

RESEARCH ARTICLE

***In situ* determination of copper (II) and cobalt (II) using adsorptive cathodic stripping voltammetry with hydroxamic acid modified carbon paste electrode**

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Abstract: A chemically modified carbon paste electrode (CMCPE) was prepared with N-phenylbenzohydroxamic acid and its derivative containing N-phenyl ring substituents such as o-Cl, o-Br, o-Me, o-OH, o-COOH and o-SO₃H to determine the levels of copper and cobalt in *in situ* biological and environmental systems. The stripping peak current was optimized with respect to various experimental and operational parameters. N-(o-chloro) phenylbenzohydroxamic acid (CPBHA) modified carbon paste electrode was found to accumulate copper(II) and cobalt(II) preferentially from solutions of analytes. It gives an excellent operational stability at pH 5 (acetic acid/acetate buffer), through a good linear dependence of the stripping peak current over a metal ion concentration range of $2 \times 10^{-6} - 7.5 \times 10^{-5}$ mol dm⁻³ and selectively for copper and cobalt ions with linearity (r^2) 1.0000 and 0.9997 respectively. The detection limits for copper and cobalt were 1×10^{-7} mol dm⁻³ and 3×10^{-7} mol dm⁻³ respectively.

The versatility of the application of this novel CMCPE was assessed by *in situ* determination of the copper and cobalt contents in six different synthetic samples and five real sample matrices, under the same optimum conditions. The interference from some co-existing common ions competing with the analytes by occupying the binding site of the modifier has also been studied. The results obtained by this method were compared with those obtained using flame atomic absorption spectrometer (for mg dm⁻³ levels) and electrothermal atomic absorption spectrometer (ET-AAS) (for µg dm⁻³ levels). A good agreement was observed with both methods.

Keywords: Adsorptive cathodic stripping voltammetry, chemically modified carbon paste electrode, cobalt, copper, *in situ* determination, N-Arylhydroxamic acid.

INTRODUCTION

Trace elements in biological systems have received much attention from environmental chemists because of their dual role as essential trace nutrients and as toxic elements. This interest has created a need for reliable analytical methods for the determination of biologically important trace elements. Great strides have been made in the last two decades in trace metal complexation,

particularly through the application of the techniques of competitive ligand exchange, including adsorptive cathodic stripping voltammetry (AdCSV).¹ Immobilization of organic reagents forming metal complexes with analyte species at carbon paste electrodes is highly perspective and widely used for fabricating various electrometric sensors for analytical purposes. AdCSV utilizes a suitable complexing agent as an integral part of the electrode, to enhance the electrode performance, and is considered to be one of the most sensitive methods for the determination of trace elements. It is a convenient method to minimize matrix interferences by selecting a suitable modifier to improve the sensitivity and selectivity of the electrochemical measurements by controlling the accumulation of residual species or ions during the preconcentration and reduction steps. Compared with ion selective electrodes based on polymeric membranes, the chemically modified carbon paste electrodes possess many advantages such as low ohmic resistance, very stable response, non-requirement of an internal electrode solution² and easy renewal of its surface.²

Hydroxamic acids have a strong affinity to form metal complexes, particularly, with transition metals. N-arylhydroxamic acid derivatives, in particular, are very insoluble in aqueous solution. This character has been utilized for removing toxic trace heavy metals from solutions of analytes, by using it as a modifier for carbon paste electrodes. Studies based on matrix modifiers and various techniques that eliminate spectral and chemical interference to identify the metals from the matrix^{3,4} have already been reported. However, to the best of our knowledge, a reliable direct detection method for

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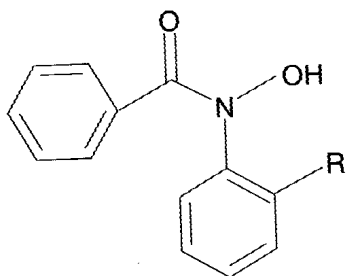


Figure 1 Structure of ortho substituted N-phenylbenzohydroxamic acid analogue

in situ determination of copper and cobalt has not been described. The main goal of this study is to identify a sensitive and a selective modifier to determine copper and cobalt *in situ* in a biological system using N-aryhydroxamic acid derivatives containing an ortho substituted N-phenyl ring (Figure 1).

METHODS AND MATERIALS

Reagents, chemicals and apparatus: Voltammetric measurements were performed with YANACO AC / DC cyclic polarograph P-900 interfaced with Graphtec X-Y plotter WX 1000. GBC 932 plus atomic absorption spectrometer was used to measure the concentration of the metal ions in the analyte and stock solutions. Nuclear magnetic resonance spectra were recorded using a Bruker 200 MHz NMR spectrometer. Infrared spectral data were recorded on Thermo Nicolet AVATAR-320 FT/IR spectrophotometer.

All chemicals were of analytical grade from Aldrich or Merck of highest purity available and used without any further purification except for vacuum drying. The solutions were prepared with triply distilled water. All glassware were soaked overnight in a 5% nitric acid solution and carefully cleaned with triply distilled water and dried in a dust-free environment prior to use. N-phenylbenzohydroxamic acid and its analogues used as the modifier for the carbon paste electrode, were synthesized as described in the literature^{5,6} and characterized by NMR and IR spectroscopy.

Stock solutions of copper(II) and cobalt(II) (1000 mg dm^{-3}) for atomic absorption spectrometry were prepared by dissolving 1.000 g of corresponding metal in a minimum volume of 1:1 conc. nitric acid and distilled water and diluting to 1.0 dm^3 with triply distilled water. Metal ion stock standard solutions of copper and cobalt for stripping voltammetry were prepared from their corresponding sulphate salts. Concentrations of metals in solutions were determined by atomic absorbance spectrometry. Calibration

standards were prepared by suitable dilution of the stock standard solutions.

Preparation of working electrode: Modified carbon paste was prepared by direct mixing of the modifier with spectral grade carbon powder and an appropriate amount of paraffin oil (approximately 0.6 g of carbon powder needs $0.20\text{-}0.25 \text{ cm}^3$ of paraffin oil) in a small mortar. As prescribed in the earlier work⁷, a pyrex glass tube (10 cm long and 3 mm inner diameter) was used to make the working electrode. Heating the tube and partially sealing at the desired position prepared a cavity of 1 cm at one end. The tube had a cut at an angle of 45° at one extreme to avoid air bubble accumulation on the carbon surface, when the electrode was submerged in the accumulation or stripping solution. Squeezing a small amount of paste into the cavity, scraping off any excess and smoothing the tip with zero grades polishing paper until the surface became a homogeneous monolayer with a shiny appearance obtained a characteristic electrode surface. An electric contact was made by means of a copper wire immersed about 5 mm into the paste. The paste was carefully removed after each measurement, prior to filling a new portion into the electrode cavity.

Procedure for obtaining voltammograms: A three-electrode electrochemical cell was used for electrochemical measurements, where a saturated calomel electrode (SCE) was used as reference and a platinum electrode was used as counter (auxiliary) electrode. The working electrode (chemically modified carbon paste electrode- CMCPE) was immersed partially in 10.0 cm^3 of the supporting electrolyte solution (acetic acid/acetate buffer, 0.01 mol dm^{-3} , pH = 5.0) and a metal ion solution of known concentration for 10 min to accumulate the metal ion on the working electrode surface under open circuit, while stirring. Then the electrode surface was washed thoroughly with triply distilled water, dipped into a fresh electrolyte solution (without metal ions) and after 14 min the stripping voltammogram of potential range 0.00 V to -0.70 V with 40 mV/s scan rate was recorded. A blank measurement was recorded without any metal ions in the electrolyte under identical conditions. All measurements were carried out at room temperature ($27 \pm 2^\circ \text{C}$) using unstirred solutions.

RESULTS AND DISCUSSION

Dependence of voltammetric response on the composition of the modifier

The voltammetric response was examined with all synthesized hydroxamic acids at seven different modifier

compositions (0, 5, 10, 20, 30, 40, 50 % w/w) of carbon paste under identical conditions. The stripping peak became increasingly sharper and more intense with increasing modifier content and the highest response was observed at 40% N-(o-chloro) phenylbenzohydroxamic acid modifier. Further increase in N-(o-chloro)phenylbenzohydroxamic acid percentage reduced the peak current. This might be due to the reduction of conductive area at the electrode surface. Hence, an electrode containing the 40% modifier was used for all subsequent measurements.

Sensitivity and selectivity of the modifier

The sensitivity and the selectivity of all synthesized hydroxamic acids were examined by considering the intensities and resolutions of the voltammetric signals obtained for working electrode modified with the above hydroxamic acids. N-(o-chloro) phenylbenzohydroxamic acid modified carbon paste electrode provided a well defined sharp peak and remarkably good separation between copper and cobalt stripping potentials under identical conditions (Figure 2).

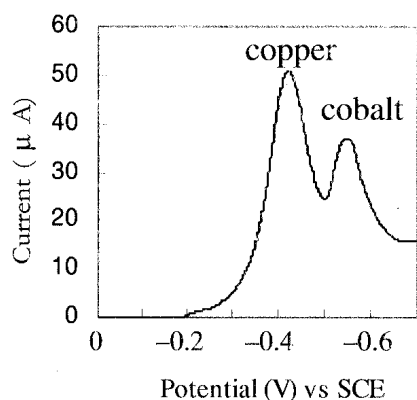


Figure 2: Variation of voltammetric stripping current with variation of working electrode potential. [$C_{Cu(II)} = 7.5 \times 10^{-5}$ mol dm^{-3} , $C_{Co(II)} = 6.5 \times 10^{-5}$ mol dm^{-3} , pH 5 (acetic acid/sodium acetate; 0.01 mol dm^{-3}) supporting electrolyte and 40 mV/s scan rate with accumulation time 10 min].

Dependence of voltammetric response on supporting electrolyte

The dependence of the composition of the supporting electrolyte on voltammetric measurements was examined for cobalt and copper ions using different electrolytes such as,

- i) pH = 3.0 (0.01 mol dm^{-3} KCl / HCl), ii) pH = 4.0 (0.01 mol dm^{-3} potassium hydrogen phthalate), iii) pH = 4.0 (0.01 mol dm^{-3} citric acid / sodium citrate), iv) pH = 5.0 (0.01 mol dm^{-3} acetic acid / sodium acetate),

- v) pH = 6.0 (0.01 mol dm^{-3} acetic acid / sodium acetate) and vi) pH = 7.0 (0.01 mol dm^{-3} KH_2PO_4 / Na_2HPO_4).

Accumulation of metal ion on the electrode was done at different pH. The height and the sharpness of the stripping peak were greatly affected by the pH of the supporting electrolyte. At low pH due to the protonation of the modifier, the stability constant of formed metal-modifier complex is low. Therefore the height of the stripping peak is comparatively low. Similarly at high pH, due the formation of metal hydroxide, the height and the sharpness of the stripping peak was diminished in magnitude. Based on the selectivity and sensitivity, pH 5 was selected as the optimum condition for the accumulation of metal ions, copper and cobalt.

Dependence of voltammetric response on accumulation time of the metal ion

The voltammetric response of both Cu-N-(o-chloro) phenylbenzohydroxamic acid and Co-N-(o-chloro) phenylbenzohydroxamic acid systems of constant metal concentration (5×10^{-5} mol dm^{-3}) with different accumulation time were examined. To ensure good hydrodynamic mass transport, a magnetic stirrer was used to stir the electrolyte during the accumulation time. The sensitivity increases with increasing accumulation time indicating the enhancement of metal ion binding on the surface of the electrode. The peak current approaches a limiting value after 10 minutes for cobalt and 12 minutes for copper. This could be due to the attainment of steady state equilibrium for metal-modifier complex formation. The accumulation time is a convenient and easy parameter to modify the saturation effect and obtain a good linear relationship between the concentrations of metal ions with peak current. Therefore, an accumulation time of 10 minutes was used for all subsequent measurements.

Dependence of voltammetric response on reduction time of the metal modifier complex

The effect of reduction time on peak current was studied for both copper and cobalt individually. The peak current increased with increasing reduction time and reached a limiting value. This could be due to the complete reduction of the metal-modifier complex on the electrode surface. Considering the linear dependence range, steady state equilibrium of accumulation and limiting value of the reduction time of both metal ions, 5×10^{-5} mol dm^{-3} metal concentration with 10 minutes accumulation time and 14 minutes reduction time was used to optimize the other parameters.

Dependence of peak current on instrumental parameter

Scan rate: The influence of the potential scan rate on the sensitivity was studied for metal ions, copper and cobalt, individually, at a metal ion concentration of $5 \times 10^{-5} \text{ mol dm}^{-3}$. An optimum sensitivity and selectivity were achieved at a scan rate of 40 mV/s. The peak width and the sharpness of the stripping peak increased with scan rate.

Dependence of voltammetric response on metal ion concentration

Under the above-described optimum conditions, the calibration graphs of copper and cobalt were obtained individually. An increase in the stripping peak current was observed with increasing metal ion concentration. The response was linear over $2 \times 10^{-6} \text{ mol dm}^{-3} - 7.5 \times 10^{-5} \text{ mol dm}^{-3}$ concentration range for cobalt ($r^2 = 0.9997$) and $2 \times 10^{-6} \text{ mol dm}^{-3} - 1 \times 10^{-4} \text{ mol dm}^{-3}$ concentration range for copper ($r^2 = 1.0000$) at 10 minutes accumulation time. To compare the linearity of both metal ions, $2 \times 10^{-6} \text{ mol dm}^{-3} - 7.5 \times 10^{-5} \text{ mol dm}^{-3}$ concentration range was used to plot the calibration curve. On the basis of the signal to background characteristics of the response, the limits of detection were found to be $1 \times 10^{-7} \text{ mol dm}^{-3}$ for copper and $3 \times 10^{-7} \text{ mol dm}^{-3}$ for cobalt at 15 minutes accumulation time. Further, lower detecting limits may be attained by allowing a longer accumulation time using standard solutions. However, in the present work, due to insufficient instrumental sensitivity, lower concentrations could not be detected. Further increase in the metal ion concentration leads to super-saturation

of metal ions on the electrode surface and results in a fluctuation of stripping peak current.

Renewal of modified electrode

In order to obtain better repeatability, the electrode surface should be renewed between measurements. This is easily accomplished by a chemical or electrochemical treatment, exposing its surface to a suitable chemical agent for dissolving the metal or complex deposited on it or by replacing the modifier containing surface by another fresh portion of the modified paste. In the present study, a completely new portion of the modified paste was used to replace the electrode surface after each measurement. The electrode surface should remain in the optimized electrolyte solution to prevent drying and destruction of the surface when it is not in use.

Analytical applications

Suitability of the new electrode: The performance of this new CMCE was evaluated by using six synthetic samples containing copper and cobalt at different concentrations. The samples were analyzed by this method and flame atomic absorption spectrometry (AAS-flame).

The calculated concentrations of metal ions in the synthetic samples and the results obtained by these two methods are summarized in Table 1. It is seen that the results obtained by this method (AdCSV) are inherently similar to those obtained by the AAS method.

Application to real samples: The performance of the proposed electrode in real sample matrices was examined with the following samples. i) Mahaweli river water

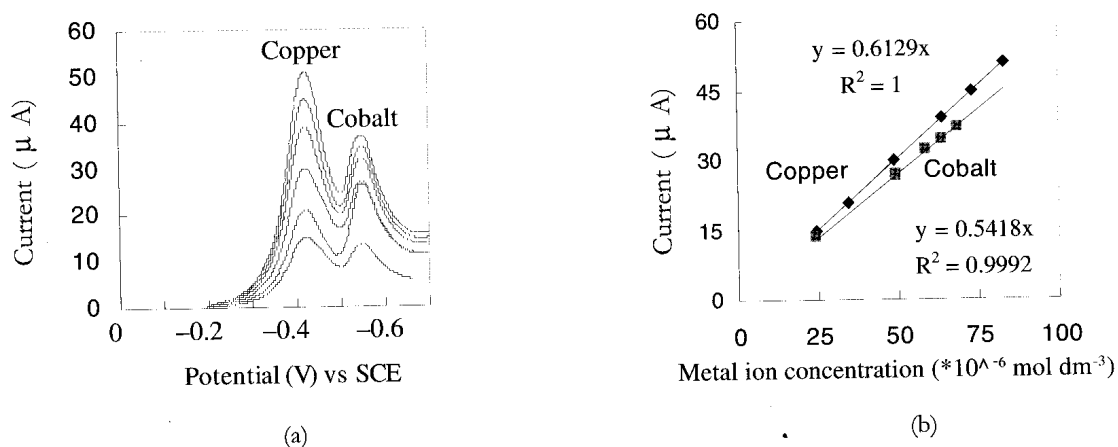


Figure. 3: a) Dependence of stripping peak current of Cu(II)/Co(II) system on potential b) Stripping peak current of copper and cobalt as a function of metal ion concentration at pH 5 (acetic acid/sodium acetate; 0.01 mol dm^{-3}) supporting electrolyte and 40 mV/s scan rate with 10 minutes accumulation time.

Table 1: Comparison of concentration of metal ions estimated by AAS and AdCSV with expected values

Sample	Metal	Concentration of Copper and Cobalt in mg dm ⁻³		
		Expected	*AdSV	AAS
1	Cu	1.5552	1.5552	1.5555
	Co	1.4470	1.4674	1.4668
2	Cu	2.1773	2.1773	2.1778
	Co	2.8941	2.8801	2.8830
3	Cu	3.1104	3.1104	3.1111
	Co	2.8941	2.9347	2.9359
4	Cu	4.0435	4.0436	4.0445
	Co	3.4729	3.4782	3.4805
5	Cu	4.6656	4.6656	4.6666
	Co	3.7623	3.7499	3.7507
6	Cu	5.2877	5.2877	5.2888
	Co	4.0517	4.0216	4.0225

* Average of three determinations: ± 0.0007 for copper and ± 0.0031 for cobalt

obtained from the Kala Oya basin (a major irrigation basin in Sri Lanka), ii) tap water obtained from the water supplying system of the city of Colombo, Sri Lanka, iii) laboratory wastewater obtained from the elementary chemistry laboratory of the University of Colombo, iv) commercially available mineral water in PET bottles bought at a local shop, v) industrial wastewater obtained from a small scale ceramic factory in Colombo and vi) a solution of AR grade salt (to monitor the assay). Due to the inability to find more real samples of certified composition, standard addition method was applied for $\mu\text{g dm}^{-3}$ levels. This minimizes the experimental error and increases the accuracy and precision. All water samples were filtered through a Teflon filter (pore size $0.45 \mu\text{m}$) and laboratory and industrial wastewater samples were boiled with 6 M HNO_3 in order to remove the interfering reducing agents, before adding the copper and cobalt stock solutions. The samples are labeled as tap water = [T], drinking water = [D], river water = [R], industrial wastewater = [I], laboratory wastewater = [L] and aqueous solution of Fluka brand sodium acetate salt = [A]. The results obtained for this analysis are given in Table 2.

From the results summarized in Tables 1 and 2, it is seen that an excellent agreement exists within the results obtained by the two methods of analyses. The

N-(o-chloro) phenylbenzohydroxamic acid modified carbon paste electrode may prove to be an extremely useful alternative electrode for *in situ* determination of copper and cobalt from solutions of analytes without any significant matrix interferences.

It was found that mixing of both metal ions did not cause any significant difference in the peak potentials. The influence of repeated measurements on the sensitivity and reproducibility of copper and cobalt peaks were examined by making five replicate measurements under identical conditions. There were no significant changes in the selectivity and the detection limit. Proper renewal of the electrode surface overcomes this problem as confirmed by the absence of the oxidized peak in the subsequent voltammograms within the stipulated potential range in the absence of metal ions.

Interferences

In order to evaluate the selectivity of this modifier, the influence of some common cationic and anionic species were investigated by systematically adding these species to synthetic samples containing copper and cobalt in the same concentrations. Because of the selective accumulation of metal ions by N-(o-chloro) phenylbenzohydroxamic acid in an open circuit at the said optimized condition, most of the common metal

Table 2: Comparison of the results obtained with the proposed method and with ET-AAS

[Metal in sample] / $\mu\text{g dm}^{-3}$							
Method	Metal	[A]	[D]	[R]	[T]	[I]	[J]
AdCSV	Cu(II)	0.045	0.054	5.248	7.162	352.590	207.430
	Co(II)	*	*	0.009	0.099	77.314	222.679
AAS	Cu(II)	0.046	0.057	5.300	7.210	355.100	209.150
	Co(II)	*	*	*	0.100	78.760	224.070

ions do not give any significant interferences in the analysis. It was observed that the determination of copper and cobalt were free from the interference of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Al^{3+} , Mn^{2+} , Cl^- , Br^- , F^- , CO_3^{2-} , HCO_3^{2-} , PO_4^{3-} , $\text{C}_2\text{O}_4^{2-}$, SO_4^{2-} , CH_3COO^- and NO_3^- upto 2000 fold molar excess, I^- upto 1000 fold molar excess, Zn^{2+} upto 500 fold molar excess and Pb^{2+} and NH_4^+ upto 100 fold molar excess with both copper and cobalt. A 50 fold molar excess of Ni^{2+} and Fe^{3+} with respect to copper did not interfere the analysis. However Fe^{3+} forms a relatively more stable complex with N-(o-chloro) phenylbenzohydroxamic acid and thus prevents complex formation and accumulation of Cu(II) and Co(II) at the electrode surface. The interference of halide ions such as Br^- and I^- could be removed before the analysis by boiling the analyte solution with $6 \text{ mol dm}^{-3} \text{ HNO}_3$.

CONCLUSION

The work presented here focuses on the use of AdCSV for the simultaneous determination of copper and cobalt using a well optimized N-(o-chloro) phenylbenzohydroxamic acid modified carbon paste electrode. This new modifier ventures into analytical application with improved qualities and utilities of trace elements compared with other modifiers used in earlier studies, with respect to simplicity of the electrode preparation, reproducibility, rapid renewal of electrode and low background current. A sensitive open circuit accumulation of the metal ions on the electrode surface is one of the great advantages of this new electrode. A previous study reported⁷ the failure of open circuit accumulation of Co(II) in N-(p-chloro) phenylcinnamohydroxamic acid modified carbon paste electrode, and a closed circuit accumulation was employed. The cathodic stripping technique with open circuit accumulation described here is free from the interference due to formation of intermetallic compounds

with interfering species which is a common problem that often plagues anodic stripping analysis⁸. Due to the very low solubility of N-(o-chloro) phenylbenzohydroxamic acid in aqueous solution, the proposed electrode generates a good remarkable operational stability for adsorptive cathodic stripping voltammetric analysis.

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