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Determination of Copper in Water by Anodic Stripping Voltammetry Using Cu-DPABA–NA/GCE Modified Electrode

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The determination of Cu by anodic stripping voltammetry using a Nafion-modified glassy carbon electrode incorporated with Cu-DPABA complex (Cu-DPABA–NA/GCE) was described. Cu was accumulated in acetic buffer pH 4 at potential of -1.4 V (vs. Ag/AgCl ref. electrode) and then determined with DPASV. Under the optimum conditions the calibration curve was linear in the range $7.0 \times 10^{-9} - 5.0 \times 10^{-5}$ mol/L. The detection limit was 3.0×10^{-9} mol/L. Different parameters and conditions, such as membrane ingredients, accumulation time and pH value was optimized. A study of the interfering substances was also performed. A significant increase in current was achieved at the modified electrode compared to a bare glassy carbon electrode. For explanation of voltammetric behavior of modified electrode in copper solution, cyclic voltammograms were recorded. The electrode was applied in the direct determination of Cu in water.

Keywords: Modified electrode, anodic stripping voltammetry, copper determination, Nafion

1. INTRODUCTION

The determination of heavy metals in naturals waters is of interest in the studies of the enviromental cycles of trace metals. Besides other methods of analysis like inductively coupled plasma (ICP), atomic absorption spectrometry (AAS), ion-selective electrode (ISE) and emission spectrometry a common method for determination of copper is anodic stripping voltammetry (ASV). Other methods require several time consuming manipulation steps, sophisticated instruments and special training. ASV is one of the most sensitive method for determination of traces of numerous ions because of its remarkably low detection limit. Other adventageus features of ASV include relatively low cost instrumentation and the capability for simultaneous multi-element determination.[1-7]

Copper is an important element in biological systems. It is an essential micronutrient present in at least thirty enzymes. On the other hand, it is toxic above a certain concentration. The World Health Organization (WHO) and the European Water Quality Directive recommends that the concentration in drinking water does not to exceed 2 mg L^{-1}. Copper (II) is found in waste water from electroplating and other metal processing industries as weel as water supply systems due to corrosion of copper in pipes. The concentration of copper is low in natural, enveromental, biological and other real samples. A sensitive method for detection of copper is of great interest. [8-11]

Chemically modified electrode (CME) have been recognized as being one of the desirable alternatives for mercury electrodes, because of the toxity of mercury enveromental regulations and health considerations may several restrict (or even prohibit) the use of mercury as an electrode materials. CME can easily and conveniely be fabricated and have some unique adventages in enhancing the selectivity and sensitivity due to the chemical nature and microstructure of modified electrode surface. In recent years many substances have been used for electrode modification and determination of copper. A amoxicillin [12], cysteine [13], calix(4)arene [14], diquinolyl-8,8'-disulfide [15], hexacyanoferrate [16], tetraethylthiuram disulfide [17], tetraphenylporphyrin [18], *p*-tert-Butylcalix(4)arene [19], 1,2-bis-methyl (2-aminocyclopentene-carbodithioate) ethane [20], polypirrole pyrocatechol violet [21] and 2-aminothiazole organofunctionalized silica [22] have been used to make chemically modified electrodes for determination of copper. Cu and other metals complexes with dipicolylamine and their derivatives are shown to be effective and selective in hydrolysis of 2'-5' and 3'-5' ribonucleotides [23], for fluorescence detection of flavin adenine dinucleotide in human eosinophilis [24], making ensemble system for detection polyphosphates in water[25], for fluorescent artificial chemosensors for phosphorylated proteins and peptides[26], and other sensors. In papers which use modified electrodes, voltammetric methods are mainly used. Therefore, chemically modified electrodes are already widely used in analytical chemistry[27].

The aim of this work was to develope a new glassy carbon modified electrode for determination of copper by ASV. Our intention was to develop an ion selective Cu electrode based on modified GC electrode immobilized with nafion using a simple construction procedure for performing Cu determinations in water.

2. EXPERIMENTAL

2.1. Reagents

Nafion perfluorinated ion-exchange resin (2% and 5%) was purchased from Aldrich. Methyl 3,5-bis{bis-[(pyridin-2-yl)methyl]amino}methyl)benzoate (DPABA) was synthesized according to previously described procedure [28]. Cu-complex was prepared by mixing Cu solution and DPABA, concentration of both were15 mg mL^{-1}. A stock solution (1 x 10^{-3} $molL^{-1}$) of Cu was prepared in deionized water. A working solution for ASV investigations was prepared by dilution of the stock solution with deionized water using variable Eppendorf micropipettes. Buffers solutions were used to control the pH. All other reagents were of analytical grade.

2.2. Instrumentation

The voltammetric changes of the sensor were measured with instrument Metrohm 797 VA Computance (Herisau, Switzerland). The triple-electrode system consisted of a working electrode, modified GC electrode, a reference Ag/AgCl potassium chloride (3M) and auxiliary platinum electrode. Cyclic voltammograms were recorded on a CHI760B instrument (CHInstruments, USA). The cell was equipped with modified GC electrode, an accessory platinum electrode of larger area (Model CHI221, cell top including Pt wire counter electrode) and an Ag/AgCl reference electrode (Model CHI111). All measurements were taken at ambient temperature. During the measurements the sample was stirred.

2.3. Preparation of modified glassy carbon electrode

Prior to each experiment, the glassy Carbon electrode was polished with alumina powder (0.5μm), rinsed with deionized water and ultrasonicated in water for 3 min.Modifying compound was prepared by mixing different volumes of 2% or 5% (v/v) Nafion-Ethanol solution with 5 μL solution of Cu–DPABA, and add freshly prepared mixture onto the dry electrode surface with micropipette. The electrode was dried (2h) to evaporate the solvent and rinsed with deionized water. Their detection limit was $3x10^{-9}molL^{-1}$. Surface of electrode was recorded using scenning electrone microscope (Fig. 1).

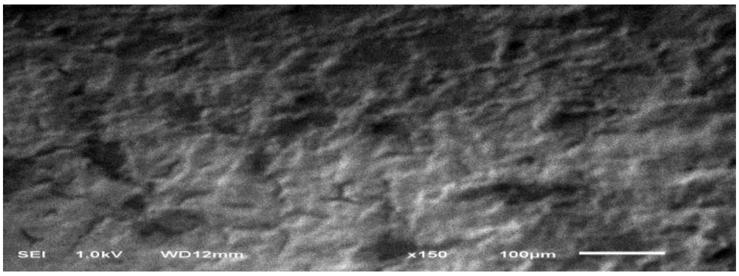

Figure 1. SEM image of modified electrode surface

2.4. Cyclic voltammetry behavior of modified glassy carbon electrode

Sweep for modified glassy carbon electrode from -0.5V to +0.6V showed one peaks (0.3V) and backwards anodic sweep (+0.6 to -0.5 V) showed one peak (-0.36 V) (Fig. 2). Modified electrode has very good reproducibility (RSD was 3.7% for n=5, concentration 50μmol/L, scan rate 100mV, average Ipa 45.8μA, standard deviation 1.68μA). Since the cyclic voltammogram of Cu solution with nonmodified electrode did not show any peak in the same potential range, the Cu-DPABA–NA/GCE modified electrode could be used for voltammetric determination of copper(Fig.4). As shown in Fig 3. that electrode has good dependence of cathodic and anodic peaks from square root scan rate.

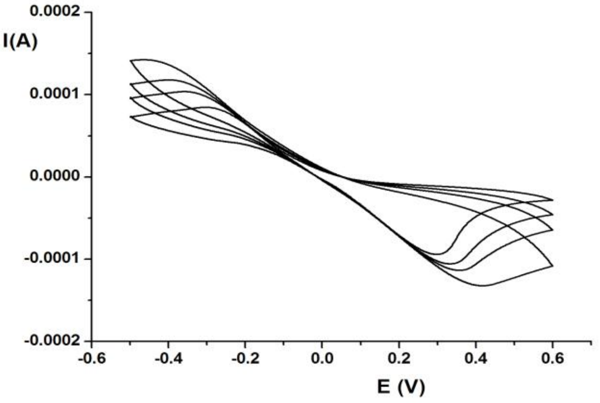

Figure 2. Cyclic voltammogram of Cu solution with modified electrode: concentration of Cu was $1x10^{-5}$, scan rate 50 mVs^{-1}, supporting electrolyte was acetic buffer

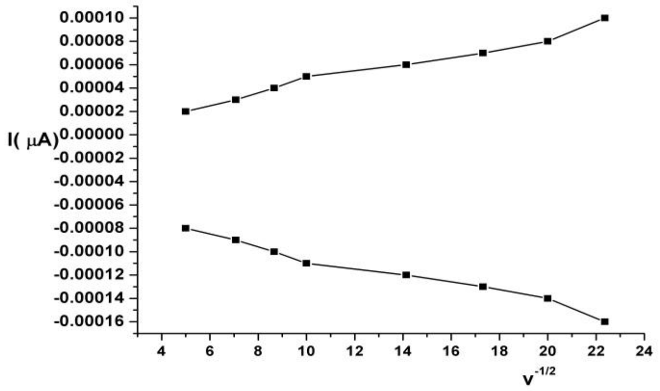

Figure 3. Dependence od cathodic and anodic peaks from square root scan rate

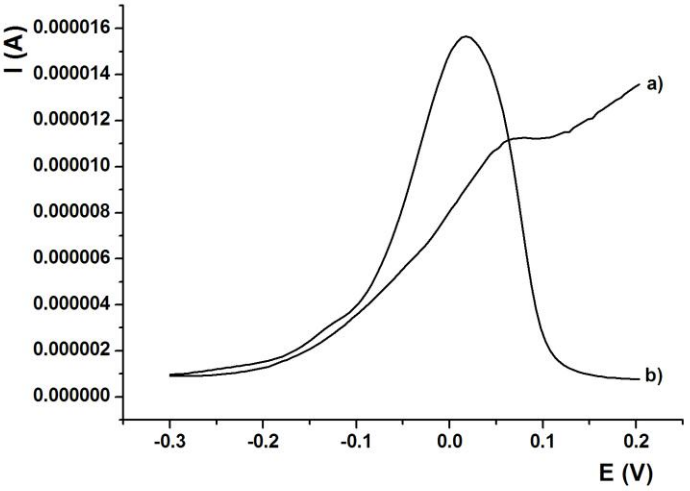

Figure 4. Pulse anodic stripping voltamogram of 2 μM of Cu at bare glassy carbon electrode (a) and modified electrode (b); electrolyte acetic buffer pH 4, accumulation potential -1.4 V, accumulation time 120s.

2.5. Optimization parameters

2.5.1. Effect of volume of modifying mixture on peak current

The effect of volume of plasticizer on the peak current was study and the results shown in Table 1 . The peak current reached its maximum when plasticizer was 2% Nafion and the volume of 2% Nafion (5 µL), mixed with 5µL of Cu-DPABA complex.. The function of Nafion was to fix complex on glassy carbon electrode, and also to serve as a barrier to prevent interferents from reaching the electrode surface. When used more then 10 µL of modifying compound layer thickness on the electrode increased which leads to an increase of accumulation time and peak current decreases. Coating the glassy carbon electrode surface with films thinner than than those created by adding 10 µL of modifying compound decreases signal [29]. So ideal volume of modifying compound for preparing modified glassy carbon electrode was 10 µL and for all others experiment was used this electrode. The selected electrode, with lowest detection limit and widest linear range, from Table 1. is the electrode from second row, No.2. The detection limit of selected electrode was $3x10^{-9}molL^{-1}$.

Table 1. The effect of volume of modifying compound on the peak current: electrolyte acetic buffer pH 4, accumulation potential -1.4 V, accumulation time 120s

No.	Volume of Cu-DPABA (µL)	Volume of 2% Nafion (µL)	Volume of 5% Nafion (µL)	Limit of detection for Cu $molL^{-1}$ $(x10^{-9})$	Linear range for Cu $molL^{-1}$
1.	5	2		3.1	$8.3x\ 10^{-9} – 5.8\ x\ 10^{-5}$
2.	5	5		3.0	$7.0x10^{-9}– 5.0\ x10^{-5}$
3.	5	10		4.2	$8.3x\ 10^{-9} – 5.7\ x\ 10^{-5}$
4.	5	15		4.9	$9.8\ x\ 10^{-9} – 5.9\ x\ 10^{-5}$
5.	5		2	3.3	$7.5\ x\ 10^{-9} – 5.8\ x\ 10^{-5}$
6.	5		5	3.3	$7.4\ x\ 10^{-9} – 5.5\ x\ 10^{-5}$
7.	5		10	4.6	$8.3\ x\ 10^{-9} – 6.0\ x\ 10^{-5}$
8.	5		15	5.2	$9.1x\ 10^{-9} – 5.8\ x\ 10^{-5}$

2.5.2. Effect of pH

The peak current of Cu in various electrolytes, such as HCl and different acetic buffers, was investigated. To cover the entire range of pH used differente supporting electrolyte same concentration ($1x10^{-3}$ mol/L). For lowest pH used HCl, then acetic buffer. It was found that a well-defined and sensitive anodic stripping peak current with best conditions (5 µL Nafion, 5 µL of Cu-complex) was with acetic buffer. The effect of different pH values in Fig. 5. The pH value 4 was selected as optimum.

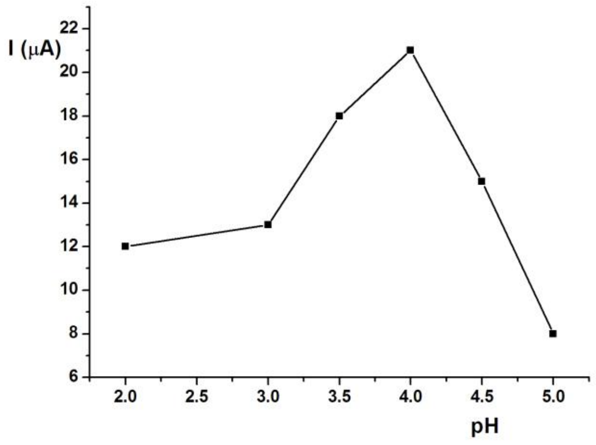

Figure 5. Effect of pH on peak current: accumulation potential -1.4 V, accumulation time 120s.

2.5.3. Effect of accumulation time

The depedence of the different pulse anodic stripping current on the accumulation time was examined. As expected for anodic stripping experiment the peak current increased with incresing accumulation time. At longer deposition time than 120s the stripping signals for Cu become almost constant. Because the preconcentration time dependsd on the analyte concentration, it took longer for the peak current to level off at lower concentration of metal ions. On the other hand, at higher concentration the rate of the metal ion uptake was faster and the binding sites of the modifyed electrode could be saturated during shorter time. Thus, the measurement range can be controlled by the adequate selection of the preconcentration time. The stripping analysis with new modified glassy carbon electrode had already reached to the range of trace metal analysis level at 120s preconcentration time.

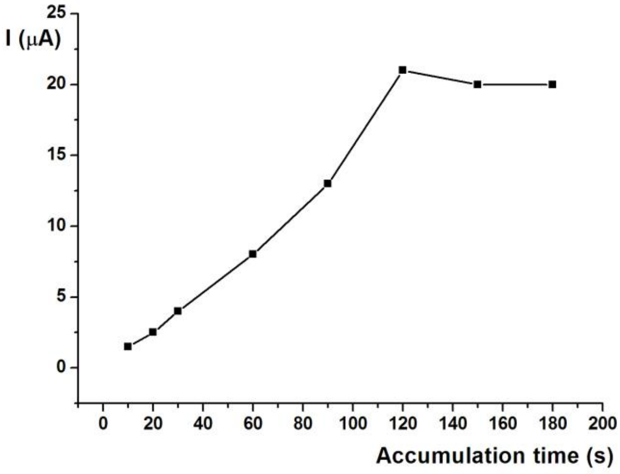

Figure 6. Effect of accumulation time on peak current; electrolyte acetic buffer pH 4, accumulation potential -1.4 V

2.6. Interferences

Perhaps the main adventage of the modifyed electrode for determination of of metals ions lays in its inherest selectivity. Any electroactive species that forms a precipiated with DPABA might present an obstacle in the successful analysis. No alteration of the voltametric signals of copper was exprienced in excess of followinf ions: Li^{+}, Na^{+}, K^{+}, Cs^{+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+} and Cd^{2+}. However in presence of Hg^{2+} and Bi^{3+} ions the stripping response has altered significantly because there is a match signal and increase the peak current of copper.

2.7. Analytical applications

Calibration plots for the determination of Cu on the Cu-DPABA–NA/GCE were achieved by SWASV under the optimal conditions. The DPASV for different concentrations of Cu and calibration curves were presented in Fig. 7. The corresponding equations and correlation coefficients were I=1.243+0.248 C, r = 0.9985 for Cu where C was concentration in µgL^{-1} and I, current in µA. The resulting calibration plots were linear over the range from 7.0x10^{-9}– 5.0 x10^{-5}. The detection limit was 3.0 x10^{-9} mol/L based on three times the background noise. The reproducibility of Cu-DPABA–NA/GCE was evaluated by 10 repetitive measurements of Cu. The relative standard deviations were 1.95% for 40µgL^{-1}of Cu. The results demonstrated that the modified electrode could improve both the sensitivity and the reproducibility of modified electrode.

Application of the new Cu modified electrode in real samples was one of the primary requirements for its validation. Standard additions of 5µgL^{-1} Cu caused current increments at the sample potentials and made the determination of Cu in the river water possible. The concentration was estimated by ASV from the calibration curve of the proposed Cu modified electrode Fig. 7. Accuracy was evaluated with recovery experiments. (Table 2). It was found that the copper contents obtained from five measurements are in satisfied agreement with prepared solution.

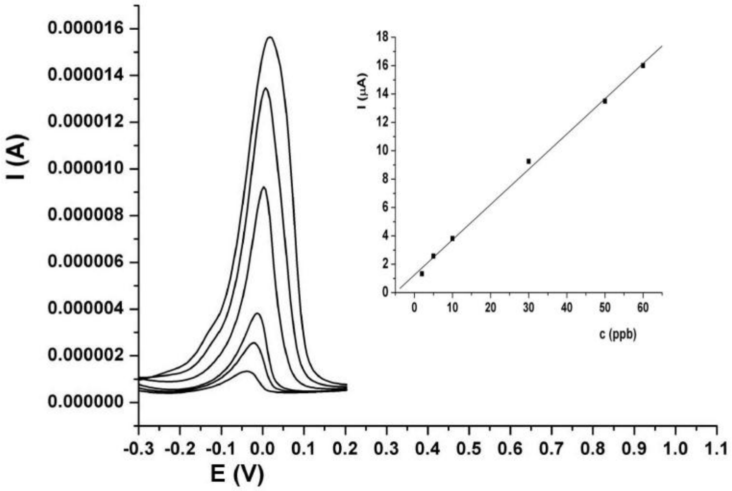

Figure 7. DPASV and calibration curve for differente concentation of Cu at optimized paremeters

Table 2. Results of determination of copper in samples of water

Sample	Sample conc. x10^{-7} mol/L	Cu-added x10^{-7} mol/L	Cu-found x10^{-7} mol/L	Recovery %
1.	0.01	5.00	5.03	100.4
2.	ND	5.00	4.95	99
3.	0.04	5.00	5.06	100.4

ND-non detectable

Limits of detection of Cu in our work are almost among the lowest ones reported previously (Table 3).

Table 3. Summary of previous ASV determination of Cu with various electrodes.

Detected metal	Electrode type	Accumulation time and potential	Electrochemical stripping technique	Detection limit (M)	Reference No.
Cu, Hg	Teetraethyl thiuram disulfide		POTEMTIOMETRIC	Cu = $10^{-7.4}$	17
Cu	DQDS	−0.05V, 300 s	DPASV	Cu=3*10^{-9}	15
Cu, Cu	2-aminothiazole pyrocatechol Violet	-0.3V, 1200s /. 600s	DPASV DPASV	Cu= 3.1*10^{-8} Cd = 15*10^{-9}	22 21
Cu,	Chitosan and crosslinked chitosan	-0.3V,300s	DPASV	Cu=1*10^{-8}	30
Cu	Nafion-Cu-DPABA modified GC electrode	-1.4V, 120s	DPASV	Cu=3*10^{-9}	This work

Among DP ASV determinations, our electrode had the lowest detection limit. Furthermore, our electrode had a short preparation time and it does not require special aparaturs. This electrode has long life (hundred measurements) in comparison with other modified electrodes reported previously.

3. CONCLUSION

A new type of modified glassy carbon electrode for ASV determination of copper was developed. The new sensor was based on readily available Cu- complex. The obtained results showed that these modified electrodes are comparable with other conventional electrode. The realization of new Cu-DPABA–NA/GCE complex modified glassy carbon electrode enhances the selectivity and detection limit for ASV determination of copper. Although the life time of suggested sensor was relatively long (hundred measurements) and it could be easily prepared for another determinations.

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Reference

1. J. Wang *Stripping Analysis Principles, Instrumentation and Application.* VCH Publisher, Deerfield Beach DL, 1985
2. J. Wang, *Analitical Electrochemistry*, 3rd ed., Wiley and Sons Inc., Hobokun, NJ, 2006
3. IM. Stinberg, A. Lobnik, OS. Wolfbies, *Sensors Actuators B* 90 (2003) 230
4. N. Mahedra, P. Gangaiya, S. Sotheeswaran, R. Narayanaswamy, *Sensors Actuators B* 81 (2002) 196
5. BF. Reis, M. Knochen, G. Pignalosa, N. Cabrera, J. Giglio, *Talanta* 64 (2004) 1220
6. S. Nelms, *Am Biotechnol Lab* 21 (2003) 3
7. G. Herzog, DWM. Arrigan, *Anal Chem* 75 (2003) 319
8. X. Dai, RG. Compton, *Electroanalysis* 17 (2005) 1835
9. NW. Solomons, *J Am Coll Natr* 4 (1995) 83
10. U, Forstner, GT Wittman (1981) Metal pollution in the aquqtic enveronment. Springer, Berlin
11. European Commission (1998) Water Quality Directive 98/83/EU, Brussels
12. A.A. Ramadan, H. Mandil, A.M. Saleh, *J. Appl. Electrochem.* 38 (2008) 1715
13. Y. Bai, X. Ruan, J. Mo, Y. Xie, *Anal. Chim. Acta* 373 (1998) 39
14. E. Canpolat, E. Sar, N. Coskun, H. Cankurtaran, *Electroanalysis* 19 (2007) 1109
15. K. Suagawara, S. Tanaka, M. Taga, *Analyst* 116 (1991) 131
16. H. Yu, JB. Zheng, *Chinese J Chem* 25 (2007) 503
17. MJ. Gismera, D. Hueso, JR. Procopio, MT. Sevilla, *Anal Chem Acta* 524 (2004) 347
18. Y. Zhang, X. Lu, K. Zhu, Z. Wanf, J. Kang, *Anal Lett* 35 (2002) 369
19. H. Zheng, H. Dong, Z. Yan, L. Wen, S. Zhang, B. Ye, *Electroanalysis* 18 (2006) 2115
20. A. Safavi, M. Pakniat, N. Maleki, *Anal Chim Acta* 335 (1996) 275
21. MR. Nateghi, A. Bagheri, A. Massoumi, MH. Kazemeini, *Syntetic Met* 96 (1998) 209 30
22. RM. Takeuchi, AL. Santos, PM. Padilha, NR. Stradiotto, *Talanta* 71 (2007) 771
23. H.W. Rhee, H.Y. Choi, K. Han, J.I. Hong, *J.Am.Chem.Soc.* 129 (2007) 4524
24. S.Y. Kim, J.I. Hong, *Tetrahedron letters* 50 (2009) 1951
25. A. Ojida, I. Hamachi, *Bull. Chem. Soc. Jpn.* 79 (2006) 35
26. T. Li, J. Du, T. Li, Z. Wu, J. Zhu, Z. Guo, *Chemistry & Biodiversity*. 5 (2008) 1495
27. A.H. Arida, P.J. Kloock, J.M. Schoning, *Sensors* 6 (2006) 435
28. S. Foxon, J. Xu, S. Turba, M. Leibold, F. Hampel, F. Heinmann, O. Walter, C. Würtele, M. Holthausen, S. Schindler, *Eur. J. Inorg. Chem* 3 (2007) 429
29. D. Stankovic, D. Manojlovic, G. Roglic, S. Kostic-Rajacic, I. Andjelkovic, B. Dojcinovic, J. Mutic, *Electroanalysis*, 23 (2011), 1928
30. B. C. Janegitz, L. H. Marcolino-Junior, S. P. Campana-Filho, R.C. Faria, O. Fatibello-Filho, *Sensors and Actuators B* 142 (2009) 260