^{2+} oxidation, there is a good linear relationship between the concentration of Ag^+ and luminescence intensity. Under optimized conditions, the linear range of this method for Ag^+ is from 0.2 to 150 nM with a detection limit of 0.06 nM. The method was applied for determination of Ag^+ in various water samples with satisfactory results.

1. Introduction

Silver (Ag) is a precious metal and an important industrial raw material which has been widely used in cosmetics, building materials and medical products. However, the abuse of Ag^+ may lead to many serious diseases to human beings, including cytotoxicity, organ failure, and mitochondrial dysfunction [1–3]. In view of the impact of Ag^+ ions on the animals and human body, the content of Ag elements in tap water cannot exceed 0.05 mg/L [4]. In addition, based on the strong interaction of Ag ions with proteins/DNA, the two can become detection probes for each other [5–12]. Therefore, it is very important to establish a rapid, highly sensitive and selective method for Ag ions detection.

Currently, the methods for detection of Ag ions are mainly concentrated on absorptiometry [13–15], atomic emission spectrometry (AES) [16,17], atomic absorption spectrometry (AAS) [18–20], fluorescence [21–23], and electrochemical methods [24–26]. The chemiluminescence method generates excitation and light emission based on the chemical energy at normal temperature. Compared with other spectral analysis methods, the chemiluminescence method has no interference of the spectral background, and thus is a highly sensitive detection method. The chemiluminescence determination of Ag ions has also been widely reported [27].

Since potassium permanganate is an important luminescent reagent, the generation of permanganate through catalyzed oxidation of

ammonium peroxydisulfate by silver ion has been reported [7]. The chemiluminescence detection of Ag ions was conducted in this method. Furthermore, a DNA detection method has also been established. However, the above method requires the conditions of heating, and excess amount of the pre-oxidation reagent such as ammonium persulfate, which can oxidize manganese ions, thus interfere with the chemiluminescence reaction.

The ECL method [28–34], which generates chemiluminescence reagents by electrochemical method, can eliminate the above shortcomings. Currently, ECL methods based on ruthenium compounds have attracted wide attention [35–39], while based on manganese are rarely reported.

In this work, a new ECL method has been proposed for the detection of Ag ions. Ag(II), the electro-oxidized product of Ag(I), can oxidize Mn^{2+} to produce MnO_4^- in the sulfuric acid medium, while MnO_4^- and luminol can generate strong chemiluminescence. To the best of our knowledge, this is the first time to establish an ultrasensitive ECL determination method for trace Ag ions based on its catalyzed electro-oxidation of Mn^{2+} with the graphite catheter electrodes as electrodes.

2. Experimental

2.1. Apparatus and instruments

IFFS-A chemiluminescence analyzer (Xi'an Rui Mai Electronic

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Technology Co., Ltd.). UV–visible spectrophotometer (Shimadzu UV-2501CP, Shimadzu Corporation). 604D CHI electrochemical workstation (Shanghai Chen Hua Co., Ltd.). Three-electrode system: the working electrode and the counter electrode are home-made graphite catheter (6 cm in length with a diameter of 5 mm). The reference electrode was the saturated calomel electrode (SCE).

2.2. Preparation of the graphite catheter electrode

The home-made graphite catheter electrode was made by drilling along the axis of the graphite rod with diameter of 12 mm. Then the graphite catheter electrode was washed by distilled water and ethanol for three times respectively. After the electrode was soaked with 6 mol/L H_2SO_4 for 24 h. Eventually the electrode was activated by sweeping 20 cycles with a scan rate of 0.02 V/s in the range of 0–2.0 V in 6 mol/L H_2SO_4 and washed by distilled water.

2.3. Reagents and solution preparation

AgNO_3 (Shanghai Fine Chemical Materials Research Institute) was dissolved by pure water to prepare 1.00×10^{-5} mol/L AgNO_3 solution. The stock solution of manganese sulfate was 0.020 mol/L (Shanghai Fine Chemical Materials Research Institute). 0.20 mol/L H_2SO_4 , 1.0×10^{-4} mol/L luminol solution, 0.20 mol/L H_3PO_4 , 2.0 mol/L sodium hydroxide (NaOH) solution, 1.0 mol/L KNO_3 solution (Sinopharm Chemical Reagent Co., Ltd.).

5.00 mL each of MnSO_4 solution, H_2SO_4 solution and KNO_3 solution was added into a certain amount of Ag ions standard or sample solution. Later the solution was diluted with water to 100.00 mL. The mixture of 10.00 mL luminol solution and 10.00 mL NaOH solution, which was diluted to 100.00 mL, was used as a luminescent reagent.

2.4. Experimental procedure

In a typical detection procedure, the flow injection ECL system (CHI working electrode potential of 1.8 V, flow rate of 4 mL/min) was turned on, and the stable peak shape was produced when the light emission intensity was generated. Then stop flowing for 5 min for the electrolysis of Ag(I). Finally, the flow injection was turned on and the luminous intensity was determined.

3. Results and discussion

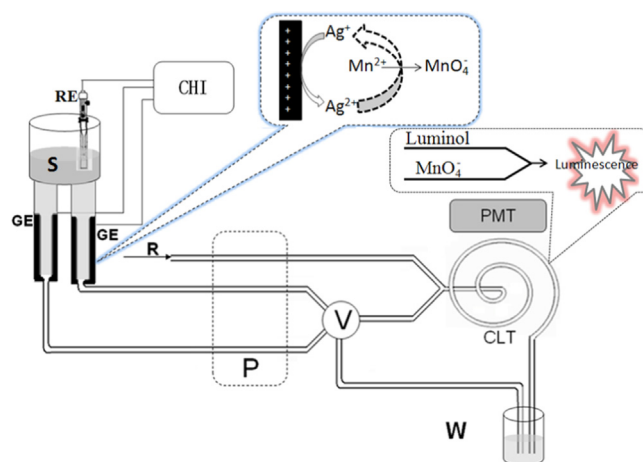
3.1. The principle and advantages of the method

The mechanism and procedure for the ECL method of Ag^+ detection was illustrated in Scheme 1. When the electrical field was applied, on the inner surface of the graphite catheter electrode (GE), Ag(I) can be electrochemically oxidized to Ag(II) which can electro-oxidize Mn^{2+} to MnO_4^- . Therefore, the luminescence intensity of the reaction of MnO_4^- with luminol in the chemiluminescence tube (CLE) is depended on the concentration of Ag(I).

3.2. The impact of electrochemical processes

3.2.1. Voltammetry curves of MnSO_4 solution under different media conditions

MnSO_4 solutions were prepared by mixing 0.50 mL each of MnSO_4 solution and KNO_3 solution, and (1) directly, (2) adding 0.50 mL H_3PO_4 solution, (3) adding 0.50 mL H_2SO_4 solution, respectively. The volume of the solution was diluted to 10.00 mL. Two glassy carbon electrodes were used as the working electrode and counter electrode respectively. The double salt bridge saturated calomel electrode was used as a reference electrode to form a three-electrode system. The linear sweep voltammetry curves were scanned in the range of 0–1.8 V. As can be seen from Fig. 1, an oxidation peak of Mn^{2+} appeared in neutral



Scheme 1. The diagram of the detection device. CHI: electrochemical workstation, GE: graphite catheter electrode, P: peristaltic pump, V: directional valve, CLT: chemiluminescence tube, PMT: photomultiplier tube, S: liquid to be detected, R: luminescent reagent, W: waste liquid.

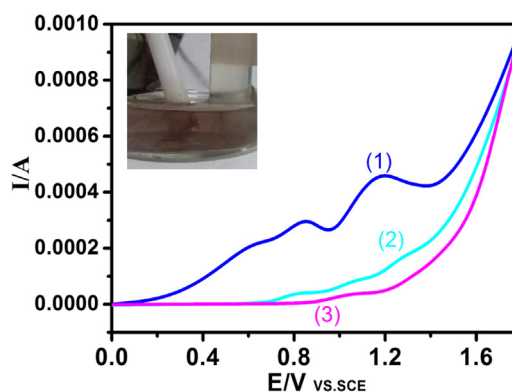


Fig. 1. Linear sweep voltammetry curves of MnSO_4 solution under different media conditions, scan rate: 200 mV/s, (1) neutral medium, (2) H_3PO_4 medium, (3) H_2SO_4 medium. Inset is the electrolytic products in neutral medium.

condition (curve 1). A large amount of brown precipitate was produced in the solution after electro-oxidation of the solution at 1.8 V for 30 min (Inset in Fig. 1), indicating the production of MnO_2 . A smaller oxidation peak at the same potential appeared in H_3PO_4 medium (curve 2). While in H_2SO_4 solution (curve 3), there was no obvious oxidation peak of Mn^{2+} in the potential range of 0–1.8 V, which indicating that Mn^{2+} cannot be oxidized in absence of catalyst under strong acidic conditions.

3.2.2. Cyclic voltammetry (CV) curves of Ag^+ solution, Ag^+ and Mn^{2+} mixture under strongly acidic conditions

CV was conducted to test the electrochemical performance of different solutions. 0.50 mL each of AgNO_3 , KNO_3 and H_2SO_4 was mixed, and then directly diluted to the volume of 10 mL to prepare solution (4). For solution (5), 1.00 mL MnSO_4 was added into the above mentioned mixture, and then diluted to 10.00 mL. As seen from Fig. 2 (curve 4), the Ag ion oxidation peak located at 1.70 V (labeled as b) appeared. And the oxidation product might be Ag(II) according to the literature [40]. The reduction peak located at 1.5 V (labeled as c) might be the reduction peak of Ag(II) which converted to Ag(I).

In the solution which containing AgNO_3 and MnSO_4 (curve 5), there was no oxidation peak appeared, but the oxidation current is obviously higher than that in the solution only containing AgNO_3 (curve 4) in the potential range of 1.6–1.7 V. In addition, the Ag(II) reduction peak c' is lower than peak c, probably due to the fact that most of the Ag(II) is

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