Simple and rapid determination of trace iodide by cathodic stripping voltammetry

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ABSTRACT

This work establishes a highly sensitive and simple stripping voltammetric method for the direct determination of trace iodide. In the presence of abounding bromide and appropriate amount of cetylpyridine bromide (CPB), the iodine was accumulated on the glassy carbon electrode surface as ion association complex ($CPBI_2Br$). After accumulation for a period of time, a linear sweep potential with negative scanning was applied and the I_2 in $CPBI_2Br$ was reduced again into the solution. Under the optimization conditions, the stripping signals (peak current) were linear relationship with iodide concentration in range of 3.81×10^{-3} µg/mL to 0.114 µg/mL and 0.127 µg/mL to 2.54 µg/mL, with a detection limit of 1.02 ng/mL ($S/N=3$) for a accumulation time of 180 s. Determination of trace iodine in pharmaceutical sample, kelp and table salt were performed with high accuracy and satisfactory recovery results.

1. Introduction

Iodine is one of the essential micronutrient for human. It plays an important role in the maintaining of the normal function of thyroid gland, which can secrete thyroxine to promote the metabolism, growth and development for human [1]. Recommended daily allowance (RDA) of iodine for adults is 140–200 µg/d [2]. For the reason that deficiency and excess of iodine both can cause thyroid disorder, and further reduce various disease. Therefore, the determination of iodine and its related compounds in many samples has important significance, such as waters [3], food [4], pharmaceutical preparations [5], clinical [6], fodder [7], biological samples [8] and environmental samples [9].

Iodine distributes widely and exists by various forms in the nature, such as iodine, iodide, iodate and methyl iodide, and cycles continuously in atmosphere, hydrosphere, biosphere and pedosphere. These features result in the problems of iodine analysis: firstly, it is easy to volatilize and lost in sample treatment; secondly, trace iodine in ecological environments is difficult to detect. At present, several types of analytical procedures have been proposed for the determination of iodide, including titrimetric [10], spectrophotometric [11], chemiluminescence [12], flow injection [13], inductively coupled plasma (ICP-MS) [14], capillary electrophoresis [15], ion chromatography [16] and neutron activation analysis (N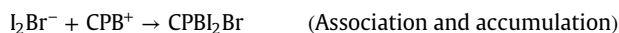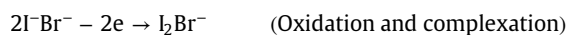AA) [17]. However, most of these techniques have some disadvantages, such as complex manipulation steps, complex sample preparation process, expensive for routine analysis, which make them unsuitable for rapid and efficient detection of iodine. By comparison, electrochemical method is less expensive and has additional advantages of fast response speed, simple operation, timesaving, high sensitivity, and real-time detection in suitable condition as an analytical technique. Hence, electroanalytical techniques, such as amperometry [18], potentiometry [20] or stripping voltammetry [19,21], have been successfully applied in the determination of trace iodine. Among them, cathodic stripping voltammetry (CSV) presents a promising way to detect trace iodide for the high selectivity and sensitivity. The basic strategy of CSV is the accumulation of iodine at the surface of working electrode is, which can be realized by the following methods : (1) Preconcentration of iodide at a modified electrode with protonated organic esters [22] or organic metal complex [23]; (2) Preconcentration of iodide according to form ion-associating compounds with surfactant, such as cetyltrimethyl ammonium bromide (CTAB) [24,25] and zephiramine [26]; (3) Preconcentration of iodide utilizing the adsorption of the analyte such as metal chelate [27]; (4) Preconcentration of iodide by formation of insoluble inorganics, such as Hg_2I_2 at mercury electrode or CuI at copper electrode [28,29]. All of the methods would dramatically improve the sensitivity, particularly to the method 2 for the enhanced sensitivity function of surfactant. Furthermore, this method is simple, inexpensive, environmentally friendly and easy to renew the electrode.

In this approach, we describe a new concept for simple and rapid determination of trace iodide in the presence of abundant

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bromide by selecting cetylpyridine bromide (CPB) as ion-associating agents (R). Iodide can be oxidized into I_2Br^- in the bromide medium and form an ion-associating compound to be immobilized on the electrode, which will increase the sensitivity remarkably. The process of the electrode reaction could be described as the following:

$$2I^-Br^- - 2e \rightarrow I_2Br^- \qquad \text{(Oxidation and complexation)}$$

$$I_2Br^- + CPB^+ \rightarrow CPBI_2Br \qquad \text{(Association and accumulation)}$$

$$CPBI_2Br + 2e^- \rightarrow 2I^- + Br^- + CPB^+ \qquad \text{(Reduction and stripping)}$$

Therefore, compared to other CSV methods reported, this method has natural immunity to the interference from Br^- or Cl^-. In addition, our procedure exhibited lower detection limit (1.02 ng/mL) and wider dynamic detection range (3.81×10^{-3} to 2.54 µg/mL) for the determination of iodine. Furthermore, the proposed method was applied to the determination of iodide in pharmaceutical dosage samples, biological samples and table salt with satisfactory results.

2. Experimental

2.1. Apparatus and reagents

Cathodic stripping voltammetric measurements were carrying out with a RST3000 electrochemical system (Zhengzhou Shiruisi Instrument Co. Ltd., Zhengzhou, China). A standard three-electrode electrochemical cell was used for all electrochemical experiments where a polished glassy carbon electrode, platinum wire and Ag/AgCl in 3.0 M KCl were utilized as working, counter and reference electrode respectively. During preconcentration, the detection solution was stirred by a magnetic stirrer bar.

All reagents were of analytical grade. Potassium iodide, potassium bromide and a variety of ionic surfactants: tetrabutylammonium bromide (TBAB), benzyltrimethylammonium bromide (BTMAB), trimethyloctylammonium chloride (TTAC), decyltrimethylammonium chloride (DTAC), dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), cetyltrimethylammonium bromide (CTAB), benzyldimethyldodecylammonium chloride (DDBAC), tetradecyldimethylbenzylammonium chloride (Zeph), benzyldimethylhexadecylammonium chloride (HDBAC), cetylpyridine bromide (CPB), octadecylamine, sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS) and non-ionic surfactants Brij, were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). Stock standard solutions of iodide (12.7 mg/mL) were prepared from dried potassium iodide by adding double distilled water and kept darkly. All ionic and non-ionic surfactant solutions were prepared as 0.01 mol/L. The potassium bromide solution was 0.1 mol/L and potassium chloride solution was 1.0 mol/L. The electrolyte was prepared daily by dilution with 1.0 mol/L H_2SO_4.

2.2. Analytical procedure

Quantitative analysis of the iodide in aqueous sample was performed using linear sweep cathodic stripping voltammetry (LSCSV). Prior to use, the glassy carbon electrode (GCE) was pre-treated by polishing with alumina (0.3 µm) water slurry and sonicating in doubly distilled water and ethanol successively. Then, the cleaned GCE was subjected to stabilization in a 0.15 mol/L H_2SO_4 by cyclic sweep between potential of 0.2 V and 0.6 V for 10 cycles at 50 mV/s scan rate. Subsequently, the electrode was inserted in known volume of standard iodide solution containing appropriate potassium bromide and surfactant. Accumulation was

performed at potential of $+0.95$ V for a certain period of time with stirring. After 30 s of quiescent time, linear sweep was carried out from 900 mV to 0 mV with 50 mV/s scan rate and the voltammogram was recorded. Finally, the GCE was maintained at least 1 min at -200 mV for renewing the electrode surface (stripping residual deposition). The sample solution was measured by standard addition method.

3. Results and discussion

3.1. Accumulation and Stripping Voltammetric behavior of iodide at GCE

The process of electrode reaction was confirmed using the analytical procedure described above with the absence of CPB, I^- and Br^- respectively (Fig. 1, curves a, b and c). When the CPB (curve a) or I^- (curve b) was absent, no any reduction peak current was discerned from 900 mV toward 0.0 mV stripping. When the Br^- was absent in solution, only a small cathodic peak could be observed at about 642 mV (curve c). It demonstrates that there is very week enrichment capacity of CPB for I^- without Br^-. In comparison, a remarkable cathodic peak became visible at 572 mV when 6×10^{-4} mol/L Br^- was spiked in above solution containing 0.381 µg/mL I^- and 4×10^{-5} mol/L CPB (curve d). These data sufficiently prove that the process of electrode reaction is just as described above.

3.2. Optimization of detection conditions

3.2.1. Selection for ionic associating agents

As described in Section 3.1, the CPB as ionic associating agent was necessary in this electrode process of determining iodine. In order to get higher detection sensitivity, a series of surfactants with different hydrophobic chain lengths and charge properties were tested as ion-associating agents. Experiments were carried out according to the analytical procedure with fixed concentration of I^- (0.381 µg/mL) and Br^- (6×10^{-4} mol/L). The added concentration for each ionic associating agent was 4×10^{-5} mol/L. The obtained results demonstrated that the cationic surfactant with
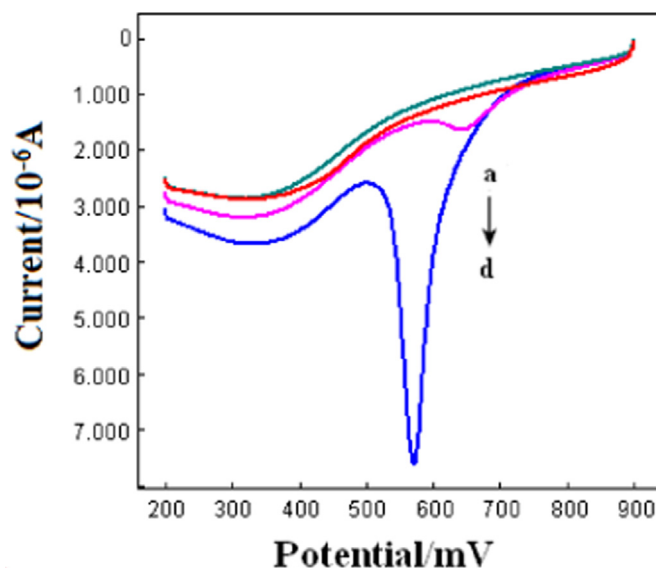

Fig. 1. Cathodic stripping voltammograms at CGE in 0.15 mol/L H_2SO_4 (a) 6×10^{-4} mol/L Br^- + 0.381 µg/mL I^-; (b) 4×10^{-5} mol/L CPB + 6×10^{-4} mol/L Br^-; (c) 4×10^{-5} mol/L CPB + 0.381 µg/mL I^-; (d) 6×10^{-4} mol/L Br^- + 3×10^{-6} µg/mL I^- + 4×10^{-5} mol/L CPB, E_{acc}=950 mV, t_{acc}=60s, scan rate: 50 mV/s.