

DETERMINATION OF COPPER BY DIFFERENTIAL PULSE CATHODIC STRIPPING VOLTAMMETRY IN THE PRESENCE OF SODIUM NITROPRUSSIDE AT pH>7

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ABSTRACT

In the present work we have studied the behaviour of sodium nitroprusside in the presence of Cu(II) using differential pulse voltammetry. For a nitroprusside solution at pH 7.7 three polarographic waves were observed. The cathodic stripping peak observed at - 0.60 V vs. Ag/AgCl for the nitroprusside-copper species, which was formed after accumulation at 0.00 V, can be used for a quantitative determination of copper in the concentration range of 10^{-7} - 10^{-6} mol dm⁻³.

INTRODUCTION

The reduction of nitroprusside ion, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ (NP), has been intensively studied for the last two decades. The electrochemical reduction of NP is an overall four electron process involving the reduction of the nitrosyl group. In alkaline solutions the NP ion undergoes two reversible one-electron reduction waves occurring at approximately - 0.30 V and - 0.60 V vs. Ag/AgCl, respectively. The first one-electron reduction gives the $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ ion which loses one CN⁻ rapidly to form $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ which is further reduced in the second wave. There are several experimental evidences of the strong adsorption of this tetracyano species. At potentials of about - 1.30 V vs. Ag/AgCl an irreversible three-electron wave occurs which is due to the reduction of the remaining $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ [1,2].

Earlier studies concerning the electrochemical determination of sodium nitroprusside in biological fluids pointed out to the occurrence of a strong interaction between copper and NP [3]. Fogg et al. [4] explored this interaction to improve the NP analytical determination by adsorptive cathodic stripping voltammetry. They observed that the second reduction peak of NP ion increases in the presence of copper (II).

They also observed a linear relationship between peak current and copper concentration in the presence of an excess of copper in solution.

In the present work, we have studied the interaction between copper and NP in order to develop a new analytical method for copper determination in water. The results presented are only preliminary.

EXPERIMENTAL

Apparatus and reagents

A Polarographic Analyser PAR 264A coupled to a Linseis 1600 x-y recorder was used. The mercury electrode stand PAR 303A was used in the HMDE mode with a medium drop size. The auxiliary electrode was a platinum wire and the reference electrode was Ag-AgCl (sat).

All chemicals were analytical-reagent grade and deionized water (Milli-Q) was used for preparing all solutions. Britton-Robinson (BR) buffer was used and pH was adjusted to 7.7 with 1 mol dm⁻³ sodium hydroxide. Nitroprusside solutions were prepared every day. For the standard metal stock solutions BDH Spectrosol metal solutions (1000 ppm) were used.

Procedure

A known volume (10.00 mL) of BR buffer was added to the voltammetric cell and the required volumes of NP or Cu²⁺ solutions were added with a micropipette. The solution was purged with nitrogen during 4 min. The experimental parameters were: accumulation time (tac) 10 s, accumulation potential 0.00 V, equilibration time 15 s, pulse amplitude 50 mV, scan rate 10 mVs⁻¹ and pulse interval 0.5 s. For each set of experimental conditions three replicate voltammograms were recorded. For the recovery tests a 10.00 mL aliquot of a Cu²⁺ solution of known concentration in BR buffer was transferred to the voltammetric cell and the required NP volumes were added directly to the cell.

RESULTS AND DISCUSSION

Figure 1 shows typical differential pulse voltammograms of a 4.50×10⁻⁶ mol dm⁻³ sodium nitroprusside solution obtained with an accumulation time of 10 s at 0.00 V. A

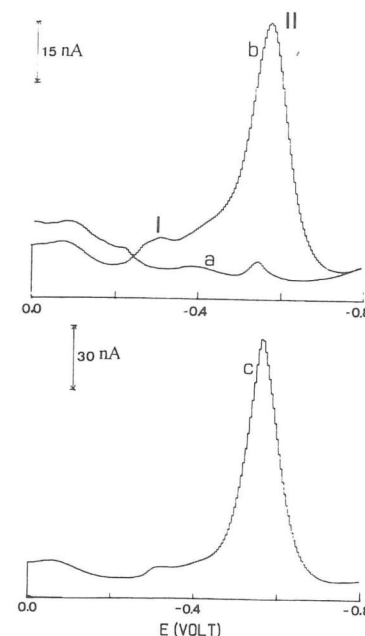


Figure 1 - Differential pulse cathodic stripping voltammograms of 4.50×10⁻⁶ mol dm⁻³ nitroprusside solution at pH 7.7. tac = 10 s at 0.00 V. a) supporting electrolyte (BR buffer); b) in the absence of copper; c) in the presence of copper ([Cu²⁺]=5.04×10⁻⁷ mol dm⁻³).

very well defined peak at approximately - 0.60 V (peak II) is clearly seen (Fig.1-b). This peak is due to the reduction of the [Fe(CN)₄NO]²⁻ ion and is considerably higher than the peak I corresponding to the first reduction of NP ion. The addition of copper (II) to this NP solution increases the peak II (Fig.1-c). However, the peak potential does not change significantly.

The variation of the accumulation time at 0.00 V changes the shape of this peak II. Fogg et al. [4] showed that, for tac=60 s and for [NP]=10⁻⁷ mol dm⁻³ at pH 6, the overall process occurring at approximately -0.60 V presented two peaks, which were very well resolved in the presence of an excess of Cu(II). These two peaks were assigned to the reduction of copper/reduced NP adsorbed species and to the reduction of the free reduced NP.

In our work all the solutions had an excess of NP and peak II presents no duplet. This single peak is suitable for the analytical determination of copper ion in solutions.

In the copper concentration range 10⁻⁷ - 10⁻⁶ mol dm⁻³ a linear relationship was observed between the current of peak II and copper ion concentration. Figure 2 shows a calibration curve of Cu²⁺ in the presence of 4.50×10⁻⁶ mol dm⁻³ NP ion. Each point is a mean value of three replicate determinations in the same solution. The calculated detection limit was 1.04×10⁻⁷ mol dm⁻³.

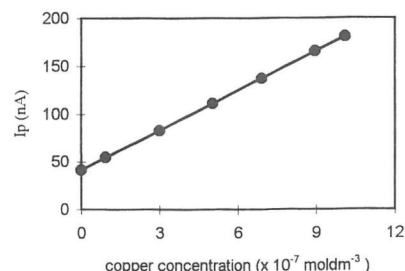


Figure 2 - Peak height vs. copper concentration. Experimental conditions as in figure 1.

This method was tested with solutions of known Cu^{2+} concentration. The recovery percentages obtained varied between 91 and 104 %.

The interference of heavy metal ions and organic matter was also studied (see table 1). We observed that the presence of Cd^{2+} , Pb^{2+} , Zn^{2+} and Fe^{3+} did not significantly affect the current signal of the copper-nitroprusside species. However, for a copper solution containing Se^{4+} , the recovery percentage was lower. The addition of fulvic acids in a concentration level near the one expected in natural waters causes a strong decrease of the signal due to copper-nitroprusside species signal. This was already expected as it is known that humic/fulvic matter is a strong complexant of copper ion.

Table 1

Recovery test for copper solution in the presence of several metal ions or fulvic acids (FA).
 $[\text{NP}] = 4.5 \times 10^{-6} \text{ moldm}^{-3}$

$[\text{Cu}^{2+}]$ added (ppm)	added metal ion	$[\text{Cu}^{2+}]$ determined (ppm)	recovery (%)
0.069	Cd^{2+} (0.1 ppm)	0.068	98.6
	Cd^{2+} (0.2 ppm)	0.068	98.6
	Pb^{2+} (0.1 ppm)	0.068	98.6
	Pb^{2+} (0.2 ppm)	0.069	100.0
0.035	Zn^{2+} (0.1 ppm)	0.034	97.1
	Fe^{3+} (0.1 ppm)	0.034	97.1
	Se^{4+} (0.1 ppm)	0.032	91.4
$[\text{Cu}^{2+}]$ added (ppm)	added fulvic acid	$[\text{Cu}^{2+}]$ determined (ppm)	recovery (%)
0.035	2 ppm	0.018	51.4
	4ppm	0.007	20.0

As the usual determination of copper by ASV is affected by the interference of Fe^{3+} , Pb^{2+} and Se^{4+} [5,6,7], this proposed analytical method using NP shows better selectivity than ASV.

Figure 3 displays the ASV peak of $5.04 \times 10^{-7} \text{ moldm}^{-3}$ copper (II) solution using

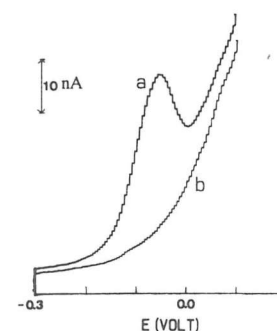


Figure 3 - Anodic stripping voltammogram of
a) $5.04 \times 10^{-7} \text{ moldm}^{-3}$ copper solution at pH 7.7
and b) supporting electrolyte. $t_{ac} = 10 \text{ s}$.

$t_{ac} = 10 \text{ s}$. Compared with the cathodic stripping voltammogram in figure 1c the ASV peak current is smaller and poorly defined than the peak of the copper-nitroprusside species in the same experimental conditions. In order to achieve the same current sensitivities in ASV, one needs a 14 fold higher accumulation time.

So, we see that the determination of copper in the presence of NP ion is more sensitive and faster.

CONCLUSION

The use of NP ion as a complexing agent may lead to the development of a new sensitive and selective method to analyse copper in waters. However, one still needs to optimize all the experimental parameters, such as NP concentration, t_{ac} , pH, E_{ac} , in order to achieve a better detection limit.

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