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Determination of copper by adsorptive stripping voltammetry of its complex with diazo-1H-tetrazole

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Introduction

Copper is an essential element to all living organisms. It takes part in a range of biological processes, from electron transport to oxidation of a range of substrates [1,2]. As an essential element and because of the ability to form complexes with organic substances, copper is virtually present in all living tissues [3]. Despite its essentiality copper is also toxic . In some cases, the gap between the concentration levels where copper is essential or toxic is very narrow [4]. This and the low concentration of copper found in the environment make it necessary to use very sensitive analytical procedures for its determination.

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Stripping voltammetric techniques such as anodic stripping voltammetry (ASV) and adsorptive stripping voltammetry (AdSV) used in the differential pulse mode, are two of the most sensitive and selective techniques used in the determination of trace metals [5 - 9].

The advantages of AdSV over ASV for use in chemical speciation studies of metals in aqueous solutions has been discussed [10].

Recently, procedures have been developed to determine copper using catechol [11] or to determine copper, cadmium and lead using 8-hydroxyquinoline [12] in seawater by differential pulse adsorptive stripping voltammetry .

In these laboratories voltammetric studies have been made of methods for the determination of some organic molecules by DPAdSV after derivatization [13-15]. It was observed that a reduction peak appeared when a solution of diazotized 5-amino-1H-tetrazole and Cu(II), at alkaline pH, was subjected to accumulation at a HMDE. In this paper the identification of this adsorbed compound ,the optimisation of the parameters for quantitative determination of Cu(II) and the possible interferences were studied.

Experimental

Adsorptive stripping voltammetry was carried out using a Metrohm 626 Polarecord with a 663 VA Stand in conjunction with a multimode electrode in the hanging mercury drop electrode (HMDE) mode. The three electrode system was completed by means of a glassy carbon auxiliary electrode and a silver-silver chloride reference electrode. All potentials given are relative to this Ag/AgCl electrode. A pulse amplitude of 50 mV was used with a scan rate of 10 mVs^{-1} and a forced drop time of 1 s. A Metrohm 646 VA Processor in conjunction with a VA 647 Stand was used for cyclic voltammetry; a drop with a surface area of 0.40 mm^2 and the medium stirrer speed (1920 rev. $min.^{-1}$) were used. pH measurements were made with a Corning combined pH/reference electrode using a Radiometer PHM 64 meter, standardised with pH 7.00 phosphate buffer and pH 9.18 borate buffer.

All the chemicals were from Sigma Chemical Company .

Stock solution of copper was prepared by dilution of BDH "Spectrosol" atomic absorption spectrophotometric standard solution.

5-Diazo-1H-tetrazole (DHT) was prepared by diazotization, in an ice bath, of 10 mg of 5-amino-1H-tetrazole, dissolved in 4.5 ml of 0.6 M HCl with 0.5 ml of 0.2 M sodium nitrite solution which was added slowly with continuous stirring. The diazo derivative was formed within 6-8 min. in a yield of 80 - 95%, as determined by reaction with excess N-acetyltyrosine [16]. The mixture was diluted to the desired volume with cold water and was maintained at 0 C. Under these conditions no modifications in the reaction between the diazotetrazole and copper were observed for at least 2 h.

To prevent contamination of the solutions with trace metals, all containers and pipettes were soaked in 1 M HCl and rinsed with deionised water before the use [17].

Deionised water was produced by a LiquiPure system.

Procedure

The general procedure used to produce adsorptive stripping voltammograms was as follows. A 15 ml aliquot of 0.02 M pH 8.8 bicarbonate buffer solution was placed in a voltammetric cell and the required amount of a standard DHT solution was added..

The stirrer was switched on and the solution was purged with nitrogen gas for 8 min. Subsequently a 15 s deoxygenation was made between adsorptive stripping cycles. After forming a new HMDE a 60 s accumulation was effected at -100mV whilst stirring the solution. At the end of the accumulation period the stirrer was switched off and, after 10 s had elapsed, a negative potential scan was initiated between the accumulation potential and -0.70 V. The procedure was repeated after a standard addition of Cu(II).

Results and discussion

When accumulation was effected at -0.1V in the presence of DHT, a well-defined peak became apparent at -0.37 V when a solution containing copper was submitted to differential pulse adsorptive stripping voltammetry , as shown in Fig 1.

This peak is due to the reduction of the copper-DHT complex adsorbed at the electrode surface. Its height was shown to be dependent on the copper and DHT concentrations, pH, accumulation potential, accumulation time and presence of interferences. The effect of these parameters was investigated in order to optimise conditions for the effective determination of copper(II).

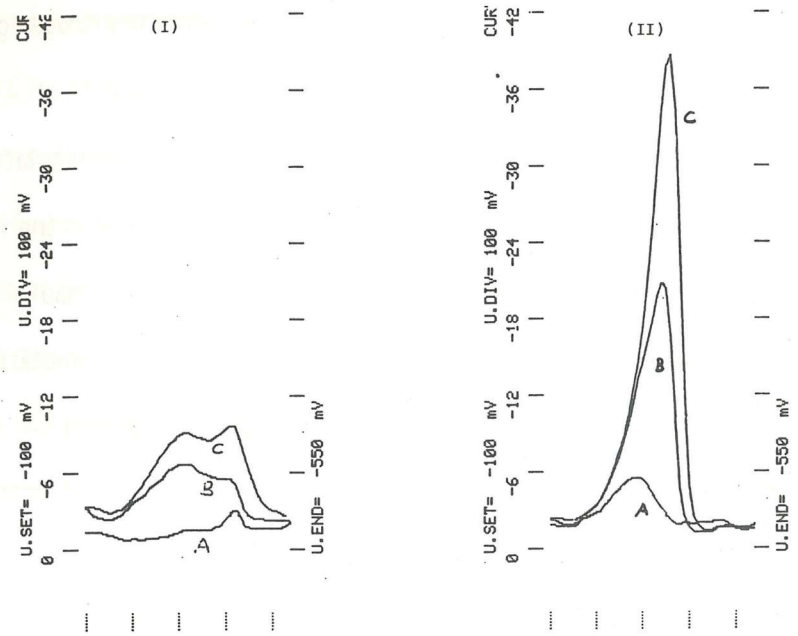

Fig 1 : Differential pulse adsorptive voltammograms of (i) Cu-AHT, and (ii) Cu-DHT complexes in 0.02 M bicarbonate buffer pH = 8.8.

Accumulation at -0.1 V for 60 s. Concentration of AHT = 5×10^{-7} M; concentration of DHT = 3×10^{-7} M. Concentrations of Cu(II) : A = blank; B = 1.0×10^{-7} M ; C = 2.0×10^{-7} M.

DC polarographic studies at the dropping mercury electrode of a 1×10^{-4} M solution of copper-DHT complex were carried out. The current was measured with a drop time of 2.4 s and a scan rate of 5 mVs^{-1}, in 0.1 M bicarbonate buffer pH = 8.8 .

Plots of applied potential as function of log $[i/i_d - i]$ gave a slope of 60 mV.

A typical cyclic voltammogram of a 5.0×10^{-7} M solution of copper-DHT complex in 0.02 M bicarbonate buffer pH = 8.8 is shown in Fig 2.

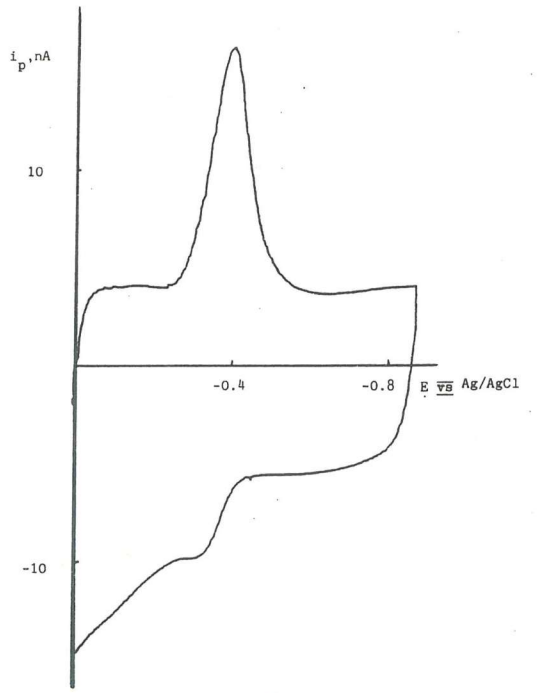

Fig 2: Cyclic voltammogram of a 5×10^{-7} M solution of Cu-DHT complex in 0.02 M bicarbonate buffer pH 8.8, accumulated at -0.05 V for 60 s. Scan rate = 50 mV/s.

The reduction process owing to reduction of copper-DHT complex is clearly seen. On the reverse scan a partially developed oxidation process associated with the copper-DHT reduction peak is observed. These experiments were carried out using the HMDE and the scans were preceded by a 60 s accumulation time. Subsequent scans were effected using the same mercury drop without further accumulation. Each scan was started at -0.05 V and scan rates of 5, 10, 20, 50 and 100 mVs^{-1} were applied.

The cathodic peak increased rectilinearly with scan rate as expected for reduction of an adsorbed species [18] and its peak potential was shifted 50 mV in the negative direction when the scan rate was increased from 5 to 100 mVs^{-1}. These shifts indicate a small degree of irreversibility at high scan rates. In the second and subsequent scans a decreasing in the copper-DHT complex peak was observed and a new peak appeared at about -0.1 V due to reduction of copper (II) accumulated at the electrode surface during the cathodic scan.

The difference in the peak potentials of the cathodic and anodic waves was found to be between 65 - 80 mV .

These results suggest a one-electron reduction process for the reduction of the copper(II)-DHT complex.

Differential pulse polarography was used in order to determine the composition of the adsorbed film. The polarograms were recorded with a drop rate of 1s, scan rate of 10 mVs^{-1} and pulse amplitude of 50 mV in 0.1 M bicarbonate buffer solution containing 1.0×10^{-4} M Cu(II) and various concentrations of DHT. The results obtained are shown in Fig 3.

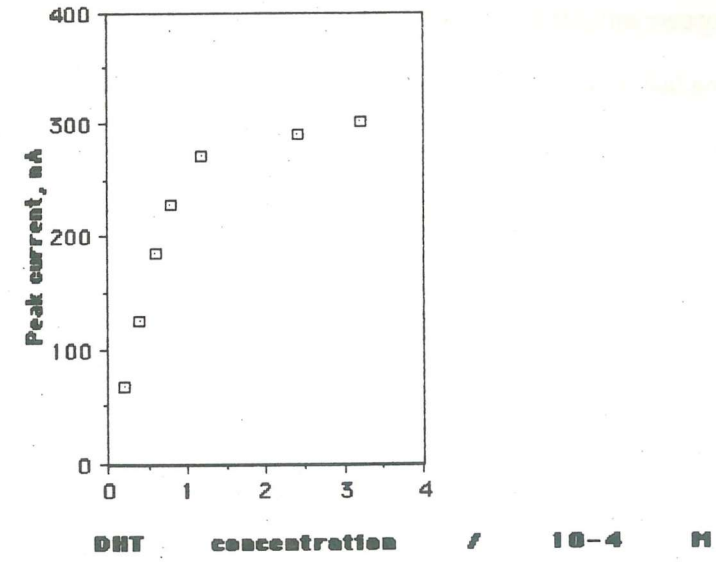

Fig 3: Effect of DHT concentration on dpp peak height of Cu(II)-DHT complex in 0.02 M bicarbonate buffer pH = 8.8. [Cu(II)] = 1×10^{-4} M

Without DHT addition the differential pulse polarogram shows the free copper(II) peak at -0.12 V. The height of this peak decreases with DHT addition and a new peak was observed at -0.37 V due to reduction of copper(II)-DHT complex. The peak potential of this peak is shifted in the negative direction with increasing in the DHT concentration. This suggests that the copper(II)-DHT reduction peak is due to adsorption of Cu(OH)DHT complex. This result supports that of Brubacker [18], Daugherty [19] and Labine [20] working with different tetrazoles.

The value for the stability constant of the copper-DHT complex was estimated from these data and was found to be 8.1×10^{11}. A value of 10^{12} is given by Brubacker [18] for the formation constant of the

copper-aminotetrazolato complex.

The DHT concentration was varied from 1 x 10^{-7} to 6 x 10^{-7} M in the presence of 1 x 10^{-7}M of copper(II). The reduction peak of the copper(II)-DHT complex increases slightly with the DHT concentration up to about 3 x 10^{-7} M and at concentration above this value a distortion was observed at the peak base. This distortion increases with the excess of DHT used and is due probably to adsorption of this excess.

The effect of accumulation potential on the height of the copper(II)-DHT complex is shown in Fig.4.

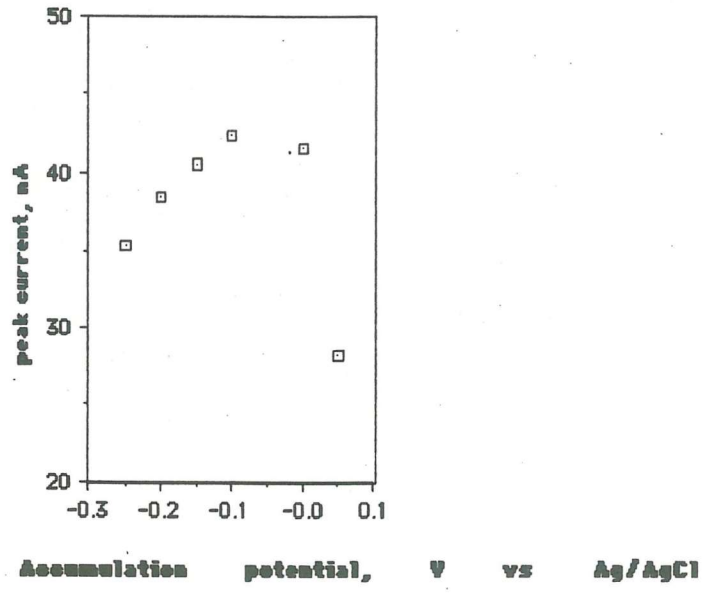

Fig. 4: Effect of the accumulation potential on the peak height of the Cu(II)-DHT complex in 0.02 M bicarbonate buffer pH = 8.8.

An accumulation potential between 0 and -0.10 V is clearly optimum. At more negative potentials the peak decreases as the reduction potential of the complex is approached. At more positive potentials strong modifications were observed on the baseline due probably to adsorption of the excess of the DHT on the electrode surface. It gives a peak ending at about -0.05 V and decreases the adsorption of the copper(II)-DHT complex.

The influence of pH on the height of the copper(II)-DHT peak is shown in Table 1.

Table 1

Influence of pH on the height of the Cu(II)-DHT peak.

[Cu(II)] = 1 x 10^{-7} M; [DHT] = 3 x 10^{-7} M; Accumulation at -0.1 V for 60 s

pH	Buffer	ip, nA
2.5	Britton-Robinson	5.2
6.9	phosphate	6.5
8.2	bicarbonate	18.3
8.8	bicarbonate	18.8
9.2	borate	14.3
9.8	borate	12.1
10.5	borate	6.0

Maximum peak height was observed at pH 8.8 but little difference in height is observed between 8.2 and 8.8. At pH 10.5 strong modifications take place at the electrode surface and the accumulation became more difficult.

Using the optimum solution conditions the peak height of the complex increases with the accumulation time up to about 3 minutes as shown in Table 2.

Table 2

Influence of the accumulation time on the height of the Cu(II)-DHT peak in 0.02 M bicarbonate buffer ph = 8.8.

[Cu(II)] = 1.5 x 10^{-7} M; [DHT] = 3 x 10^{-7} M

time, s	ip, nA
30	16.2
60	22.6
90	27.5
120	31.4
150	34.5
180	36.7

The fact that this curve does not pass through the origin suggests that the copper-DHT complex is strongly adsorbed on mercury and accumulates at the electrode surface even at very short accumulation times during the scan.

Calibration curves were prepared using the standard addition method. A typical calibration plot is shown in Fig. 5.

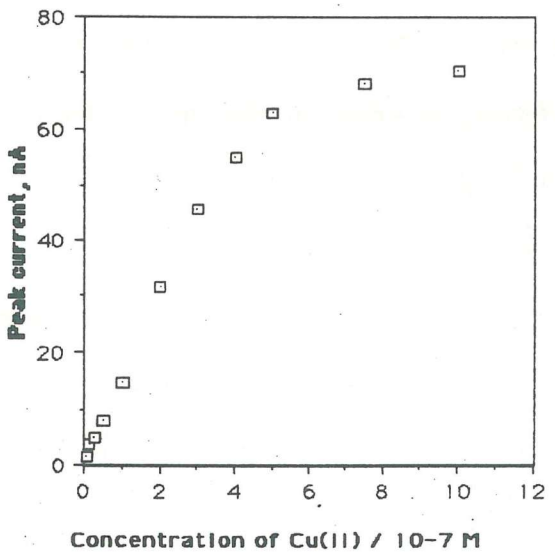

Fig 5: Calibration curve for the determination of Cu(II) with DHT in 0.02 M bicarbonate buffer pH = 8.8.

Accumulation : 60 s at -0.1 V

Calibration is clearly rectilinear up to 3 x 10^{-7} M copper(II). This point represents the stoichiometry of the 1:1 complex. Another rectilinear region was observed between 3 and 5 x 10^{-7} M of Cu(II) but the different slope suggests a formation of a new species at the electrode surface.

After this point saturation of the electrode surface was observed.

Copper concentrations as low as 5×10^{-9} M were easily determined in this laboratory without additional care.

Precision was good: six determinations at the 1×10^{-7}M copper level gave a coefficient of variation of 5.2%.

The effect of some organic and inorganic compounds capable of reacting with Cu(II) , with DHT, or of being adsorbed at the electrode surface, on the height of the copper(II)-DHT peak were investigated.

Studies of interference were made on solutions containing 1×10^{-7} M of Cu(II) and 3×10^{-7} M of DHT.

Surface active agents interfere by inhibiting adsorption of the copper-DHT complex. In the presence of 0.5 mg/l of Triton X -100 the height of the copper-DHT peak was reduced to 25% of its original.size. Other surfactants, such as quaternary ammonium compounds and sodium dodecylbenzenesulphonate gave similar results. Chelating agents (EDTA) interfere by masking the Cu(II).

No interference was observed in the presence of aniline or tyrosine even when present at 10^{-6} M levels. Cadmium (II), zinc(II), silver(I), Hg(II), Cr(III) and Pb(II) did not interfere at the 1×10^{-6} M levels.

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A STUDY OF PITTING CORROSION ON Al_2O_3-COATED STAINLESS STEEL USED IN BIOMATERIALS

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Abstract

Stainless steel has been commonly used as a biomaterial, particulary for orthopeadic applications. Recent developments have introduced not only other metallic alloys but also ceramic coated stainless steel to improve wear and corrosion resistance. In this work results are presented on the study of pitting corrosion of Al_2O_3-coated and uncoated stainless steel. A significant decrease in the passivation current was found for the coated samples.

Introduction

All materials used as substitutes of portions of bones and joints must satisfy a number of mechanical, chemical and biological requirements. A wide variety of metallic, polymeric and ceramic materials has been used in biomaterials, as attempts to satisfy all these requirements. It is however well known that most metals corrode when present in physiological environments, and those showing better corrosion resistance, like titanium, suffer from low wear resistance. On the other hand, most ceramics don't show enough toughness. An efficient way to conciliate so many different desired properties is by using ceramic coated metals [1,2].