

Determination of Cadmium(II) With a Carbon Paste Electrode Modified With an Ion-exchange Resin

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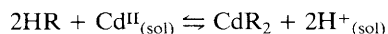
The determination of cadmium(II) was studied using a carbon paste electrode modified with an ion-exchange resin (Dowex 50W-X8) using differential-pulse and linear scanning voltammetry. Suitable conditions for the pre-concentration of cadmium(II) were determined in an open circuit by ion exchange. With the proposed method, a cadmium(II) concentration of 1.0 ng ml^{-1} could be determined.

Keywords: Modified carbon electrode; cadmium(II) determination; voltammetry

Attempts to increase the scope of application of voltammetric techniques, that are limited by the use of the classical mercury drop electrode, have resulted in the use of chemically modified electrodes. Although it is true that in electroanalytical techniques the very sensitive differential-pulse polarographic and stripping methods have been most widely used for the determination of elements at trace levels, they are also subject to the disadvantageous influences of a series of parameters that are difficult to control and which affect the reproducibility of the measurements.

In order to increase the number of elements that can be determined in the pre-concentration stage and to decrease further the determination limits of voltammetric techniques, research has been directed towards the field of electrodes, particularly those of carbon paste, by altering the pre-concentration stage. Hence, carbon paste modified with 1,2-naphthoquinone has been used to determine nicotinamide adenine dinucleotide (NADH)¹ and with 9,10-phenanthroquinone to determine 10^{-3} M ascorbic acid. Copper(II) has been determined^{2,3} by modifying the carbon paste with an exchange resin and the uranyl ion determined similarly at 5 p.p.m. ⁴ Using polyethylene as the modifier⁵ it is possible to determine phenols, chlorophenols and hydroquinones at levels of as low as 0.01 p.p.m. By a modification performed with trioctylphosphine oxide,⁶ uranyl ions have been determined with a detection limit of 0.3 ng ml^{-1} .

In this work we used a cation-exchange resin in the protonated form (HR). This was mixed to form a paste with carbon as the supporting conductor in order to determine Cd^{II} quantitatively. The resin exchanges the proton with the Cd^{II} cations that are in solution (sol) according to the reaction



One of the factors that most affects the pre-concentration is the distribution coefficient such that it is necessary to work under conditions that provide the greatest distribution coefficient and thereby allow the maximum pre-concentration.

Cadmium(II) is reduced in the analytical step and determined by linear scanning and differential-pulse voltammetry.

Experimental

Reagents and Apparatus

An Amel 448/A oscillograph with an Amel 862 X-Y recorder and a Metrohm Model E-506 Polarecord polarograph were used.

For the analysis two 50-ml cells were employed, one to perform 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, vaseline and the exchange resin was used; 0.2 g was placed in a 1.7-mm i.d. polyethylene tube. Contact with the paste was achieved with a copper wire.

A Metrohm Model 654 pH meter was used.

Stock solutions of Cd^{II} were prepared from analytical-reagent grade $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Carlo Erba) and standardised by volumetric complexometry. Polarography was used to confirm the dilutions of the stock solutions.

Spectroscopic graphite (National Trade mark, Union Carbide) with a grain size of less than $42 \mu\text{m}$ and analytical-reagent grade Dowex 50W-X8 ion-exchange resin in the protonated form were used.

Throughout, water de-ionised with Milliro and Milli-Q systems (Millipore) was used.

Preparation of Electrode

Vaseline is added to a weighed amount of electrothermally activated spectroscopic graphite at a graphite to vaseline ratio of $1:1 \text{ m/V}$; this forms the carbon paste and the ion-exchange resin (damp and ground) is added to it. After homogenisation, the mixture is placed in a polyethylene supporting tube; the carbon paste is 0.5 cm deep and is in direct electrical contact with a copper wire.

Determination of Cadmium

A measured volume (20 ml) of the Cd solution is allowed to equilibrate before analysis. The solution is stirred. The electrode is placed in the solution under open circuit conditions for a pre-determined time. The electrode is then removed from the pre-concentration solution, washed with water and placed in the measurement cell containing the supporting electrolyte. Voltammograms are recorded between 0.0 and -1.5 V versus SCE both for linear scanning and differential-pulse voltammetry.

Having made the measurement, the electrode is regenerated by successive potential sweeps until the initial residual current, corresponding to the absence of Cd, is reached. The same electrode-regenerating effect can be achieved by maintaining the electrode at a potential of -0.9 V for 5 min .

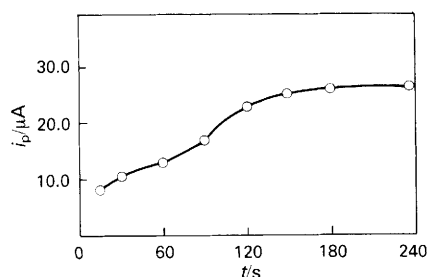
Results and Discussion

In order to establish the most suitable conditions for retention of the ion, linear scanning voltammetry was used to study the different variables in a supporting electrolyte of 0.1 M KNO_3 at pH 11.0 (modified, with KOH) using a scan rate of 100 mV s^{-1} .

To study the influence of the proportion of resin contained in the electrode, electrodes with varying amounts of resin were

Table 1. Influence of the proportion of resin paste on the peak current (i_p) and residual current for linear scanning voltammetry of Cd solutions

Resin, % m/m	$i_p/\mu\text{A}$	Residual current/ μA
2.0	9.7	1.5
3.9	23.2	3.5
10.7	11.2	6.8

**Fig. 1.** Influence of pre-concentration time. Concentration of Cd solution, 20 ng ml⁻¹**Table 2.** Influence of the pH of the solutions from which Cd is pre-concentrated on the peak potential (E_p) and peak current (i_p) for linear scanning and differential-pulse voltammetry of Cd solutions

pH	Linear scan		Differential pulse	
	$E_p/\text{mV vs. SCE}$	$i_p/\mu\text{A}$	$E_p/\text{mV vs. SCE}$	$i_p/\mu\text{A}$
4.0	-870	14.2	-870	1.6
5.0	-860	14.1	-860	1.6
7.0	-920	13.6	-870	1.6
9.0	-900	13.1	-850	1.6
10.0	-870	14.4	-840	1.6
11.0	-860	15.3	-850	2.3
12.0	-930	13.5	-900	2.0

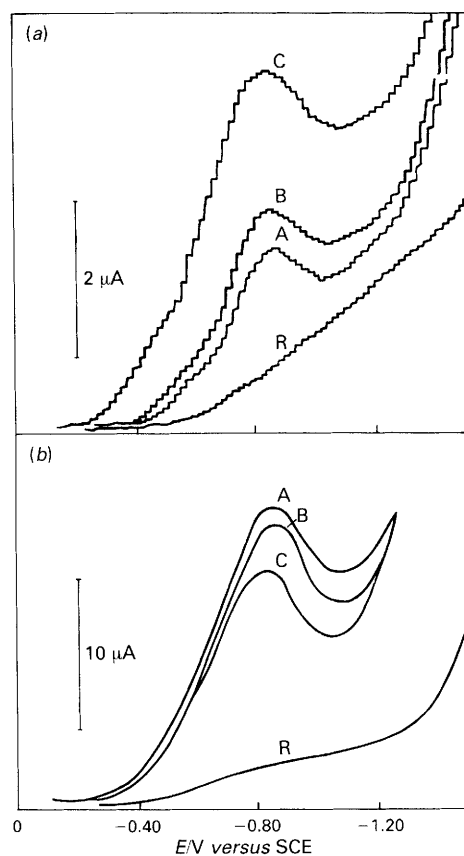
prepared using a 20 ng ml⁻¹ Cd^{II} solution stirred for 120 s at pH 7.0 (with phosphate buffer). The results obtained (Table 1) show that the residual current increases on increasing the proportion of resin until a point is reached where the wave is not defined; the most suitable amount of resin proved to be 3.9%, when large well defined peaks, of high intensity, and an acceptable residual current were obtained.

The influence of pH on the solution containing Cd^{II} was studied under the same conditions as those described above. The peak intensities change very little between pH 5.0 and 10.0; at pH 7.0, the current is 18.0 μA . At lower or higher pH the wave appears distorted. Below pH 3.0 no Cd^{II} reduction wave appears because at an acid pH the exchange reaction does not take place and the protons of the resin are reduced. A pH value of 7.0 was therefore used for subsequent studies.

The rate of exchange of Cd^{II} with the resin was studied using the above-determined conditions. It was observed (Fig. 1) that peak intensity increases with the length of time the electrode is in the pre-concentration solution; this increase is very small above 120 s. During the first few seconds a 50% pre-concentration occurs, which indicates a rapid exchange rate under the conditions chosen. According to these findings, an optimum pre-concentration time of 120 s was used.

Although the Cd^{II} solution must be stirred continuously to generate convection and to facilitate the exchange rates, no variation in peak intensity was observed on changing the stirring rate and similar results were obtained at all the rates examined.

For the measurement step, we first established the optimum conditions of the measurement solution. Having studied

**Fig. 2.** Effect of concentration of supporting electrolyte on the peak current using (a) differential-pulse voltammetry and (b) linear scanning voltammetry. Concentration of Cd solution: A, 0.10; B, 0.25; and C, 0.50 mol l⁻¹. R = Residual current

different supporting electrolytes at a concentration of 1.0 M and pH 11.0, KNO₃ was the most suitable as it yielded the greatest peak intensity for the two techniques tested. From the results obtained on modifying the pH of the electrolyte a maximum peak intensity was obtained at pH 11.0 for both techniques (Table 2). Below pH 4.0, the reduction wave of Cd^{II} was either absent or poorly defined owing to reduction of the protons. The peak potentials do not show significant changes, indicating that protons do not participate in the reduction process.

The effect of the ionic strength of the electrolyte chosen for the measurement step showed (see Fig. 2) that in the case of linear scanning voltammetry the peak intensity appears to increase as the ionic strength decreases: this effect is seen only when the peak intensity is measured from a residual current curve obtained in the absence of Cd^{II}. In differential-pulse voltammetry when the same procedure is used to measure peak intensity the opposite effect occurs. These trends are not observed if the peak heights are measured from an interpolated base line. Ionic strengths of 1.0 and 0.5 M were chosen for linear scanning and differential-pulse voltammetry, respectively.

Regarding the effect of scan rate in linear scanning voltammetry it can be seen that the peak intensity decreases as the scan rate decreases. The residual current follows the same trend and hence a scan rate of 100 mV s⁻¹ was chosen as the most suitable (Fig. 3). The peak potentials also become less cathodic as the scan rate decreases.

For differential-pulse voltammetry, with an imposed pulse amplitude of -50 mV, a decrease in scan rate leads to a decrease in intensity and causes the peaks to be less well defined. Small differences also occur in peak potential. For this technique an optimum scan rate of 40 mV s⁻¹ was chosen. The peak intensity also increases as the pulse amplitude

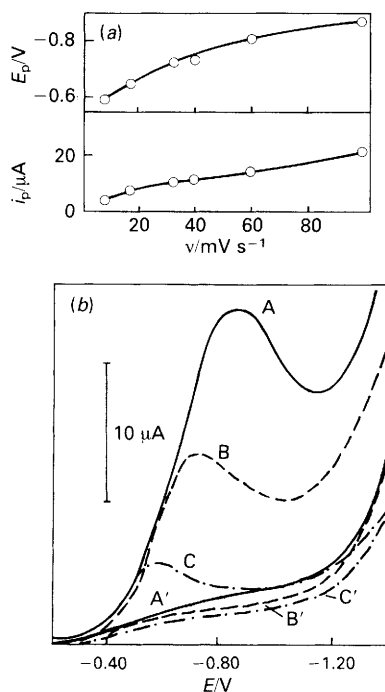


Fig. 3. (a) Variations of E_p and i_p with scan rate in linear scanning voltammetry. (b) Voltammograms obtained in linear scanning voltammetry at scan rates: A, 100; B, 60; and C, 8 mV s⁻¹. A'-C' are the corresponding residual currents

Table 3. Determination of Cd in the atmosphere of a room in which the smoking of tobacco was permitted

[Cd]/ng m ⁻³				
Day	Linear scanning voltammetry	Differential- pulse voltammetry	Graphite furnace atomic absorption spectrometry	Anodic stripping voltammetry
1	81.0	82.0	81.7	82.0
2	16.0	16.0	16.1	15.9
3	27.0	26.0	26.6	26.8

increases. The residual current follows the same trend such that a pulse amplitude of -50 mV was considered ideal.

Having chosen the most suitable conditions, measurements were made of different concentrations of Cd^{II} and the following equations were found to fit the calibration data:

$$i_p = 1.45 + 0.44c \text{ (linear scanning voltammetry)}$$

$$i_p = 0.44 + 0.037c \text{ (differential-pulse voltammetry)}$$

For concentrations in the range 20.0–60.0 ng ml⁻¹:

$$i_p = 6.78 + 0.036c \text{ (linear scanning voltammetry)}$$

$$i_p = 0.71 + 0.011c \text{ (differential-pulse voltammetry)}$$

where i_p is the peak current in μA and c the concentration of Cd^{II} in ng ml⁻¹.

Detection limits (3σ) of 0.9 and 1.0 ng ml⁻¹ were found for the linear scanning and differential-pulse voltammetry, respectively.⁷

From the statistical study it is deduced that the results obtained have a relative error of <2.0% and a relative standard deviation of <3.1%; this was for five different electrodes with 5.0 ng ml⁻¹ solutions of Cd for ten replicates.

Application

The method described was applied to the determination of Cd in the atmosphere of a room in which the smoking of tobacco was permitted. Samples were taken on each of 3 d using the NIOSH⁸ method. The duration of sampling was 3 h. The Cd concentration was then determined in each of the three samples by graphite furnace atomic absorption spectrometry, anodic stripping voltammetry at hanging mercury drop electrode and by the described method. All three methods were in close agreement (see Table 3).

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