POLAROGRAPHIC DETERMINATION OF COPPER AFTER ENRICHMENT BY ADSORPTION OF THE 2,2'-BIQUINOLINE COMPLEX ON ACTIVATED CARBON

KEY WORDS : Adsorption on activated carbon, Differential pulse polarography, Copper determination, Sea water.

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ABSTRACT

A preconcentration method based on the adsorption on activated carbon of a binary complex of copper(I) with 2,2'-biquinoline, and subsequent polarographic determination of microamounts of copper has been developed. The adsorbed complex is destroyed by a mixture of acetonitrile and perchloric acid. The free copper ions are measured by differential pulse polarography in a supporting electrolyte of 0.2M potassium thiocyanate. The detection limit was found to be 0.33 ng/ml (3σ). This method was successfully applied to the determination of copper in sea water.

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INTRODUCTION

In order to improve the sensitivity and selectivity in the trace analysis of metal ions, a process of preconcentration previous to the selected method of analysis, has recently found wide application in analytical chemistry. Solvent extraction techniques have often been used for sample treatment prior to measurements by spectrophotometry of mixed complexes in order to remove interferent substances, to preconcentrate the analyte and to enhance the sensitivity[1-4]. Similarly, extraction-voltammetry has been shown to be an important method in trace analysis because of its inherent sensitivity, broad scope of application and relatively simple instrumentation[5,6].

Attention has also been paid to the preconcentration of trace metals on a thin layer of activated carbon using chelating agents[7-9]. In this case, it is necessary that the complexing agent present an aromatic structure that could interact with the activated carbon surface. When aromatic structures are present in the complexing agent, π-orbital overlap interaction between the aromatic structure of the molecule and the activated carbon surface is possible, resulting in a larger adsorption energy.

A preliminary separation by adsorption on activated carbon provides good selectivity and selectivity for many instrumental methods of analysis avoiding the interferences from different elements and from matrix effects. This is particularly true in anodic stripping voltammetry , where high concentration of other ions, the formation of intermetallic compounds or the proximity of the stripping peaks handicap applications of this sensitive technique.

On the other hand, the primary causes of analytical error in the trace element analysis are improper sampling, especially

contamination during sample collection sample preparation and the analysis procedure itself. It is well known that contamination is strongly concentration dependent. Consequently enrichment on activated carbon can minimize contamination

In this work, the determination of trace amounts of copper was carried out by differential pulse polarography (DPP) after preconcentration, by adsorption, into activated carbon as the 2,2'-biquinoline complex. Copper ions are released by addition of a mixture of acetonitrile and perchloric acid. The proposed method was applied to the copper determination in sea water.

EXPERIMENTAL

INSTRUMENTATION

All voltammetric measurements were made with a Princeton Applied Research (PAR) Model 174A Polarographic Analyser.

The three-electrode system consisted of a droping mercury electrode as the working electrode, a saturated calomel reference electrode and a platinum wire auxiliary electrode.

The differential pulse polarographic analyses were performed with the following settings: scan rate, 5 mV/s; modulation amplitude, 50 mV; drop time, 1 s.

Cyclic voltammetric experiments were carried out using a hanging mercury drop electrode (HMDE) as working electrode.

A 150 W mercury lamp was used to irradiate the sea water samples in order to remove organic contaminants which may interfere as competing chelating agents.

REAGENTS

All chemicals were of analytical-reagent grade. All the solutions were prepared with high-purity water from a Millipore "Milli-Q Water Purification System" device.

Standard copper (II) solution (Titrisol Merck, 1000 μg/ml). A 10 μg/ml solution was prepared by diluting the standard solution and other copper concentrations were prepared by appropriate dilution. All these solutions were stored in copper-free glass bottles.

2,2'-Biquinoline solution. An approximately 0.1% solution was prepared by dissolving 0.1 g of the compound in ethanol and diluting to 100 ml.

Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) solution. This solution was prepared by dissolving 100 g of the salt in 1000 ml of water.

Sodium acetate solution. A 20% m/v solution was prepared dissolving 200 g of the salt in 1000 ml of water.

Potassium thiocyanate solution. A 0.2M solution was prepared by dissolving 19.43 g in 1000 ml of water.

PROCEDURE

To a solution volume of 1000 ml containing less than 60 μg of copper add 1 ml of $NH_2OH \cdot HCl$ solution, 1 ml of sodium acetate solution and 2 ml of 2,2'-biquinoline solution. Then transfer the mixture to a filter funnel Hahn which contains a 23 mm Φ filter paper (Schleicher & Schnell 589/2) covered with a 50 mg thin film of activated carbon. Dry the filter covered with activated carbon, which has adsorbed the complex, at 105° C for 20 min. Remove the activated carbon from the filter and add

2.5 ml of acetonitrile and 200 µl of perchloric acid and centrifuge. Transfer 2 ml of the supernatant to a polarographic cell containing 3 ml of 0.2M potassium thiocyanate. Purge oxygen-free nitrogen during 10 min and record the polarograms in the differential pulse mode.

Sea water samples were previously subjected to UV-irradiation for 6 h in order to decompose organic substances binding trace of copper as inert complex species. The Hg lamp was located at 15 cm of the sample.

RESULTS & DISCUSSION

The 2,2'-biquinoline(I) reacts with copper ions in aqueous solutions in presence of $NH_2OH \cdot HCl$, which serves as reducing agent, to give a colored bischelated copper(I) complex. The complex formed can be easily adsorbed on activated carbon giving place to a high preconcentration of this element.

To release the copper (I) ions from the carbon it is necessary to destroy the complex. This was best accomplished by using the mixture acetonitrile : $HClO_4$ (25:2). The recoveries obtained indicate that both processes adsorption and destruction of the complex are quantitatives. This mixture also served to stabilize Cu (I) ions avoiding the well known dismutation reaction that these ions undergo in aqueous solution.

In aqueous solutions the hydrated copper(II) ion gives a single polarographic wave at approximately 0.0 V, corresponding to its reduction directly to copper amalgam. In an acetonitrile medium copper(I) ions are stabilized. Cuprous ions have a general tendency to coordinate with compounds containing electron donor nitrogen atoms, such as ammonia, amines and nitriles. In an acetonitrile medium, the behaviour would be the same.

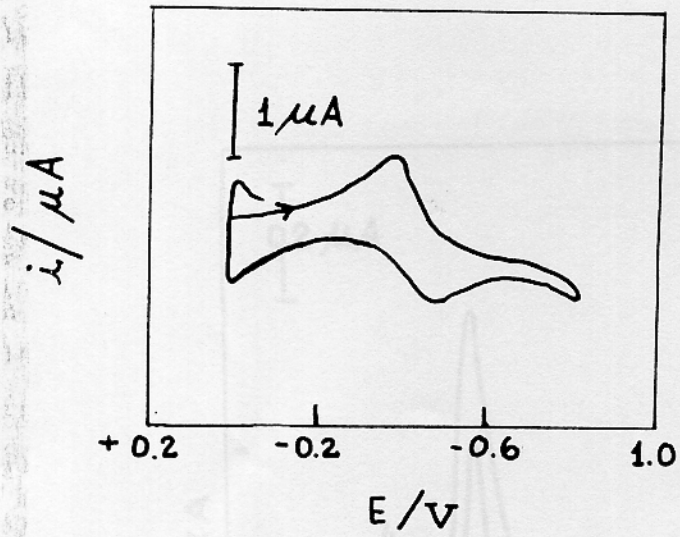

Fig. 1: Cyclic voltammogram of copper (II) at 2 μg/ml in acetonitrile-perchloric acid, HMDE, scan rate, 50 mV/s.

The cyclic voltammogram of copper (II) in 5% $HClO_4$ in acetonitrile is shown in fig.1 . The peak observed at -0.45 V can be assigned to the reduction of Cu(I) to Cu(0). The reduction of Cu(II) to Cu(I) can not be seen because it is more anodic than the dissolution of mercury[10]. In this context, aqueous solutions of Cu(II) were used to perform the standard addition method.

The differential pulse polarograms of copper(II) ions in a supporting electrolyte containing 3 ml of 0.2M KSCN and 2 ml of perchloric acid-acetonitrile mixture can be seen in fig. 2. Without KSCN in the supporting electrolyte, the differential pulse polarographic determination using the cathodic wave does not give a linear relationship between i_p and the copper concentration. Furthermore the residual current is very high which lowers the sensitivity. The same waves as in fig. 2. resulted following the abstraction of copper(I) from its bis-

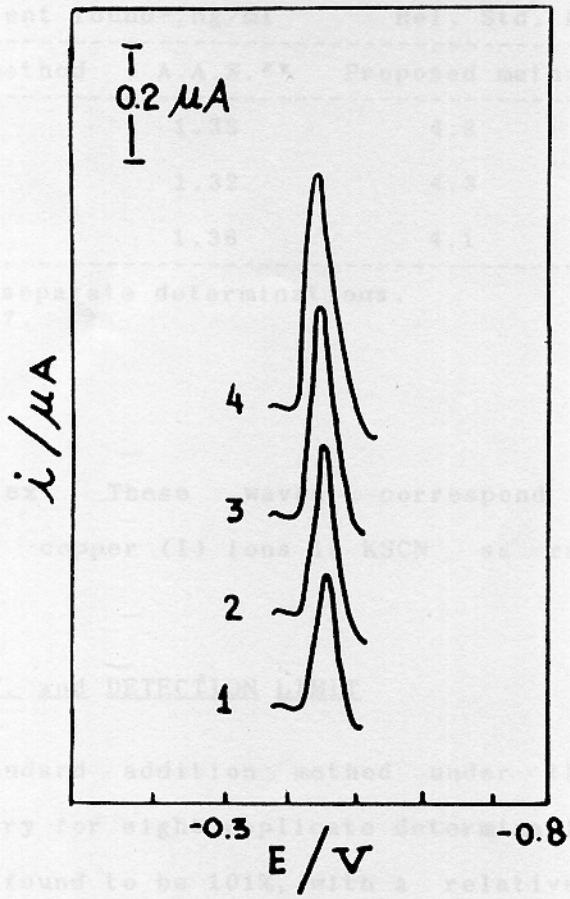

Fig.2: Differential pulse polarograms of copper ions in the mixture of acetonitrile-perchloric acid. The supporting electrolyte was KSCN 0.12M. (1) 0.4 μg/ml Cu(II) (2) 0.5 μg/ml Cu(II). (3) 0.6 μg/ml Cu(II). (4) 0.7 μg/ml Cu(II).

Table 1

Determination of Copper in sea water

Sample	Copper content found*, ng/ml		Rel. Std. Dev., %	
	Proposed method	A.A.S.**	Proposed method	A.A.S.
1	1.36	1.38	4.8	5.3
2	1.37	1.32	4.3	4.1
3	1.42	1.36	4.1	4.3

* Averages of eight separate determinations.
** Berndt et al. ref 7.

biquinoline complex. These waves correspond to the electroreduction of copper (I) ions in KSCN as reported by Meites[11].

RECOVERY, SENSITIVITY, and DETECTION LIMIT

Using the standard addition method under the chosen conditions the recovery for eight replicate determinations at the 20 ng/ml level was found to be 101%, with a relative standard deviation of 2%.

A recovery of 105% and a relative standard deviation of 4% were found for eight replicate determinations at the 1 ng/ml level of copper using the 2,2'-biquinoline complex.

The detection limit of 0.33 ng/ml was estimated on the basis of the detection limit being three times the standard deviation of the blank signal.

INTERFERENCES

Metal ions such as Ag, Cd, Co, Hg, Sn, and Sb may form complexes with 2,2'-biquinoline [12]. This makes them susceptible

to be adsorbed on the thin film of the activated carbon converting them in possible interferences. However, in a KSCN supporting electrolyte Ag(I) does not undergo reduction and the other named ions have a reduction potential peak far away from that one observed for copper ions.

It was found that the most common anions did not interfere. Cyanide ion and EDTA inhibit the biquinoline complex formation reaction at all levels. Fortunately these interferent agents are not normally present in natural waters.

APPLICATION

A synthetic sea water sample was prepared according to Berndt[7] adding 10 ng/ml of copper ions. The quantity of copper ions found was 10.36 ng/ml with a relative standard deviation of 3,5%.

The proposed procedure was applied to the determination of copper ions in sea water from the Concepción Bay (Chile). Samples of 1000 ml were taken and the enrichment factor was around 160 times. The results showed in Table 1 are in good agreement with those obtained by an independent method like atomic absorption spectroscopy[7].

It should be noted that the proposed method, using known additions of a standard solution, ensured the determination of copper without any interference from components of the matrix.

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