Determination of Copper with 5-(dimethylamino)-2-((4-methyl-4H-1,2,4-triazol-3-yl)diazenyl) benzoic acid in Water Samples of River Nile (Egypt) by Adsorptive Stripping Square Wave Voltammetry

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Summary. The complex of copper (II) with 5-(dimethylamino)-2-((4-methyl-4H-1, 2, 4-triazol-3-yl) diazenyl) benzoic acid (DATAZB) and 5,5-dimethylcyclohexane-1,2,3-trione-1,2-dioxime-3-thiosemi-carbazone (DCDT) was analyzed by adsorptive stripping square wave voltammetry (A_d-SSWV). The electrochemical behavior of copper (II)-DATAZB and copper (II)-DCDT complexes was studied, in 0.08 mol l^{-1} potassium hydrogen phthalate (PBS) buffer solution, 1×10^{-6}M DATAZB and 7.86×10^{-5}M DCDT, 2.4% ethanol, and 1 M HCl, respectively. Cu(II) and (DATAZB & DCDT) ligand could form Cu(II)-DATAZB & Cu(II)-DCDT complexes. These complexes have adsorptive characteristics on the hanging mercury drop electrode (HMDE) and can be reduced in an irreversible reduction step. Calibration graph for copper (II) has been constructed from 0.4 ng mL^{-1} to 70 µg mL^{-1} and the detection limit of the method was 0.40 ng mL^{-1}. In Ad-SSWV, the complexes Cu(II)-DATAZB and Cu(II)-DCDT experiments an adsorptive reductive process occurs which promotes the appearance of a peak at -0.135 and -0.570V. The effect of chemical and instrumental parameters on the sensitivity and selectivity was studied. The method has been applied to water samples and the amounts of Cu found are very similar to those obtained when samples are analyzed by atomic absorption spectrometry (ASS).

Introduction

Copper is an essential constituent of enzymes, therefore it is biologically an essential trace element [1], and plays an important role in water as pollutant or essential element[2]. The main problem in anodic stripping voltammetry (ASV) is that the positive peak potential of copper (II) is near the oxidation of mercury, and the peak is broad. In addition, the accuracy of the measurement is adversely affected by the formation of intermetallic compounds. In the literature, many procedures have been reported for determination of copper in water and biological samples. Most of these are developments of flame atomic absorption spectrometry and striping voltammetry [3, 4].

Copper exists in nature extensively, but the concentration in various samples is usually low, so developing sensitive and selective methods to determine copper is required. In particular, stripping-analysis following absorption accumulation of the metal chelates has

become a widely accepted analytical tool because of it high sensitivity [5, 6]. The development of the stripping square wave voltammetric method for the determination of copper is described in biological samples [7]. Afterwards copper reacts with the DCDT reagent giving rise to the complex Cu-DCDT. This complex is reduced at the surface of the mercury electrode after being absorbed on it. 5,5-Dimethylcyclohexane-1,2,3-trione-1,2-dioxime-3-thiosemicarbazone, DCDT, a compound which belongs to the thiosemicarbazones groups and also possesses two oxime groups as complexing groups. DCDT reacts in acid medium with some inorganic compounds to form complexes [8], copper ion being between them. The use of the DCDT reagent is described to determine iron in waters, fruit juices and wines in acids by polarography [9].

The development of a stripping square wave voltammetric method for the determination of copper in water samples is described in this paper. The aim of the present work is to evaluate copper element adsorptive stripping voltammetry schemes based on the formation of metal chelates of DCDT and DATAZB reagents. Consider the equilibria involved in adsorptive stripping voltammetry of copper metal ion M, with sensitization by an appropriate ligand DCDT or DATAZB, that is, the solution-phase complexation and interfacial accumulation processes:

$$M + DCDT \longrightarrow MDCDT \qquad (1)$$

$$M + DATAZB \longrightarrow MDATAZB \qquad (2)$$

$$(MDCDT)_{soln} \longrightarrow (MDCDT)_{surf} \qquad (3)$$

$$(MDATAZBT)_{soln} \longrightarrow (MDATAZB)_{surf} \qquad (4)$$

In assessing schemes for adsorptive stripping voltammetric measurements, it is important to consider the competition for the chelating ligand (reactions 1 and 2) and coadsorption effects (reactions 3 and 4). In addition, experimental variables affecting the resolution between two chelate peaks should be assessed. Our data demonstrate the suitability and flexibility of adsorptive stripping voltammetry for copper element determination.

In the present paper, a new method was found a highly sensitive and selective method to determine Cu (II) in water samples using a new chelate reagent, 5-(dimethylamino)-2-((4-methyl-4H-1, 2, 4-triazol-3-yl)diazenyl)benzoic acid (DATAZB). DATAZB is a ligand that has azo-and heterocyclic functional groups (**Scheme 1**) making it a strong chelate agent for copper. Although this other derivate reagent has been reported for the determination of cobalt and copper by spectrophotometry and stripping voltammetry [10], up to now, there has been no report on its use to determine copper in water samples in this paper, and the results were consistent with those of spectrophotometry method.

Scheme (1)
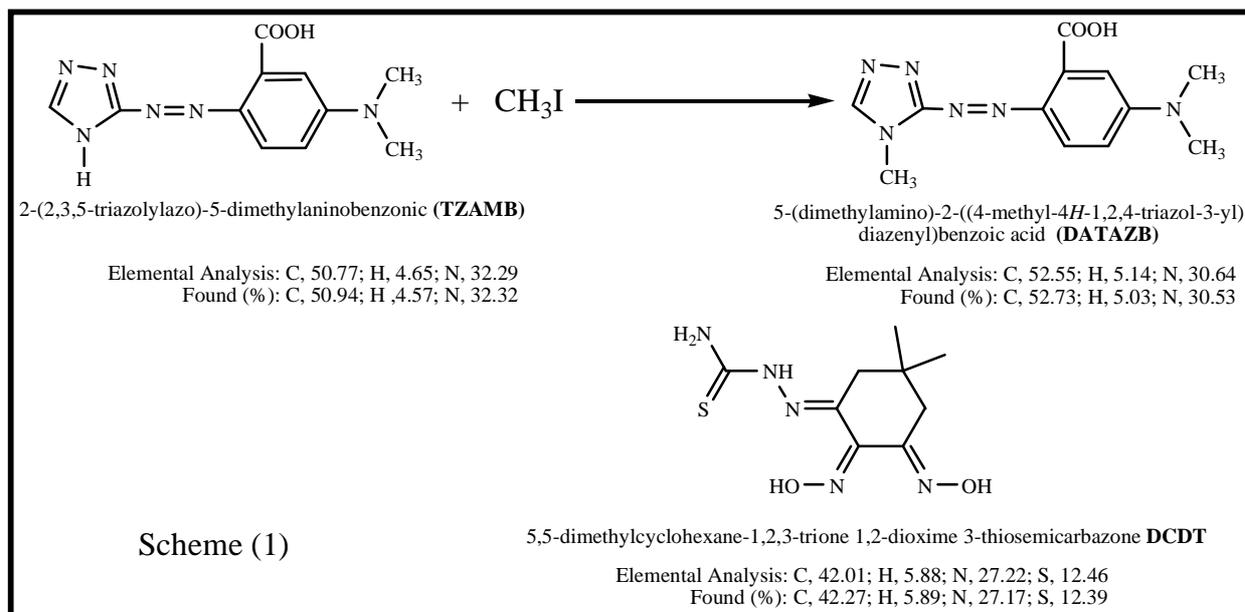
The electrochemical behavior of copper(II)-2-[2,3,5-triazolylazo]-5-dimethyl-aninobenzonic [Cu(II)–TZAMB] complex was studied. In 0.05 mol l^{-1} potassium hydrogenphthalate (PBS, pH 2.5) buffer solution, Cu(II) and TZAMB can form Cu(II)–TZAMB complex. This complex has adsorptive characteristics on hanging mercury drop electrode (HMDE) and can be reduced in an irreversible reduction step[11].

Experimental

Apparatus

For the voltammetric measurements, an EG&G PAR Model 273A potentiostat with 250/270 research electrochemistry software version 4.0, manufactured by Princeton Applied Research Corporation (NJ) was used with a three electrode system, a hanging mercury dropping electrode as working electrode, an Ag/AgCl saturated KCl reference electrode and a Pt wire auxiliary electrode. Stirring was performed with a Teflon-coated bar at approximately 400rpm using a magnetic stirrer (KIKA Labortechinik, Germany). A Pyrex glass cell was used for the measurements with magnetic fusion energy (MFE). Atomic absorption spectrophotometric (AAS) measurements were carried out using a Buck Scientific Model 210 VGP. pH measurements were made with an Orion model 601 digital pH meter.

Reagents

DATAZB was prepared by interaction of free ligand TZAMB (2.60g, 1mol) with CH$_3$I (1.14ml, 1mol) in ethanol with strong stirring (in presence of 2ml 0.01 mol KOH). The resulting solution was filtered, and washed thoroughly with pure ethanol. After removal of the solvents DATAZB was recrystallized with ethanol five times. To obtain DCDT, 5,5-

Dimethyl-1,2,3-cyclohexanetrione-1,2-dioxime was previously obtained by the Haas's procedure [12], was modified as described later [13].

A 1×10^{-3} mol l^{-1} DATAZB stock solution was prepared by dissolving 0.0137 g in ethanol and then diluting with double-distilled water in 50-ml volumetric flask. A 1.95×10^{-4} M DCDT stock solution was prepared by dissolving0.00251g DCDT in 5 ml ethanol and then diluting with water in 50 ml volumetric flask.

Stock standard Cu (II) solution (1000 mg l^{-1}) was used to prepared series of standard solutions. All standard solutions were obtained by successive dilution of the stock solution with double –distilled water. Unless otherwise specified, all solutions were prepared from analytical grade reagents and double-distilled water.

Samples collection and procedure

In this paper, one hundred and twenty water samples (for 15 days starting from 1-6-2005 to 1-6-2006) were collected from the River Nile, since water samples were collected for five positions in Egypt River Nile. The fist position was Aswan city at G.P.S. N 24° 07`04.04``, E $32^{o}$ 53`55.13`` twenty four samples were collected. The second position was Assiut city at G.P.S. N 27° 11``07.71``, E 31° 11`42.26`` twenty four samples were collected. In Cairo city at three position at G.P.S. N $30^{o}$ 10` 25.80``, E 31° 08` 20.20`` twenty four samples were collected. In Rashid city at four position at G.P.S. N $31^{o}$ 27`41.17``, E 30° 22` 15.17`` twenty four samples were collected. In five position, Damiatta city at G.P.S. N $31^{o}$ 31` 17.37``, 31° 50` 34.89`` was collected twenty four samples.

The peak current of Cu-DCDT complex obtained in square-wave voltammetry is dependent on various instrumental parameters such as square-wave amplitude, square-wave frequency and step potential. These parameters are interrelated and affect the response, but here only the general trends will be examined. It was found that these parameters had little effect on the peak potential. The results of this optimization study show that the set of square-wave amplitude of 60 mV; frequency 200Hz step potential 5 mV are best suited for routine determination of Cu(II) in the River Nile water samples. Since the step potential together with frequency defines the effective scan rate, an increase of either the frequency or the step potential results in an increase in the effective scan rate. By maintaining both the frequency and step potential at 200Hz and 5mV, respectively, the effective scan rate is 100 mV/s

0.5 ml of (2×10^{-5}M) DATAZB in 3% ethanol and 0.05mol l^{-1} PBS are added to water samples. The sample is stirred while accumulation takes place. After the accumulation period, the stirring is stopped and, after 15s of equilibrium time, the voltammograms of the sample

are recorded. The instrumental conditions are as follow: t_{ac} =30 s, E_{ac}= 0.05V, Scan rate= 100 mV s^{-1}, step potential=5mv, amplitude= 60mV, stirring rate=500 rpm. From the analytical signal, peak current (I_p) the concentration is calculated by using a suitably prepared calibration graph. Each measurement was performed with a fresh drop and always of the same size.

0.4 ml of 0.05% (1.95x10^{-3}M) DCDT in 2.4% ethanol and 1 M HCl are added to water samples. The sample is stirred while accumulation takes place. After the accumulation period, the stirring is stopped and after 15s of equilibrium time, the voltammograms of the sample are recorded. The instrumental conditions are as follow: t_{ac}=60 s, E_{ac}= -0.350V, frequency= 200Hz, step potential=5 mv, amplitude= 60 mV, stirring rate=500 rpm. From the analytical signal, peak current (I_p) the concentration is calculated by using a suitably prepared calibration graph.

Results and discussion

Effect of pH

Influence of HCl concentration on the peak height of DCDT (7.8x10^{-5}M) was varied between 0.1 and 2M HCl. Peak currents of Cu (II)-DCDT complex showed maximum values at 0.5 and 1M HCl and the peak potential (E_p) was displaced towards more negative potentials as the HCl concentration increased. Thus, 1M HCl concentration was selected as the most suitable for this study. Also, the potassium hydrogenphthalate (PBS) buffer solution concentration was varied from 1.5- 5.0. Peak current height of Cu (II)-DATAZB complex showed a maximum value in 0.08 mol l^{-1} PBS buffer solution(An optimum pH of around 2 was found).

Effect of concentration of DCDT and DATAZB reagents and ethanol concentrations

The DATAZB concentration was varied from 1X10^{-5} to 5x10^{-4} g L^{-1} and a redox peak current was not observed. A 1x10^{-6} g L^{-1} concentration of DATAZB was selected for subsequent experiments. Taking into account that the presence of ethanol in the samples is necessary as it is the solvent used to prepare the solutions of DATAZB, different concentrations of ethanol ranging from 1.5 % to 5.5 % were also tested and it was found that the peak current did not vary over this range of ethanol concentration. A 3% of ethanol was

used thereafter. The DCDT concentration was varied from 1×10^{-4} to 1.6×10^{-4} g L^{-1} and it was found that the peak current remained constant with concentration of reagent above 7.5×10^{-4} g L^{-1}. A 8×10^{-4} g L^{-1} concentration of DCDT was selected for subsequent experiments. Different concentrations of ethanol ranging from 1.6% to 9.6% were also tested and it was found that the peak current did not vary over this range of ethanol concentration. A 1.6% of ethanol was used thereafter.

Effect of instrumental variables

The accumulation potential (E_{ac}) was varied from 0 to -0.500 V. The maximum value of peak current (i_P) for Cu-DCDT complex was obtained between -0.30 and -0.45V. For subsequent experiments -0.35 V was selected. Also, the value of peak current (i_P) for Cu-DATAZB complex reaches a maximum highest of the peak current while the (E_{ac}) at 0.01V (Fig. 1).
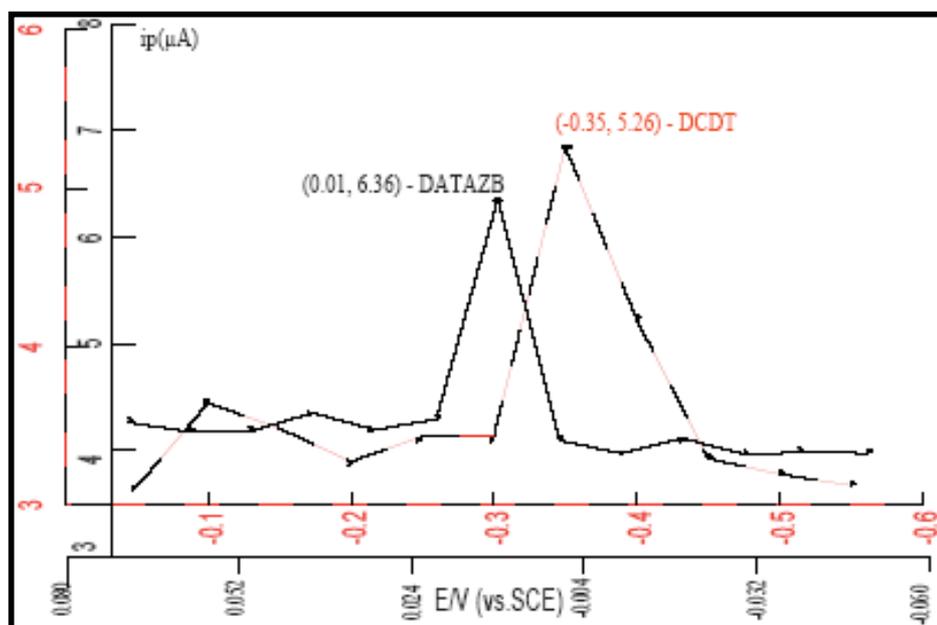

Fig.1: The effect of accumulation potential on the peak current.
a- $C_{DCDT} = 7.8 \times 10^{-5}$ M DCDT, 2.4% ethanol and 1M HCl, 500 ng mL^{-1} of Cu, $t_{acc} = 60$ s.
b-$C_{DATAZB} = 1 \times 10^{-6}$ M DATAZB, 3% ethanol and pH=2 (0.08M PBS solution), 1×10^{-7} mol l^{-1} of Cu, $t_{acc} = 30$ s, scan rate 100 mVs^{-1}.

A linear increase of peak current of the complex was observed when frequency was varied from 25 to 200 Hz. Peak current increased linearly with variations of step potential from 2 to 10 mV at 200Hz. However, this increment of the I_p was accompanied with a loss of the peak definition; therefore 5 mV was chosen to carry out subsequent experiments because it offered good values of peak current. Regarding to the influence of the square wave amplitude, the maximum value for I_p is produced at 60mV when the amplitude was increased

from 20 to 100 mV. With regard to the instrumental variables, the relationship between peak current and accumulation time (t_{ac}) was studied for solution of 20 ng mL^{-1} of copper with DCDT and DATAZB reagent, and t_{ac} was varied from 0 to 200s. Linearity was found for Cu-DATAZB and Cu-DCDT complexes up to 120 and 160s, respectively. The peak shape for the two complexes (Cu-DATAZB and Cu-DCDT) changes when accumulation time (t_{ac}) increases above 120s and 160 s, respectively. On linearity is only up to 100s and 120s, increasing the concentration of Cu-DATAZB and Cu-DCDT complexes to 50 ng mL^{-1}, respectively. A study of the influence of copper concentration was performed in aqueous solutions, under the optimal conditions mentioned, and by using different accumulation times (Fig. 2).
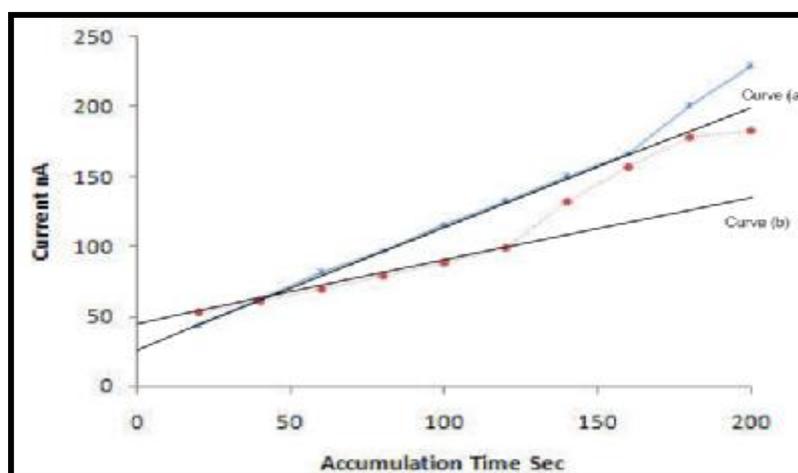

Fig. 2: Influence of the accumulation time on the Cu-DCDT and Cu-DATAZB peaks current.
a-Cu-DCDT =20 ng mL^{-1} of Cu, 4x10^{-5} % DCDT, 0.8% ethanol and 1M HCl, Eac= 0V; frequency =50 Hz, amplitude= 50 mV.
b-Cu-DATAZB= 20 ng mL^{-1}of Cu, 1x10^{-6} M DATAZB, 3% ethanol and pH=2 (0.08 M PBS solution), tacc= 30 s. scan rate 100 mVs^{-1}

It is important to remark that DATAZB and DCDT reagents produce a signal at a potential very close to that of the Cu-DATAZB and Cu–DCDT complexes, and the voltammograms of the complexes have been obtained by subtracting the corresponding blank signal. The stripping current of Cu-DATAZB and Cu–DCDT complexes after being preconcentrated during 120 s yielded a linear dependence in a concentration range 0–20 ng ml^{-1} of copper. For 100 s, the peak current increased linearly with copper concentration from 0 to 50 ng ml^{-1}. Finally for 60s the response is linear from 0 to 10 µg ml^{-1}. To construct the calibration plot we decided to use 60s as accumulation time. This time allowed us the copper

determination in a wider range of concentration and we ensured that the electrode was not getting saturated and that the nature of the process was not changing.

The properties of polargraphic peaks

In preliminary studies, there were no redox peaks of DATAZB in PBS buffer solution. Cu^{2+} (2×10^{-8} mol l^{-1}) did not give any redox peaks also. When a micro-amount of Cu^{2+} was added to the solution containing DATAZB, a new peak appeared at -0.15V. This suggests that the Cu(II)–DATAZB complex causes this peak. The peak height increases with increasing Cu^{2+} concentration, so this peak can be applied to the determination of trace Cu^{2+}.
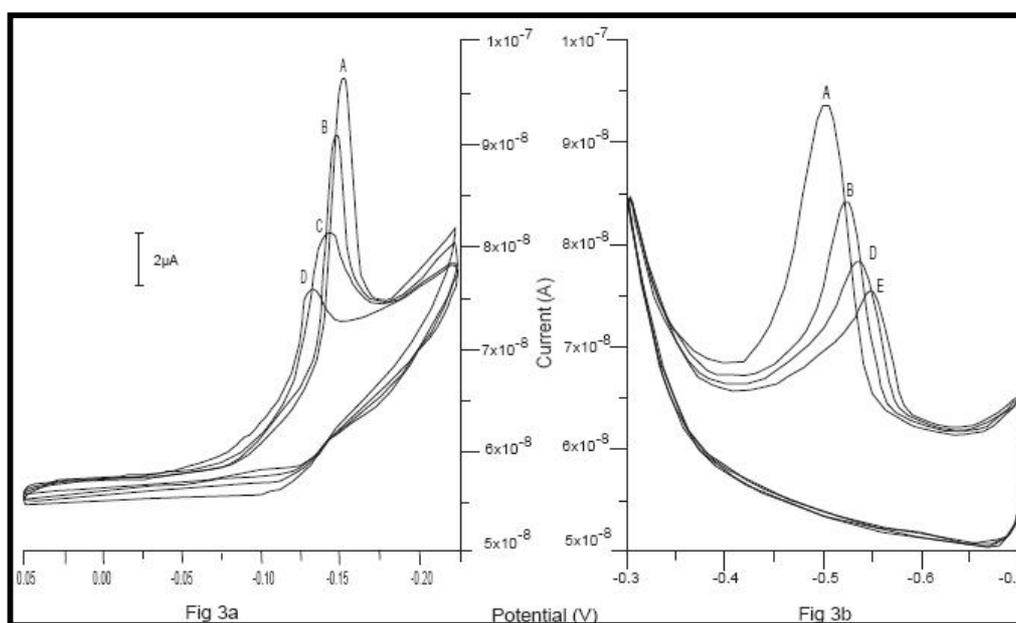

Fig. 3: The repetitive cyclic voltammograms of Cu (II)–DATAZB and Cu(II)-DCDT complex.
a-C_{DATAZB}=1×10^{-6} M DATAZB, 3% ethanol and pH=2 (0.08M PBS solution), 1×10^{-7} mol l^{-1} of Cu, scan rate 100 mVs^{-1}
b-C_{DCDT}=7.8×10^{-5} M DCDT, 2.4% ethanol and 1M HCl, 500 ng mL^{-1} of Cu, scan rate 100mVs^{-1}. Where A= First cyclic, B, C, D, E= final cyclic

The repetitive voltammograms are shown in Fig. 3a. By scanning four cycles, it was found that the peak current of first cycle (curve A) is much higher than those of the next cycles (curves B, C, D), which indicates that the complex has adsorptive characteristics. A cathodic peak was observed during the scan in the negative direction. Scanning in the reverse direction did not produce an anodic peak, indicating the irreversibility of the oxidation process. As shown in Fig. 3b, it may be calculated that Cu(II)–DCDT complex is reduced irreversibly on the electrode, producing a cathodic wave. The non-reversibility of the process

has also been confirmed by applying the Birke`s criterium, since the shape of the reduction peak changed when the amount of adsorbed product was higher than a certain value (i.e., when the concentration of copper or DCDT or the accumulation time increased excessively).
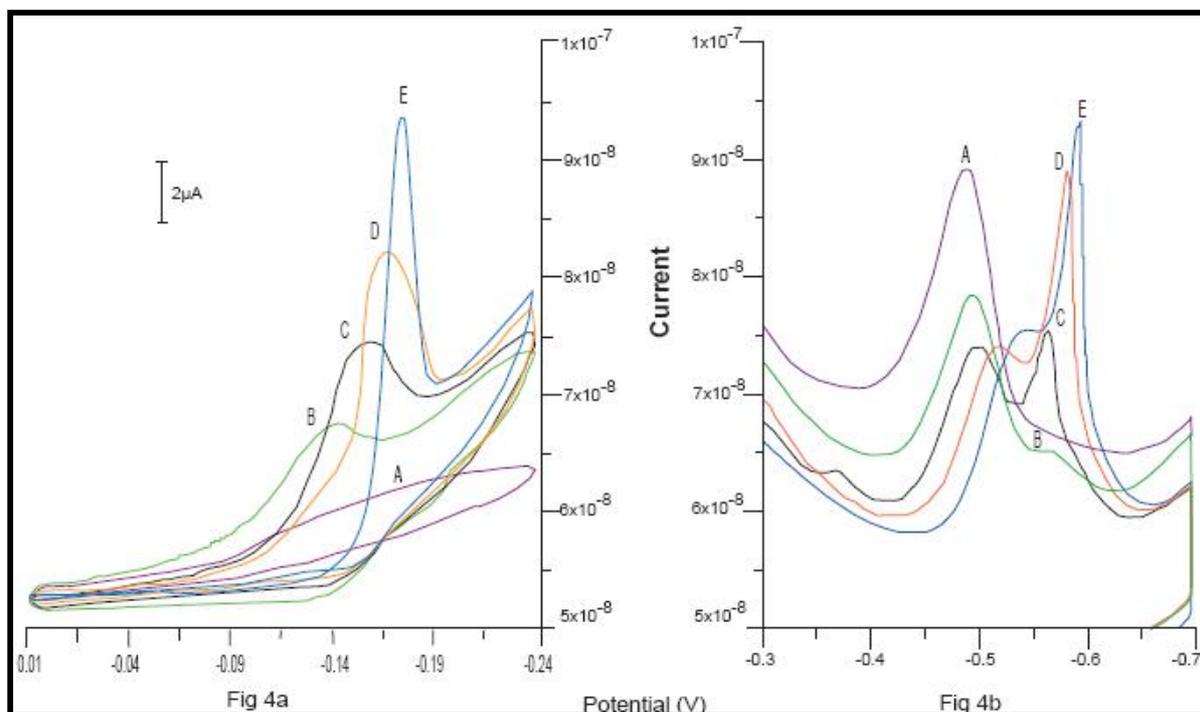

Fig. 4: Cyclic voltammograms of Cu–DATAZB and Cu-DCDT complex with different Cu concentrations.

4a- C_{DCDT} =7.8x10^{-5} M DCDT, 2.4% ethanol and 1M HCl, 500 ng mL^{-1} of Cu, scan rate 100 mVs^{-1}. A-DCDT; B, 300 ng mL^{-1} Cu; C, 500 ng mL^{-1} Cu; D, 700 ng mL^{-1} Cu; E, 1000 ng mL^{-1} Cu.

4b-C_{DATAZB} =1x10^{-6} M DATAZB, 3% ethanol and pH=2 (0.08M PBS), 1x10^{-7}mol l^{-1} of Cu, scan rate 100 mVs^{-1}. A-DATAZB; B, 300 ng mL^{-1} Cu; C, 500 ng mL^{-1} Cu; D, 700 ng mL^{-1} Cu; E, 1000 ng mL^{-1} Cu.solution containing 3 mg mL^{-1} of Cu and 4.72x10^{-4} M DCDT 2.4% ethanol, and 1M HCl was registered. It is observed that DATAZB and DCDT reagent originates a cathodic wave very close to that due to Cu-DATAZB and Cu–DCDT complexes. In Fig. 4a the peak appears at -0.15 V and its increases as the Cu^{2+} increased, so this peak can be applied to determination of trace Cu^{+2} and thus this peak must be produced by reduction of the complex, voltammograms of a solution of 1x10^{-6} mol l^{-1} DATAZB with different concentrations of Cu have been registered in CV. With the aim of determining whether the second wave is really originated by Cu–DCDT complex, voltammograms of a solution of 7.86 · 10^{-5}M DCDT with different concentrations of Cu have been registered in CV. Fig. 4b showing that the second wave increased as the Cu increased and thus this wave must be produced by the reduction of the complex. Therefore, the presence of the first wave is due to the reagent.

In preliminary studies, sampled DC, DPV and SWV techniques have been used to examine the electrochemical behavior of 0.08 mol l^{-1} potassium hydrogen phthalate (PBS) buffer solution of copper (500 ng mL^{-1}) and 1x10^{-6} M DATAZB and strongly acidic solutions (1M HCl) of copper (500ng mL^{-1}) and 7.86x10^{-5} M DCDT, and 2.4% ethanol at the surface of the HMDE electrode, respectively. The voltammogram of the solution was registered in DPV and SWV. Since sampled DC technique is less sensitive than the other techniques, the DC voltammogram of a solution containing 7 mg mL^{-1} of Cu and 8.32x10^{-4} M DATAZB, 3% ethanol, and 0.08 mol l^{-1} PSB was registered. On the other hand, the DC voltammogram of a

Electrode Reaction Mechanism

Number of Electrons Transferred and Reversibility of the System

Controlled-potential coulometry was used to determine n, the number of electrons transferred in the reduction process. Electrolysis of the Cu(II)-DCDT complex, with a slight excess of Cu(II), gave about six electrons, indicating that the wave may be due to complexed-reagent reduction. Logarithmic analysis, for 1M HCl shows a linear behavior, obeying the relationship

log i/(i$_d$ - i) = -7.96 + 26.87E (E in V) where (i= applied current nA and i$_d$= peak current in nA)

indicating that the reduction is irreversible. In linear-sweep cyclic voltammetry, the Cu(II)-DCDT complex yields one well defined reduction wave but an oxidation wave is not observed. The reduction wave is displaced to more negative potentials when the scan rate (mv s^{-1}), increases, and this behavior reflect the characteristic of irreversible processes.

In this paper, the reduction peak of Cu (II)-DATAZB complex by cyclic voltammetry was examined to check its possible adsorptive processes. As shown in (Figure 4), there were no peaks observed when Cu^{2+} (2x10^{-8}mol l^{-1}) or DATAZB were alone in PBS buffer solution, but when Cu^{2+} and DATAZB co-existed, a sensitive peak was observed at the hanging mercury drop electrode (HMDE). A reduction peak is formed when the potential is scanned between 0.05 and -0.20 V (vs. Ag/AgCl saturated KCl). This indicates that Cu (II)–DATAZB complex produced was responsible for the peak. In order to obtain more information, electrolysis was used. An electrolysis potential of -0.15 V (vs. Ag/AgCl saturated KCl) was applied. After electrolysis for 10 h, the reduction peak current of Cu (II)–DATAZB did drop down to zero (due to presence of methyl group on nitrogen in triazole the heterocyclic ring).

The reagent DATAZB (1×10^{-6} mol l^{-1}) was added to the cell, by using cyclic voltammetry, a reduction peak (at -0.15 V, vs. Ag/AgCl saturated KCl) of Cu(II)–DATAZB in this solution was obtained again. It is evident that the reactant is DATAZB in the Cu(II)–DATAZB. The number of electrons (n) transferred in an irreversible surface reaction can be calculated from the peak width at half height, $W_{1/2}$, by the equation $n = 3.52\ RT/FW_{1/2}$. $W_{1/2}$ was found to be 54 mV (at 25 ^{O}). From this value, n = 2, confirming that the reduction peak (-0.15V) is due to reduction of the azo group (-N=N-) to a hydrazo group (-NH-NH-) [14-16].

Calibration and precision of the method

A calibration plot was also constructed with double-distilled water samples (free of copper) fortified with organometallic copper standard, applying the proposed method for the determination of copper. Voltammograms of these samples are shown in Fig.5.
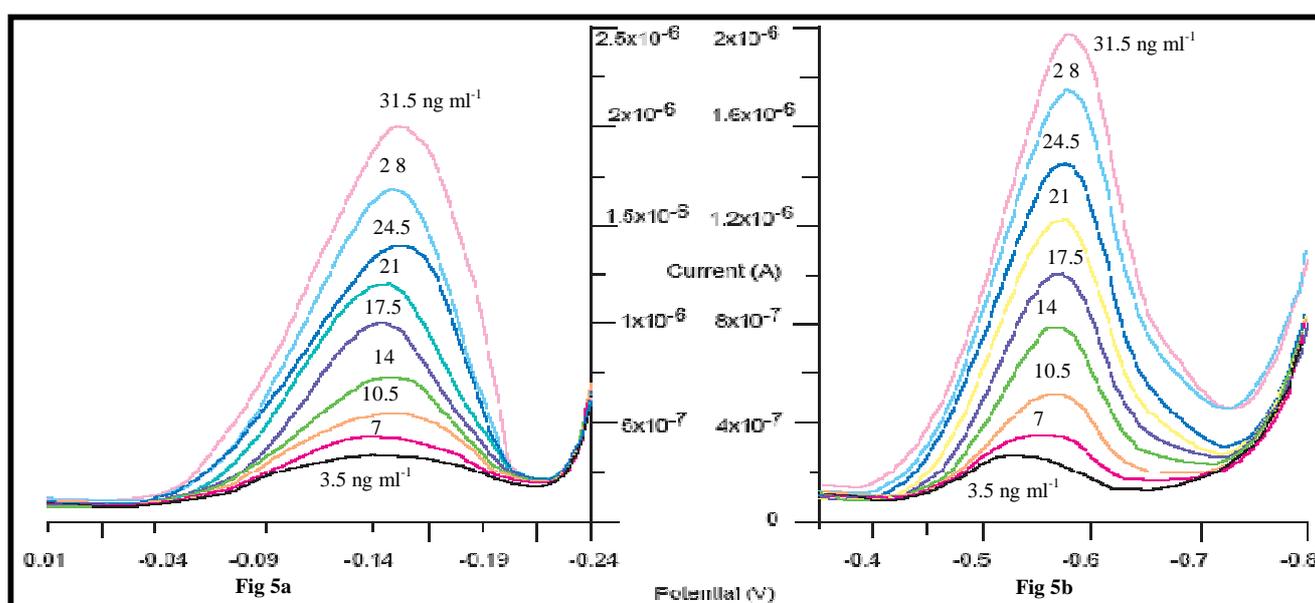

Fig. 5: Ad-SSWV voltammograms of Cu-DATAZB and Cu-DCDT obtained for Cu concentration between 0 to 35 ng ml^{-1}
5a- C_{DCDT} = 8×10^{-5} M DCDT, 1.6% ethanol and 1M HCl, E_{ac}= -0.35 V; t_{ac}=60 s; frequency =200 Hz, step potential=5 mV; amplitude = 60 mV
5b- C_{DATAZB} =1×10^{-6} M DATAZB, 3% ethanol and 0.08 M PBS, E_{ac}= 0.05 V; t_{ac}= 60 s; frequency = 200 Hz, step potential = 5 mV; amplitude= 60 mV

Slopes of Cu(II)-DCDT and Cu(II)-DATAZB plots were compared and no significant differences were observed. Taking into account that there are no differences between results obtained from aqueous solutions and from Nile river samples, Determination of copper in

Nile water samples was carried out by the standards methods. The correlation coefficient of the calibration plot was 0.999 and detection limit calculated by the method of Winefordner was 0.017 ng ml^{-1} [17]. The precision was determined by analysing 5 samples of Nile water samples by the proposed method.

Table 1, gives the results obtained in the determination of copper in Nile water samples. These results were compared with those obtained by the standard method based on atomic absorption spectrometry (AAS) and using different electroanalysis method. In order to validate the proposed procedure, we applied a regression analysis to the two sets of results according to the model:

y = a + b x; where y is the result produced by the proposed method and x is the result obtained by AAS.

The regression procedure used takes into account the errors associated with variables x and y (VALFIT program) [18]. This leads to the equation

y = (0.049 ± 0.024) + (0.997±0.018) x   with a correlation coefficient of 0.9999

Table 1:Results for determination of copper (II) in Nile water(means of triplicate or pentaplicate determination)

Location	Using DATAZB reagent (ng ml^{-1})				Using DCDT reagent (ng ml^{-1})				Using AAS (ng ml^{-1})		
	RSD%	Mean^f ± SD	M	Min.-Max.	Mean^f ± SD	M	Min.- Max	Mean^f ± SD	M	Min.- Max
A	0.106	17.82± 0.019	17.83	17.79-17.84	17.884±0.024	17.89	17.85-17.91	17.797±0.009	17.75	17.71-17.76
B	0.296	9.342±0.0277	9.35	9.30-9.37	9.384±0.0241	9.39	9.35-9.41	9.321±0.021	9.36	9.29-9.45
C	0.032	24.832±0.008	24.83	24.82-24.84	24.860±0.022	24.86	24.83-24.89	24.849±0.032	24.87	24.72-24.90
D	0.085	19.776±0.017	19.78	19.75-19.79	19.762±0.019	19.76	19.74-19.79	19.752±0.027	19.83	19.60-19.84
E	0.037	21.812±0.008	21.81	21.80-21.82	21.842±0.017	21.84	21.82-21.87	21.808±0.054	21.74	21.63-21.93

A= Aswan; B= Assiut; C= Cairo; D= Rashid; E= Dumyat; f = Confidence interval, p = 95%; M=Medium

The program indicates that the point corresponding to a = 0 and b = 1 belongs to the so-called elliptic joint confidence region of the fitted straight line. Alternatively, the common procedure based on t-test for the intercept and slope leads to the same conclusion; there is no difference, statistically, between the results obtained by the proposed procedure and the results obtained by AAS and different electroanalysis methods. Precision and accuracy were determined as relative standard deviation RSD by analyzing the same reference standard solution three times for various concentration levels. Table 2 shows RSD for three concentration levels of each element. The detection limits D_L of the investigated metals, defined as the metal concentration yielding an analytical peak equal to the minimum detectable one, can be calculated as:

$$D_L = 5\frac{S_d}{m}$$

Where, S_d is the standard deviation of the blank and m is the slope of the calibration line

Table 2, shows the calculated detection limits of all elements under study. The given detection limits of the elements under investigation revealed that the proposed scheme of analysis under the optimal conditions is very sensitive and useful for ultratrace determination of elements.

Table 2. Comparing the analytical figures of various methods for determination of copper by adsorption stripping analysis

Reagents	LOD[a] (ng/ml)	LOD[a] (M)	LDR[b] (ng/ml)	Interference	Reference
BAE[c]	4.027	6.34×10^{-8}	60-2000	Fe^{3+}	(19)
8-HD[d]	1.103	1.74×10^{-8}	1-10	-	(6)
BME[e]	0.204	3.21×10^{-9}	1-850	I^-, Br^-, SCN^- (1500)	(5)
DCDT	0.390	6.14×10^{-9}	1-35	Fe^{3+} (100)	(3)
TZAMB[f]	0.061	9.59×10^{-10}	0.6-30	Zn^{2+}, Se^{4+} (100)	(11)
DATAZB	0.017	2.68×10^{-10}	0.4-50	Fe^{3+}, Cd^{2+} (100)	This method

a- Limit of detection, b- Linear dynamic range, c- Bis(acetylacetone)ethylendiimine, d- 8-HD=8-Hydroxyquinoline, e-Benzylmonooxime. F- 2-(2,3,5-triazolylazo)-5-dimethyl-aminobenzoic

Effects of Foreign Ions

In the determination of 1×10^{-7} mol.l^{-1} of copper (II) at the optimum reagent concentrations studied, foreign ions could be tolerated (less than a 5% change in peak current) at the levels given in Table 3. The great selectivity of the method should be emphasized because only iron and cadmium interfere seriously.

Table 3. Tolerance of foreign ions in the determination of 1×10^{-7} mol.l^{-1} Copper (II)

Minimum interfering foreign ion to Cu(II) ratio (M/M	Ions tested
10000	Na^+, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{-2}, I^-, Mn^{2+}, Ba^{2+}, NO_3^-
1000	Zn^{2+}, Al^{3+}, Mo^{4+}, Ni^{2+}, Se^{4+}, Cr^{5+}, Sn^{2+}, Pb^{2+},
100	Fe^{3+}, Cd^{2+}
No interfere	Equally amount Co^{2+}

Several metals have been reported to be present in Nile water samples; iron is the most abundant one. Therefore, the effect that this metal produces over the copper determination was studied. To detect the possible interference from iron, samples of 1×10^{-7} mol.l^{-1} of Cu and

with different amounts of iron were prepared. Ratio (w/w) Cu:Fe was varied from 1:1 to 1:10. The voltammetric signal obtained for Cu was compared with that corresponding to a sample of this ion, without iron. Signals were considered affected by the iron if the difference (1:10) was 5% at least, and it was found that Fe did not interfere in the concentration range tested.

The determination of copper was performed, following the method proposed in this paper. On the other hand, Nile water samples were also analyzed by atomic absorption spectrophotometry. In conclusion, the method of copper determination by Ad-SSWV this paper is a very low-cost method because reagents and techniques are not expensive. Another advantage is that the time required to carry out the analysis is shorter than other polargraphic methods in which determination of copper in Nile water samples was made. It should be pointed out that with this method it is possible to determine very low quantities of copper because the detection limit is 0.017 ng ml^{-1}.

Conclusions

A novel method to determine Cu^{2+} using a new reagent DATAZB was discussed in this paper. Using different electroanalytical methods, the electrochemical behavior of this complex was studied. This method was applied to determine Cu^{2+} in water samples in different locations in River Nile water samples and the results were compared with data for these samples, obtained by using different ligand and atomic absorption spectrometry.

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