

## Graphite electrode modified with Indigo Carmine for Cu(II) ions detection

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**Abstract.** An electrochemical method for Cu(II) determination, based on its reaction with indigo carmine (IC) in alkaline medium and differential pulse voltammetry performed at graphite electrode, was elaborated. The experimental parameters affecting the Cu(II) - IC complex formation (reaction time and pH) were optimized. The linear range of the calibration curve, obtained by representing the IC oxidation current ( $E_{\text{appl}} = 0.175 \text{ V vs. Ag/AgCl, KCl}_{\text{sat}}$ ) versus the Cu(II) concentration (pH 10), was from 10  $\mu\text{M}$  up to 70  $\mu\text{M}$  Cu (II) and the detection limit was 4.74  $\mu\text{M}$ .

**Keywords:** Cu(II), indigo carmine, differential pulse voltammetry

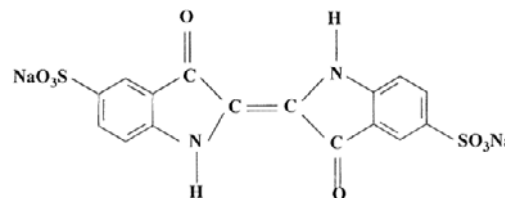
### Introduction

Monitoring trace or ultra trace copper in natural environment, biological and other real samples is very important, since the ingestion of copper can lead to toxicosis, affecting first the liver and later the central nervous system, kidneys and eyes [Barceloux. and Barceloux, 1999]. Because the concentration of copper is extremely low in various natural samples, a selective and sensitive method for reliable determination of copper would be of great interest.

Modified electrodes are suitable for the preconcentration of metal ions by formation of complexes and could be created by grafting of some complex-forming ligands to the surface of the electrode [Zen *et al.*, 2003 ].

In this work, an electrochemical method for the determination of copper (II) by complexation with indigo carmine has been proposed. For this purpose, the oxidation current of indigo carmine in basic medium was measured in the presence and in the absence of Cu (II) ions. The decrease of the oxidation current of indigo carmine caused by the formation of an electro-inactive complex was studied. The experimental parameters were optimized, such as pH and time of reaction.

### Materials and Methods



Indigo carmine (3,3'-dioxo-2,2'-bis-indolyden-5,5'-disulfonic acid disodium salt) (Scheme 1) was purchased from Sigma Aldrich (St. Louis, MO, USA).

#### Scheme 1

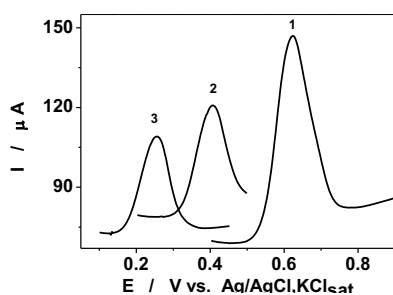
A 1 mM Cu (II) stock solution was prepared from  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Microchim - Romania). All used chemicals were of analytical grade. Aqueous solutions were prepared with distilled water. All experiments were carried out at room temperature.

Cyclic and differential pulse voltammetric measurements were performed using a computer-controlled potentiostat (Autolab PGSTAT 10, Ecochemie, Utrecht, The Netherlands) and GPES 4.8 software. A conventional three electrodes cell (30 mL) consisting of a graphite electrode as working electrode, a  $\text{Ag/AgCl, KCl}_{\text{sat}}$  as reference electrode

and a Pt wire as counter electrode, was used. Before using, the graphite electrode was cleaned by wet polishing with emery paper and filter paper, followed by 2 minutes ultrasonication, in an ultrasonic bath (Elma S10, Elmasonic, Germany). The solutions pH was measured using a digital pH meter (Hanna Instruments, USA). Each individual experiment was performed at least three times and the results were averaged.

## Results and Discussion

Differential pulse voltammetry (DPV) measurements were carried out to investigate the pH effect on the redox couple Indigo carmine (IC) / Dehydroindigo carmine (DHIC). As expected for a redox process involving protons and electrons, the pH increase induces a negative shift of the oxidation peak potential of IC, simultaneously with a monotone decrease of the peak currents (Figure 1).



**Fig. 1.** DPV response of IC recorded at graphite electrode. Experimental conditions: scan rate,  $0.03 \text{ V}\cdot\text{s}^{-1}$ ; pulse amplitude,  $100 \text{ mV}$ ; supporting electrolytes, (1) acetate buffer (pH 2.5); (2) and (3) phosphate buffer pH 6 and pH 8.5, respectively; IC concentration,  $10 \mu\text{mol}\cdot\text{L}^{-1}$ .

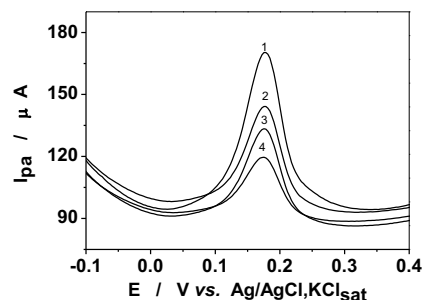
Using DPV data for IC/DHIC couple, a linear correlation between the anodic peak potential ( $E_{\text{pa}}$ ), and the pH was found, described by the equation  $E_{\text{pa}} = 0.750 - 0.061 \cdot \text{pH}$  ( $R^2 = 0.9933$ ), which points out to an equal number of protons and electrons participating to this process.

When Cu(II) ions are added to an alkaline solution of IC, the  $\text{Cu}_2\text{IC}$  complex is formed [Zanoni *et al* 2010]. Because at the working potential this complex is electro-inactive, a decrease of the oxidation peak current will appear for IC/DHIC redox couple. Moreover, as can be seen from Figure 2, the peak current decrease is depending on Cu(II) concentration in the  $\mu\text{M}$  range.

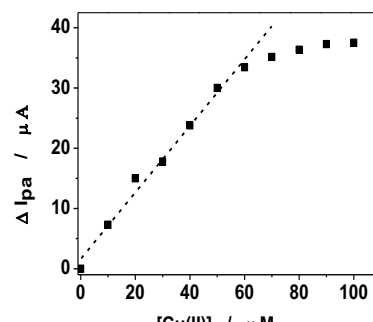
The influence of the solution pH on the  $\text{Cu}_2\text{IC}$  complex formation was investigated by measuring of the decrease of oxidation peak

current ( $I_{\text{pa}}$ ) of IC/DHIC redox couple induced by Cu(II) addition at different pH values.

The maximum decrease of  $I_{\text{pa}}$  was observed at pH 11 (76%), but pH 10 was chosen as working pH, considering that: (i) at this pH the  $I_{\text{pa}}$  decrease was still significant (63%) and (ii) at pH 10 the buffering capacity of the carbonate solution is maximum. The decrease of the oxidation peak current for IC/DHIC redox couple due to Cu(II) addition



**Fig. 2.** Typical DPV response obtained before (1) and after the addition of different Cu(II) ions concentrations in a solution containing  $100 \mu\text{mol}\cdot\text{L}^{-1}$  IC: (2)  $40 \mu\text{mol}\cdot\text{L}^{-1}$  Cu(II); (3)  $80 \mu\text{mol}\cdot\text{L}^{-1}$  Cu(II); (4)  $100 \mu\text{mol}\cdot\text{L}^{-1}$  Cu(II). Experimental conditions: supporting electrolyte,  $0.1 \text{ M}$  carbonate buffer (pH 10); scan rate  $0.03 \text{ V/s}$ ; pulse amplitude,  $100 \text{ mV}$ . into the alkaline (pH 10) IC solution and as a function of the copper ions concentration is depicted in Figure 3. The linear domain, from  $10$  up to  $70 \mu\text{M}$  Cu(II), corresponds to the following regression equation:  $\Delta I_{\text{pa}} = (1.63 \pm 0.99) + (0.55 \pm 0.03) \cdot [\text{Cu(II)}]$ ;  $R^2 = 0.9853$ ,  $N = 7$ . The detection limit (DL) was estimated at  $4.7 \mu\text{M}$  for a signal-to-noise ratio of 3.



**Fig. 3.** Calibration plot for Cu(II) DPV detection. Experimental conditions:  $100 \mu\text{M}$  IC; supporting electrolyte,  $0.1 \text{ M}$  carbonate buffer (pH 10); reaction time,  $30 \text{ min}$ .

**Conclusion**

DPV measurements performed at graphite electrode were successfully used for copper determination, exploiting the Cu(II) reaction with IC in alkaline medium (pH 10). Due to the electro-inactivity of Cu(II)-IC complex, the decrease of the IC oxidation current, measured at an applied potential of ~150 mV vs. Ag/AgCl, KCl<sub>sat</sub>, was used to draw a calibration curve allowing the determination of Cu(II) concentrations.

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