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Determination of Copper(II) with a Carbon Paste Electrode Modified with an Ion-exchange Resin*

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The determination of copper(II) was studied using a carbon paste electrode modified with an ion-exchange resin (Dowex 50W-X8) using differential-pulse voltammetry. The conditions necessary for the pre-concentration of copper were determined in an open circuit by ion exchange; copper levels down to 18 nM were determined. The method was applied to the determination of copper in pharmaceutical products.

Keywords: *Copper(II) determination; modified electrode; carbon paste electrode; ion-exchange resin; differential-pulse voltammetry*

In electroanalysis the most commonly used technique in the determination of elements at trace levels is undoubtedly the stripping method, as it is the most sensitive. However, numerous parameters influence its use and these are sometimes difficult to control in order to achieve excellent reproducibility of the working conditions; this directly influences the measurements performed.

With a view to minimising these physical factors, interest is growing in replacement of the mercury drop electrode or mercury film by electrodes whose active surface is more reproducible or, if not, is not critical. At the same time one also aims at avoiding the problems of diffusion towards the inside of the electrode and of the formation of metallic complexes. Further, electrodes are sought that can be used for elements that cannot be determined with mercury electrodes, either because no amalgam is formed because the substance is not adsorbed on its surface in the pre-concentration or accumulation phase, or because it is not electroactive in the range of its use.

These aims can be partially achieved by using carbon electrodes, in particular the glassy carbon variety, or using electrodes composed of modified graphite. With this kind of electrode it is possible to conserve the advantages of great sensitivity and selectivity, owing to a selective pre-concentration, and to eliminate to a large extent the drawbacks mentioned above.

Pre-concentration on the modified electrode takes place through a non-electrochemical process, after which the analyte accumulated on the surface is measured by simple voltammetry. These non-electrochemical mechanisms of pre-concentration include complexing,[1–5] ion exchange[6,7] and covalent bonding.[8]

In this paper we describe the behaviour of a carbon paste electrode modified with an ion-exchange resin used for the determination of Cu^{2+} ions; the method was chosen owing to the simplicity of the construction of the electrode, with direct incorporation of suitable amounts of an ion-exchange resin in the carbon paste. This incorporation offers a beneficial alternative for the accumulation of ions because one is dealing with a cationic resin in the acid formed and the pre-concentration reaction may be expressed as

$$nRSO_3 + M^{n+} \leftrightarrow (RSO_3)_nM + nH^+$$
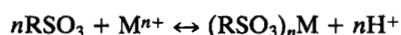
according to the efficiency of the pre-concentration phase of the distribution coefficient.

The measurement phase is performed by application of a potential to the electrode, in this instance producing reduction of the ion retained:
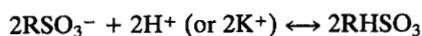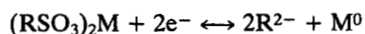
$$(RSO_3)_2M + 2e^- \longleftrightarrow 2R^{2-} + M^0$$

$$2RSO_3^- + 2H^+ \text{ (or } 2K^+) \longleftrightarrow 2RHSO_3$$

Experimental

Reagents and Materials

Copper(II) solution. Prepared from electrolytic copper.
Spectroscopic graphite. Particle size less than 42 μm.
Dowex 50W-X8 ion-exchange resin in the protonated form.
Water de-ionised using a Milli-Q and Milli-R system (Millipore) was employed throughout.

Apparatus

An Amel 448 oscillopolarograph with a Hewlett-Packard Model 862 X-Y recorder and a Metrohm Model E-506 Polarecord polarograph were used.

Throughout the study two cells of 50 ml were used, one for carrying out the pre-concentration and the other for measuring; the latter was equipped with a platinum counter electrode and a saturated calomel reference electrode (SCE).

As the working electrode a mixture of carbon paste and Dowex 50W-X8 ion-exchange resin was employed, using as the support a polyethylene tube with a geometric surface area of 1.62 mm². Contact with the carbon paste was made with a platinum wire.

A Metrohm Model 654 pH meter was used.

Preparation of Electrode

To a weighed amount of spectroscopic graphite activated electrothermally is added vaseline at a graphite to vaseline ratio of 1 : 1 m/V; this forms the carbon paste. To this product is added moist, ground ion-exchange resin and the mixture is homogenised, then introduced into the polyethylene supporting tube, achieving direct contact with the platinum wire.

Determination of Copper

A 25.0-ml volume is taken from the solution containing copper, adjusted to the conditions appropriate for each study and with constant stirring, and into it is introduced the electrode at previously chosen times under open-circuit conditions.

The electrode is then placed in the measuring cell, which contains the supporting electrolyte, and the intensity - potential curve is recorded between +0.2 and −0.9 V against SCE when a linear potential scan is made and between +0.2 and −0.4 V in differential-pulse voltammetry.

Having performed the measurement, the electrode is regenerated by successive potential sweeps in both techniques until it reaches the initial residual current that it has in the absence of copper.

The regeneration of the electrode in differential-pulse voltammetry can be achieved with the same effectiveness by maintaining the electrode at a potential of −0.8 V or at the peak potential for 5 min.

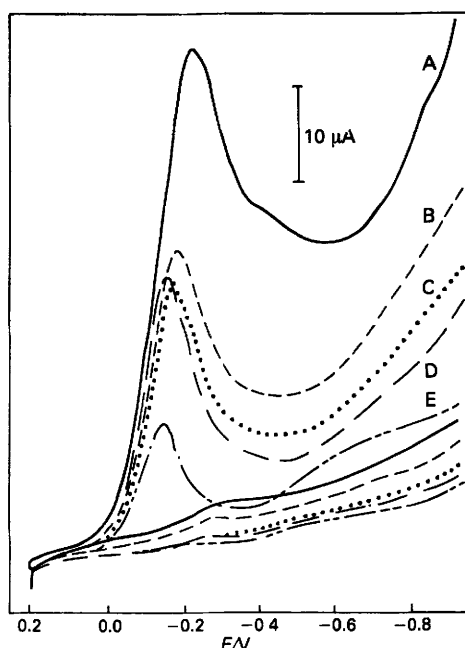The carbon paste is changed daily and the measurement solution after every ten determinations.

Fig. 1. Voltammograms obtained at different scan rates: A, 250; B, 150; C, 100; D, 60; and E, 40 mV s^{-1}

Fig. 2. Effect of sample pH in pre-concentration cell: (A) 2.0; (B) 4.0; (C) 6.0; and (D) 10.0

Results and Discussion

The studies conducted to establish the procedure for the determination of copper(II) with a carbon paste electrode modified with an ion-exchange resin consisted of two steps, one directed towards establishing the pre-concentration conditions and the other towards carrying out the measurement itself. In the former step linear scanning voltammetry was used with the aim of choosing the most suitable conditions for the retention of the ion because, in spite of knowing these conditions,[9] such characteristics are modified as the grain size of the resin decreases and because it is mixed with the carbon paste.

In order to be able to follow the retention process it is essential to establish the optimum response conditions in the linear scanning technique; to do so a study was made of its stripping variables in a non-complexing support electrolyte consisting of 1 M KNO$_3$ at pH 7.4.

The reduction of the retained copper ions converts them into metallic copper with an E_p close to -0.2 V; reversibly, the variation in E_p with the scan rate is in agreement with what is expected for this kind of system.

Fig. 1 shows the modification of the voltammograms at different scan rates, with an increase occurring in the peak as the scan rate increases and showing a linear variation with $v^{1/2}$, the residual current increasing slightly with the scan rate. For rates greater than 200 mV s^{-1}, distortion of the waves takes place, which hinders measurements; its use is therefore not recommended.

Throughout the process of ion exchange the pH of the solution to be determined plays an important role because, as is well known, the proton concentration of the solution affects the resin - solution balance and pH is therefore an important variable. It was found (Fig. 2) that for acidic solutions of pH <1 no copper ions are retained on the electrode; maximum retention is observed at pH 2.0; the retention decreases rapidly with increase in pH and shows an absence of waves at pH higher than 10. The conditions for maximum retention differ from those found for the same resin when used in a column[10]; this is logical in view of the fact that the particle size had been altered.

Another variable that must be established is the time during which the electrode should be kept in contact with the solution
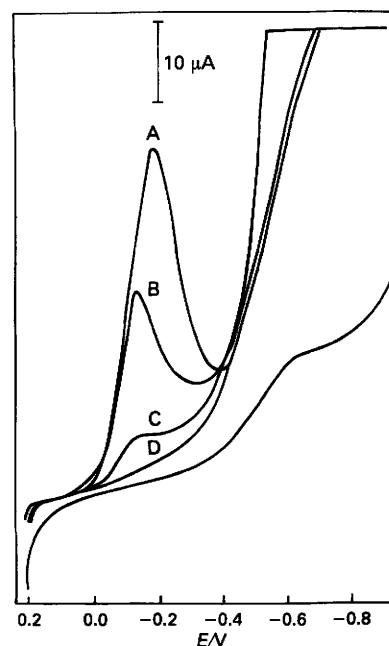

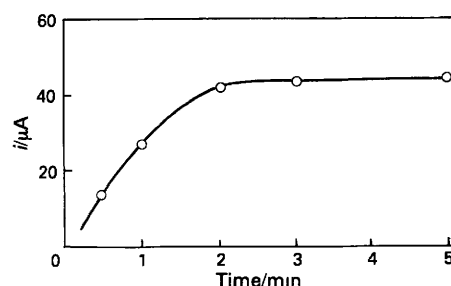**Fig. 3.** Effect of pre-concentration period on peak current from 1 µg ml^{-1} Cu^{2+} solution

Table 1. Influence of proportion of resin on peak intensity

Resin, %	i_p/µA	i_R/µA	$i_p - i_R$/µA
2.0	13.2	3.2	10.0
3.9	33.0	9.0	24.0
7.8	53.0	12.0	41.0
10.7	53.0	40.0	13.0
16.7	—	80.0	—

to be determined. Fig. 3 shows the variation in peak intensity with contact time; an increase can be seen in peak intensity up to 120 s, the time at which exchange equilibrium is reached. Variations in the stirring rate do not influence the process; as long as stirring is maintained, no control is necessary.

An increase in the proportion of resin in the carbon paste will endow the electrode with a greater capacity for exchange but, owing to the greater conductivity of the resin, this increases the resistance of the electrode, which will lead to an increase in the residual current. With a view to studying this variable, electrodes were prepared with varying proportions of resin and pre-concentration of copper(II), and measurement by linear potential scanning under the optimum conditions found earlier were performed. The results are shown in Table 1, from which it may be inferred that the proportion of resin that provides the highest peak intensity is 7.8%.
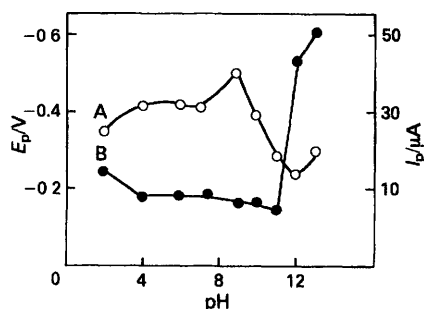
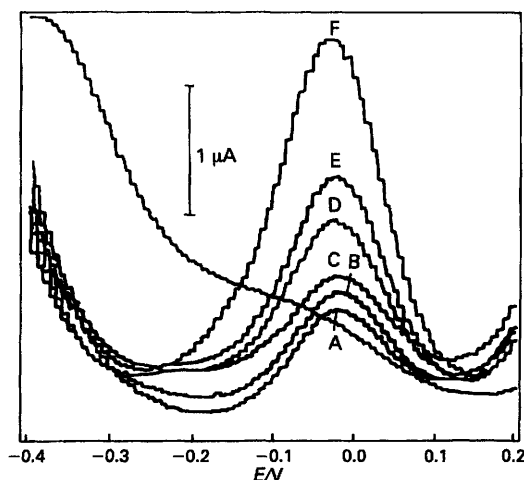**Fig. 4.** Dependence of E_p and i_p on pH in measuring cell: (A) i_p; and (B) E_p
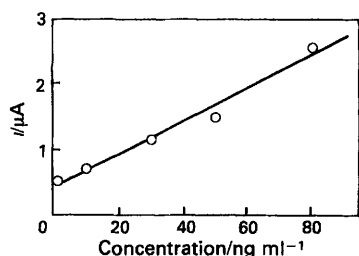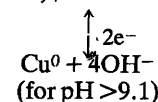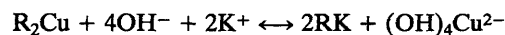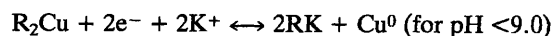

Fig. 5. Differential-pulse voltammograms obtained with increasing copper concentration: (A) 1; (B) 5; (C) 10; (D) 30; (E) 50; and (F) 80 ng ml⁻¹

electrode - solution interphase. The following are the most probable mechanisms:

$$R_2Cu + 2e^- + 2K^+ \longleftrightarrow 2RK + Cu^0 \text{ (for pH} <9.0)$$

$$R_2Cu + 4OH^- + 2K^+ \longleftrightarrow 2RK + (OH)_4Cu^{2-}$$

$$\uparrow \cdot 2e^-$$
$$Cu^0 + 4OH^-$$
$$\text{(for pH} >9.1)$$

This would account for the reduction at more negative potentials, owing to losses in the interphase produced by the diffusion of copper ions from the resin towards the solution because of the formation of hydroxy complexes.

Differential-pulse voltammetry was chosen for the measurement step, performing the retention of 80 ng ml⁻¹ Cu^{II} solutions at pH 2.0 in solutions stirred for 120 s, the measurement cell containing 0.5 M KNO$_3$ (pH 9.1). The best results were obtained with a scan rate of 8 mV s⁻¹ and a pulse amplitude of −60 mV. Increases in pulse amplitude, although they do produce greater intensities, also increase the residual current and the width of the peak, and peaks are deformed at $\Delta E = -100$ mV.

Having chosen the optimum conditions, measurements were performed for different concentrations of copper(II). Fig. 5 shows the results obtained for different solutions of copper(II), with a linear behaviour for concentrations between 1.0 and 80 ng ml⁻¹, which after treatment by least-squares yields

$$i_p \text{ (μA)} = 0.42 + 0.026 \text{ ng ml}^{-1}$$

with a correlation coefficient $r = 0.995$. From the statistical study it is concluded that the results obtained have an error of 1% and a relative standard deviation of 6%.

The method was applied to the determination of copper in pharmaceutical products containing as major species camphor, undecylenic acid, boric acid, resorcinol, salicylic acid and zinc sulphate. A good correlation was found between the results obtained with the proposed method and those obtained using atomic absorption spectrometry.

Regarding the measurement step, it is first essential to establish the optimum conditions for the measurement solution, choosing the supporting electrolyte and pH of the solution. The best electrolyte found was 1 M KNO$_3$, as it gave the best defined waves; no modifications were observed when KClO$_4$ or Na$_2$HPO$_4$ was used at the same concentration.

Fig. 4 shows the variation in potential and peak intensity found on modifying the pH of 0.5 M KNO$_3$ solution. A small variation can be seen in E_p at pH 11.0, leading to the reduction of copper(II) retained in the resin at more negative potentials and with a decrease in i_p for pH values greater than 9.0, this being the pH at which the maximum peak intensity is found.

These observed modifications may be accounted for in terms of the influence that the concentration of OH⁻ ions may exert on the mechanism of the reduction process, as the substance is converted into metallic copper and an increase in OH⁻ ions produces a competition between the ions and the exchange groups that affects the reduction process in the

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