

The versatility of salicylaldehyde thiosemicarbazone in the determination of copper in blood using adsorptive stripping voltammetry

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Abstract

The adsorptive cathodic stripping voltammetry technique (AdCSV) is used to determine copper(II) using salicylaldehyde thiosemicarbazone (N, S- donor) as a complexing agent on hanging mercury drop electrode at pH 9.3. Variable factors affecting the response, i.e. the concentration of ligand, pH, adsorption potential and adsorption time are assessed and optimized. The adsorbed complex of copper(II) and salicylaldehyde thiosemicarbazone gives a well defined cathodic stripping peak current at -0.35 V, which has been used for the determination of copper in the concentration range of 7.85×10^{-9} to 8.00×10^{-6} M with accumulation time of 360 s at -0.1 V versus Ag/AgCl. This technique has been applied for the determination of copper in various digested samples of whole blood at trace levels.

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1. Introduction

Copper is a metal of prime environmental concern. The technique of voltammetry is suitable for determination of trace elements in environmental and biological samples, because it is highly sensitive, simple and only a very simple pretreatment of the sample is required [1].

The application of voltammetric techniques in the determination of trace copper has been reviewed [2]. Of these methods, anodic stripping voltammetry on a hanging mercury drop electrode (HMDE) has gained wide acceptance for copper determination [3]. The disadvantages of this method are the formation inter-metallic compounds with co-existing metal ions at the electrode, which can cause serious error [4], and the presence of ligand such as chloride in the sample solution, which disturbs the stripping wave [5]. To solve the disadvantages of anodic stripping voltammetry for copper determination, an organic ligand was

used to complex with copper(II) with adsorptive property rather than electrolytic accumulation on the surface of the electrode.

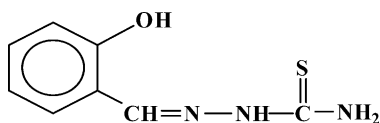
The method of adsorptive accumulation is useful to concentrate an analyte selectively for voltammetric analysis or to concentrate the ions of metals, which have low solubility in mercury. It is well known that copper forms inter-metallic compounds with other metals at electrode in anodic stripping voltammetry. These compounds interfere considerably in copper determination. So the determination of copper by measuring its reduction current after accumulation without its electrolysis is the better method. A number of studies on the use of AdSV for the determination of copper have been reported and compared [6–9]. These methods present advantages and disadvantages in relation to the sensitivity, selectivity and resolution of the adsorptive stripping peak current.

Salicylaldehyde thiosemicarbazone (Hstsc) has been used as an ionophore for the detection of mercury using PVC based ion selective electrode technique [10]. In view of excellent properties of Hstsc towards Cu(II) [11], it was

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desired to extend the analytical applications of this reagent using AdCSV. In this paper, the adsorptive cathodic stripping voltammetry of the copper complex with salicylaldehyde thiosemicarbazone is investigated.



Salicylaldehyde thiosemicarbazone

2. Experimental

2.1. Apparatus and reagents

A polarograph, Metrohm, (μ -Autolab, Type-II) equipped with static mercury dropping electrode was used. The three electrode system consists of a working hanging mercury drop electrode (HMDE), platinum auxiliary electrode and Ag/AgCl saturated with KCl as reference electrode, was used to measure the cathodic current. pH measurements were made on pH meter (Elico, LI-120).

All the reagents used were of Analytical Reagent grade. A stock solution of 1×10^{-2} M copper was prepared by dissolving 99.99% pure metal (Aldrich) in 5% nitric acid. A 1.0×10^{-3} M stock solution of salicylaldehyde thiosemicarbazone (synthesis given below) was prepared in tetra-hydrofuran. The supporting electrolyte was 0.1 M ammonia/ammonium chloride buffer (pH 9.3). Working solutions were prepared by diluting the stock solutions with de-ionized double distilled water.

2.2. Synthesis of salicylaldehyde thiosemicarbazone

Thiosemicarbazide (0.746 g) was dissolved in 75 mL de-ionized double distilled water by heating. It was then added to salicylaldehyde (1 g) and the reaction mixture was refluxed for 3–4 h. Crystals of salicylaldehyde thiosemicarbazone were obtained on cooling which were separated by filtration and were dried by vacuum pump. Crystals so obtained were re-crystallized from ethanol. A yield of 80% was obtained.

2.3. Blood sample preparation

Approximately 2 mL blood samples were taken from 40 children with special care, by vein puncture using disposable syringes and needles, and were placed into heparinized pretreated clean polypropylene tubes. The samples (1 mL) were then digested with nitric acid and perchloric acid (3:1). Digested samples were made up to 5 mL using 0.25% nitric acid. Special care was taken to avoid all contaminations. Only reagents with low background impurities were used.

2.4. Procedure

Twenty millilitres of 0.1 M ammonia/ammonium chloride buffer of pH 9.3, was pipetted into the cell along with 1.6×10^{-8} M Hstsc. Nitrogen gas was purged for 4 min. A new mercury drop was made to form and deposition was conducted for 6 min at -0.1 V, while stirring the solution. At the end of the deposition, the stirrer was switched off and 10 s elapsed to allow the solution to become quiescent. Voltammograms were then recorded by scanning the potential in the negative direction up to -0.8 V versus Ag/AgCl electrode by differential pulse stripping voltammetry with a scan rate of 5 mV/s, pulse amplitude of 50 mV/s, pulse repetition time of 1 s. The peak so obtained was labeled as $I_{p,b}$. After the background (blank) voltammogram has been obtained, aliquots of Cu(II) solution was added into the cell while maintaining the inert atmosphere inside the cell with nitrogen gas. Scanning of the potential was again performed by same method. The current amplitude was labeled $I_{p,s}$. Net peak current ($\Delta I_p = I_{p,s} - I_{p,b}$) was plotted against Cu(II) concentration to get calibration graphs.

3. Results and discussion

Figs. 1 and 2 show adsorptive stripping voltammograms of salicylaldehyde thiosemicarbazone and its complex with copper(II), respectively. These voltammograms were obtained in the presence of 0.1 M buffer of ammonia/ammonium chloride (pH 9.3), accumulation time of 6 min and deposition potential of -0.1 V versus Ag/AgCl. The reduction peak of the ligand with concentration 1.6×10^{-8} M appeared at -0.62 V. Two potential reduction sites in the ligand are C=N and C=S and these are associated with π^* molecular orbital. The π^* molecular orbital of C=S group are at low energy vis-a-vis π^* molecular orbital of C=N group. It is likely that this group (C=S) gets reduced at the said potential. This peak at -0.62 V was confirmed by the fact that there was a proportional increase in peak current/area with increase in both the concentration of reagent and increase in accumulation time. A new peak at -0.35 V appeared on adding copper(II), (in concentration range, 1.0×10^{-8} to 1.0×10^{-9} M) which was due

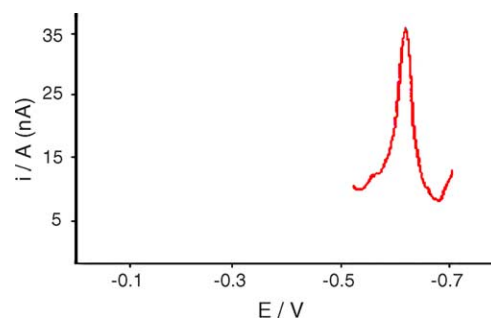


Fig. 1. Voltammogram for 1.6×10^{-8} M Hstsc after deposition of 6 min at -0.1 V in 0.1 M ammonia/ammonium chloride buffer (pH 9.3).

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