

Differential Pulse Cathodic Stripping Adsorption Voltammetric Determination of Trace Amount of Copper Using Artificial Neural Network for Optimization

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Résumé

Nous présentons une nouvelle méthode hautement sélective pour la détermination du cuivre(II) ; elle est basée sur la redissolution cathodique après adsorption du complexe de Cu(II) avec le xylénol orange à une électrode de mercure à gouttes tombantes. Les conditions instrumentales et les facteurs chimiques ont été optimisés en se servant du réseau neuronal artificiel. Les conditions optimales ont été obtenues à pH 2.0, avec une concentration en xylénol orange de 3.0 μM , un potentiel d'accumulation de -0.60 V , un temps d'accumulation de 90 s, une vitesse de balayage de 15 mV/s et une amplitude d'impulsion de 80 mV. Sous ces conditions optimisées, nous avons obtenu une droite de calibration pour les concentrations de Cu(II) dans la gamme de 1.0-50.0 ng/mL, pour un temps d'accumulation de 90 s. Une limite de détection de 0.35 ng/mL Cu(II) a été atteinte. Pour dix déterminations successives de 10 et 40 ng/mL de Cu(II), nous avons obtenu des écarts-types de 2.6% et 1.2% respectivement. Nous avons évalué la validité de méthode en analysant le cuivre dans l'eau et dans des échantillons d'alliage.

Abstract

A highly selective new method is presented for the determination of copper(II) based on cathodic adsorptive stripping of the complex of Cu(II) with

xylénol orange at a hanging mercury drop electrode. The instrumental and chemical factors were optimized using an artificial neural network. The optimized conditions were obtained at pH 2.0, xylénol orange concentration of 3.0 μM , accumulation potential of -0.60 V , accumulation time of 90 s, scan rate of 15 mV/s and pulse height of 80 mV. Under the optimized conditions, a linear calibration curve was obtained for the concentration of Cu(II) in the range of 1.0-50.0 ng/mL with an accumulation time of 90 s. A detection limit of 0.35 ng/mL Cu(II) was achieved. For ten successive determinations of 10 and 40 ng/mL of Cu(II), relative standard deviations of 2.6% and 1.2% were obtained, respectively. The ability of the method was evaluated by analysis of copper in water and in alloy samples.

Keywords: copper, cathodic absorptive stripping, hanging mercury drop electrode, xylénol orange

Introduction

Copper has widespread use in industries such as metallurgy, electronics, heating, etc. In addition, copper is a metal of prime environmental concern. Several electrochemical stripping procedures, including anodic stripping voltammetry (ASV) and adsorptive cathodic stripping voltammetry (AdCSV), have been reported for the determination of copper (1-7) based on electrolysis or adsorptive accumulation of the ions onto a hanging mercury drop electrode (HMDE). Although these procedures offer the desired sensitivity, they suffer from practical difficulties. The main problems with ASV are the overlapping of positive peak potentials of copper with

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mercury and the formation of inter-metallic compounds. In order to eliminate the limitations of anodic stripping voltammetry for copper determination, an organic ligand is used to complex copper(II); this complex has an adsorptive property rather than an electrolytic accumulation on the surface of the electrode. A number of studies on the use of AdSV for the determination of copper have been reported (3,5). All of the above methods suffer from many interference ions and/or have a higher limit of detection or a smaller linear dynamic range. The proposed method has a large dynamic range plus better selectivity for copper determination.

The selection of the voltammetric factor values and the number of experiments was performed using an experimental design method. It can be shown that in order to produce an orthogonal experimental design, the number of experiments must be a multiple of a power of the number of levels, l , so that $N=kl^r$, where r is at least 2, k is equal to 1 and r to the minimum value; this implies that $N=l^2$. Hence, for a five-level design, 25 experiments should be performed. In fact, at least the number of experiments should be equal to the square of the number of levels (8).

There are many methods for optimization of factors, such as factorial design, simplex and artificial neural network. Artificial neural network (ANN) is a modeling method that can deal with non-linear systems, and there is no need to know the exact form of the analytical function on which the model should be built (9-12). Therefore, ANNs are suitable for experimental condition optimization since the relationship between the evaluating signal and the experimental input factors is complex, nonlinear and cannot be expressed with a certain mathematical formula. The feed-forward neural network consists of an input layer, one or more hidden layers and an output layer. The network trains by calculating an error between desired and actual output and propagating this error back to each node in the network. The basic configuration used here consisted of a linear input layer, a hidden layer of neurons with sigmoidal transfer function, and an output layer with one neuron with linear transfer function. The sigmoidal hidden layer is critical as it allows the network to learn non-linear relationships between inputs and output (13). The general equation for the correction of weights with momentum was used to decrease the time for convergence and also to prevent networks from becoming trapped in a local minimum (14).

In this paper, a selective and simple method for the adsorptive voltammetric determination of Cu(II) is

proposed. The method is based on the effective accumulation of Cu(II)-xylenol orange complex on a HMDE followed by reduction. An artificial neural network has been used to optimize the experimental variables, and it works very well for the nonlinear system.

Experimental

Apparatus:

A Princeton Applied Research (PAR, EG&G) Model 384B polarographic analyzer system was used. A computer (Pentium III) with Sigma Plot software and a plotter, Model DMP 40-44, were used for data processing and printing. A conventional three electrode system, A PAR 303A, comprised of a small-sized hanging mercury drop electrode (HMDE) with a surface area of 1.6 mm², a platinum wire counter electrode, an Ag/AgCl (in saturated with KCl) reference electrode, and a PAR Model 305 stirrer were used in all experiments. All reported potentials were referred to the Ag/AgCl electrode. Solutions were deoxygenated with high-purity nitrogen for 4 minutes prior to each experiment, and the experiments were performed under a nitrogen atmosphere. A Perkin-Elmer atomic absorption spectrometer (Model 2380) was used during real sample analyses.

Reagents:

All reagents used were analytical reagent-grade, and doubly distilled water was used throughout.

A xylenol orange (XO) solution, 1.0×10^{-4} M, was prepared by dissolving an appropriate amount of the compound (Merck) in distilled water.

A stock solution of Cu(II), 1000 mgL⁻¹, was prepared by dissolving an appropriate amount of copper nitrate (Merck) in distilled water.

The buffer solution was prepared from Briton Robinson buffer (0.5 M) (14).

Recommended procedure:

The supporting electrolyte solution (10 mL of 0.02 M Briton Robinson buffer solution, pH 2.0) containing 3.0×10^{-6} M xylenol orange was pipetted into the cell and purged with nitrogen for at least 4 minutes. The adsorption potential at -0.60 V vs. Ag/AgCl was applied to a fresh mercury drop in quiescent solution, and adsorption was carried out from the stirred solution for a period of 90 seconds. After that, a differential pulse stripping

Table 1. Selected levels for each factor

Level	pH	XO (μM)	E_{ac} (V)	t_{ac} (s)	scan rate (mV/s)	pulse height (mV)
-2	1.3	0.3	0.2	30	2.0	40
-1	2.0	2.0	-0.1	60	5.0	50
0	3.0	4.0	-0.4	90	10.0	60
+1	4.0	6.0	-0.7	120	15.0	70
+2	5.3	10.0	-1.0	180	25.0	80

voltammogram was recorded from 0.20 to -0.15 V with a potential scan rate of 15 mV/s and pulse amplitude of 80 mV. After the background voltammogram was obtained, aliquots of copper(II) standard solution were introduced into the cell while maintaining a nitrogen atmosphere, and a differential pulse stripping voltammogram was recorded as described above to give the sample peak current. All data were obtained at room temperature.

The experiments were designed as described by R. G. Brereton (8). In this experiment, we studied the effects of 6 factors including pH, concentration of XO, potential and time of accumulation, scan rate, and pulse height on the peak current. Then five levels for each factor were selected (Table 1). Twenty five solutions were prepared with different pH and XO concentration, and 25 experiments were designed based on the experimental design. The ANN input layer consisted of the six voltammetric factors which are shown in Table 1. The output layer consisted of Cu(II)-XO peak current. A back propagation program was written in MATLAB (the Math works Inc., version 6.0) by the authors using a Pentium(III) computer. The optimum values of the factors were calculated with the program. Under the optimized conditions, the calibration graphs were prepared by plotting peak current against Cu(II) concentration.

Sample preparations:

Water samples were used directly after filtering with a filter paper (Whatman, No. 1) and UV irradiation for 2 hours with a 160-W UV-lamp.

The preparation of alloy samples was conducted by weighing 0.10 g of sample to the nearest 0.1 mg and transferring the sample into a 250 mL Erlenmeyer flask. Then 10-12 mL of HNO_3 -HCl (1:3) plus a few drops of concentrated HF was added. The mixture was heated until dissolution was complete. Then, the solution was

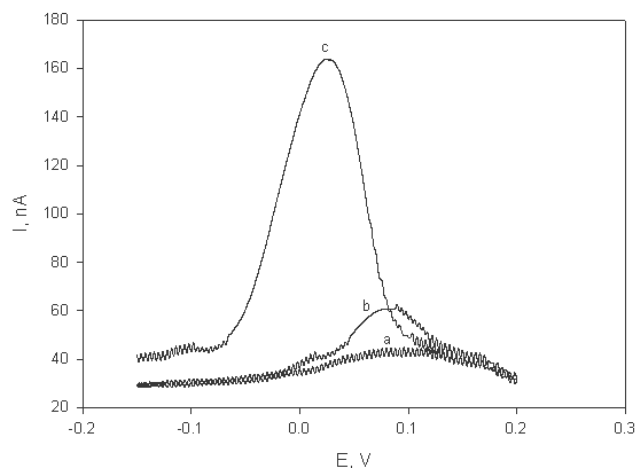


Figure 1. Differential pulse voltammograms of: a) blank solution; b) Cu(II) ion without the ligand; c) Cu(II) complex with xylenol orange. Conditions: Cu(II) concentration, 40.0 ng/ml; pH 2.0; XO concentration, 4.0 μM ; accumulation potential, -0.50 V; accumulation time, 90 s; scan rate, 10 mV/s; and pulse height 80 mV.

diluted with water to 100 mL in a 100 mL volumetric flask.

Results and Discussion

Preliminary experiments were carried out to identify the general features which characterize the behavior of the copper(II)-xylenol orange system on a HMDE. Xylenol orange can form a complex with Zn(II), Pb(II) and Cu(II) at different pH values. The formation constant of the complex of Cu(II)-xylenol orange at pH 2.0 to 3.5 is 2.5×10^4 . Figure 1 shows the stripping voltammogram for the ligand-buffer, copper(II)-buffer and copper(II)-ligand-buffer system in the potential range of 0.20 to -0.15 V vs. Ag/AgCl reference electrode. As can be seen, no obvious current is observed in this potential range for the ligand-buffer system (Figure 1a) and/or for a solution containing 40.0 ng/mL Cu(II) in the buffer solution, as indicated in Figure 1b. With the addition of xylenol orange, as indicated in Figure 1c, a large cathodic peak current located at about 0.0 V appeared. Addition of 10 $\mu\text{g}/\text{mL}$ Triton X-100 reduced the peak current to about 7.5% of the initial value. This phenomenon shows the adsorptive characteristic of the complex.

Optimization of Variables:

In this experiment, we studied the effects of instrumental and chemical factors on the peak current by artificial neural network. Twenty five experiments

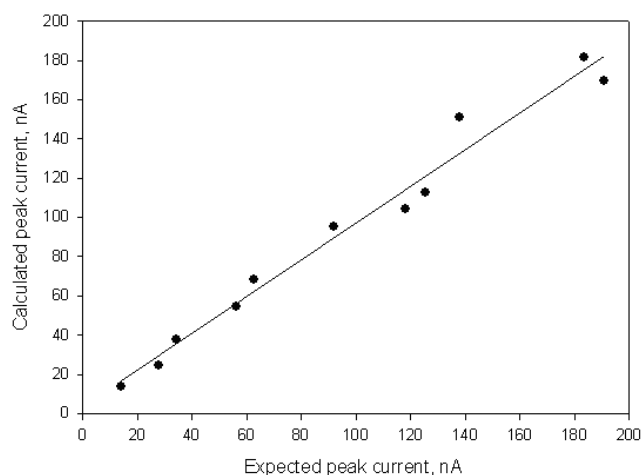


Figure 2. Relation between expected peak currents and calculated peak currents of Cu(II) that was determined by ANN (6:6:1).

were designed based on the experimental design as the training set of ANN, and eleven random experiments were designed as a prediction set of ANN. A preliminary study showed that increasing the pulse height above 80 mV cause peak broadening. Therefore, the maximum value of pulse height that was studied was 80 mV. The differential pulse voltammograms were recorded from 0.20 to -0.15 V, and peak currents were measured. A three layer back propagation network was used with an input layer with one bias, an output layer, and a hidden layer with sigmoidal transfer function. The input layer consisted of six experimental factors, which were pH, xylenol orange concentration (C_{XO}), accumulation potential (E_{ac}), accumulation time (t_{ac}), scan rate, and pulse height (see Table 1), and five levels for each factor were selected. The output layer consisted of Cu-XO peak current. The hidden layer with a certain number of nodes was inserted between the input and hidden layers. The number of nodes in the hidden layer was not fixed but was itself adjusted for optimal results. In order to obtain the best neural network structure, several ANN systems with different numbers of hidden nodes (from 2 to 12) were tested. The root mean square errors of calibration (RMSEC) and prediction (RMSEP) between the true and desired outputs over the entire training set and prediction set for each of the architectures was calculated. From RMSEP values after iterating 10000 times, the 6-6-1 system was better than the others. Therefore, we chose the 6-6-1 structure as the optimized system.

The initial architecture of the neural network (the number of neurons and weights) is only a guess, and

therefore it must be modified after performing calculations. Since the feed-forward neural network is a nonlinear optimization system, there is a possibility that the procedure may end in a local minimum if the learning rate and the momentum constant are not selected very carefully. Therefore, we optimized learning rate and momentum. According to the minimum value of RMSEP, the optimum value of the learning rate (ζ) and the momentum (μ) were 0.1 and 0.6, respectively. After obtaining the optimal value of $\zeta = 0.1$ and $\mu = 0.6$, the 6-6-1 system was trained 10000 times. Figure 2 shows the results obtained from voltammetric experiments and neural computation. The equation of this plot is $I_{cal} = 0.075 + 0.967I_{exp}$ ($n=11$, $r = 0.9930$). The high correlation coefficient ($r = 0.9930$) and small error of prediction (8.2%) indicate good performance of the model.

In optimized parameters of the ANN architectures, the Cu(II)-XO peak current was calculated for different values of the inputs or voltammetric factors. The Cu(II)-XO peak current was maximum at: pH of 2.0, ligand concentration of 3.0 μM , an accumulation potential of -0.60 V, an accumulation time of 90 s, a scan rate of 15 mV/s, and a pulse height of 80 mV. The study of the effect of pH and XO concentration on the peak current of 40 ng/mL of Cu(II) solution showed that with increasing pH values from 1.3 to 2.0, the peak current increases, whereas for higher pH, values decrease. In addition, when increasing the XO concentration up to 3.0 $\times 10^{-6}$ M, the sensitivity increases and then decreases. This is due to the fact that for higher concentration of XO, the ligand competes with the complex for adsorption at the surface of the electrode.

The study of the effect of accumulation potential on the peak current of 40.0 ng/mL Cu(II) solution showed that with increasing accumulation potential from +0.20 to -0.60 V, the peak height increases and then decreases for higher potential values. This is attributed to the fact that, at higher potential values, the ligand competes with the complex for adsorption at the surface of the electrode. In addition, the influence of scan rate on the peak current showed that when increasing scan rate from 2 to 15 mV/s, the sensitivity increases and then decreases.

Calibration Curve:

Under the optimized conditions: pH of 2.0, a xylenol orange concentration of 3.0 μM , an accumulation potential of -0.60 V, an accumulation time of 90 s, a scan rate of 15 mV/s, and pulse height of 80 mV, a calibration

Table 2. Interference study

Species	Tolerance limit ($W_{\text{ion}}/W_{\text{Cu(II)}}$)
Na ⁺ , K ⁺ , Cs ⁺ , NH ₄ ⁺ , Mg ²⁺ , Ca ²⁺ , Ba ²⁺ , Ag ⁺ , Zn ²⁺ , Cr ³⁺ , Mn ²⁺ , Cd ²⁺ , Co ²⁺ , BrO ₃ ⁻ , Fe ²⁺ , Fe ³⁺ , Hg ²⁺ , NO ₃ ⁻ , Cl ⁻ , Br ⁻ , F ⁻ , ClO ₃ ⁻ , N ₃ ⁻ , SO ₃ ²⁻ , SO ₄ ²⁻ , CO ₃ ²⁻ , ClO ₄ ⁻ , NO ₂ ⁻	1000
Al ³⁺ , Ce ⁴⁺ , IO ₄ ⁻	750
Ni ²⁺ , Rh ³⁺ , IO ₃ ⁻ , C ₂ O ₄ ²⁻	500
Pb ²⁺ , V ³⁺ , CN ⁻	120
Ga ³⁺ , S ₂ O ₃ ²⁻	75
I ⁻ , S ²⁻ , CrO ₄ ²⁻	20
Bi ³⁺	5

graph was obtained for Cu(II) concentration from 1.0 to 50 ng/mL with a regression equation of $\Delta I = 1.43 + 5.40C_{\text{Cu(II)}}$ (n=8, r = 0.9996), where ΔI is the peak current vs. nA and C is Cu(II) concentration in ng/mL.

The limit of detection, ($C_{\text{LOD}} = 3s_b/m$, where s_b is the standard deviation for ten replicates determination of the blank signal and m is the slope of the calibration curve), is equal to 0.35 ng/mL Cu(II).

The relative standard deviation for ten replicate measurements of 10.0 and 40.0 ng/mL of Cu(II) were 2.6% and 1.25%, respectively.

Interference Studies:

The possible interference of other ions in the adsorptive currents of Cu(II)-XO was studied under the optimum conditions and with 40.0 ng/mL Cu(II). The results are shown in Table 2. The tolerance limit was defined as the concentration which gains an error of $\leq 5.0\%$ in the determination of Cu(II). The results show that the method is free from many interferences from foreign ions.

Applications:

In order to examine the performance of AdSV in a practical solution, the proposed method was performed for the determination of copper in alloy samples, tap water, and well water. In order to eliminate matrix effects, the standard addition method was used.

Alloy samples were analyzed after dissolution of the sample in 10-12 mL of HNO₃-HCl (1:3) plus a few drops

Table 3. Determination of copper in some industrial alloys

Alloy	Actual Cu(II) (ng/mL)	Cu(II) found (ng/mL)	Recovery (%)
Si/Cu/Al	23.7	23.0 (± 0.8)	97.0
G-sNbZ10	25.7	26.7 (± 1.0)	103.8

Number in parenthesis is the standard deviation for five replicate measurements. Alloy contents: Si/Cu/Al (3.16% Cu, 0.10% Mg, 8.78% Si, 0.64% Fe, 0.18% Mn, 0.67% Ni, 2.46% Zn, 0.19% Pb, 0.26% Sn, 0.09% Ti, 0.11% Cr, and 83.36% Al). G-SnBz10 (87.71% Cu, 10.6% Sn, 0.56% Zn, 0.74% Pb, 0.11% Fe, 0.112% Ni, 0.0019% Mn, 0.002% Bi, 0.0213% As, 0.033% Sb, 0.0267% P, 0.0014% Cd, 0.059% Ag, and 0.0011% Se).

Table 4. Determination of Cu(II) in water samples

Sample	Cu(II) found by AdSV (ng/mL)	Cu(II) found by AAS ^a (ng/mL)	Recovery (%)
Tap water	32.5 (± 1.4)	31.0 (± 1.1)	104.8
Well water	12.8 (± 1.0)	12.0 (± 0.8)	103.2

Number in the parenthesis is the standard deviation for five replicate measurements. ^aAfter 50-fold preconcentration with boiling.

of concentrated HF. The water samples were analyzed directly after filtering the sample using a filter paper (Whatman No. 1). The samples also were analyzed for Cu(II) contents by an atomic absorption method. The recovery for the method reveals the capacity of the voltammetric method for determination of the Cu(II) ion in water and alloy samples. The results are given in Table 3. They are satisfactory.

Water samples were used directly after filtering with a filter paper (Whatman, No. 1) and UV irradiation for 2 hours with a 160-W UV-lamp to destroy any organic compounds that were present, especially surfactants. The results are given in Table 4.

Conclusion

An artificial neural network has been used to optimize the variables, and it works very well for nonlinear systems. A new method is developed using xylenol orange for the determination of trace amounts of Cu(II) by means of adsorption cathodic stripping voltammetry. The proposed method is more sensitive, precise and selective than flame atomic absorption spectroscopy and is more selective than the other existing electrochemical methods. This method is suitable for determining low levels of copper in real samples such as water and alloys.

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