

DETERMINATION OF 4-CHLOROPHENOL USING TWO TYPES OF GRAPHITE-BASED COMPOSITE ELECTRODES

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The severe toxicity of 4-chlorophenol requires the development of simple, sensitive and reliable analytical methods. Two types of graphite based composite electrodes, *i.e.*, expanded graphite-polystyrene (EG-PS) and expanded graphite-epoxy (EG-Epoxy) with 20% graphite (wt.) were evaluated as alternative electrodes for the determination of 4-chlorophenol. The electrochemical performances of these electrodes were studied by cyclic voltammetry (CV), linear-scan voltammetry (LSV), chronoamperometry (CA), and differential pulsed voltammetry (DPV). The both electrodes exhibited useful features for the amperometric determination of 4-CP, related to its mechanical resistance, very low cost, simple preparation and easy renewal of the active electrode surface, with better performance of EG-Epoxy composite electrode.

INTRODUCTION

Carbon electrodes are widely used in electroanalysis due to their low background current, wide potential window suitable for the investigation of an electrochemical oxidation process, chemical inertness, low-cost, and suitability for various sensing and detection applications.¹⁻¹⁸

Recently, electrodes and detectors based on conductive composites comprised of an insulating organic polymer matrix filled with electrically conducting carbon powders have been used for analytical, biological and electroanalytical applications due to their mechanical and chemical stability.^{1,9}

The advantage of these composite electrodes is that they are readily prepared and can be easily polished in comparison to the standard carbon electrodes. Other convenient features are related to their easy renewable surface, sufficient stability and a long lifetime.¹⁹

Expanded graphite (EG) is a low dense form of graphite, prepared by thermal expansion of intercalated natural graphite. Very few reports about its use for electroanalytical applications are available.^{13,14}

4-Chlorophenol (4-CP) is a toxic and non-biodegradable organic compound that is used for the production of dyes, drugs, pesticides, and fungicides, and can be often found in high quantity in the waste waters from various industrial sectors. The severe toxicity of 4-CP requires the development of a simple, sensitive and reliable analytical method. The electrochemical methods are playing an important role in the determination of environmental pollutants as they exhibit high sensitivity, good selectivity, rapid response, low cost, availability for *in-situ* measurements, and in principle need simple instruments.

The main objective of this work is to determine 4-CP using two types of carbon-based composite electrodes, *i.e.*, expanded graphite-polystyrene (EG-PS) and expanded graphite-epoxy (EG-Epoxy). The capability of EG-PS to detect 4-CP was reported in our previous work.²⁰ The detection results of 4-CP using the two types of graphite-based composite electrodes have been compared and allow us to investigate the role of the insulating matrix phase to enhance the detection performance of the material.

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RESULTS AND DISCUSSION

SEM images of fractured surfaces of both composites were taken to qualify the bulk distribution and the structure of the conductive filler (Fig. 1). The appearance of both composites, on the shown length scale of 50 μm , is very similar. Generally, the graphite flakes are well distributed within both organic matrices. However, some differences that can be explained by the different preparation conditions are present. A layering of the graphite flakes parallel to the surfaces of the plate is visible for the EG-Epoxy electrode, due to the pressing of the plate in the hot press. Such layering is absent in the EG-PS electrode which has been prepared by casting a film from a solution. For this composite one can distinguish closely spaced zones of graphite flakes

with a random orientation. The last observation is also confirmed by the different resistivities measured for the two composites. A random orientation of the conductive filler, as in the case of the EG-PS composite, provides with better conditions for conduction of the electrical current across the thickness of the electrode in contrast to the case where a layering parallel to the surfaces of the electrode exists, as for the EG-Epoxy composite. Therefore, the resistance of the EG-PS composite is slightly lower than the resistance of the EG-Epoxy one. The morphological differences, however, are relatively small and, therefore, the different detection results observed for both composites can be entirely related to the different natures of the matrices and the orientation of graphite flakes.

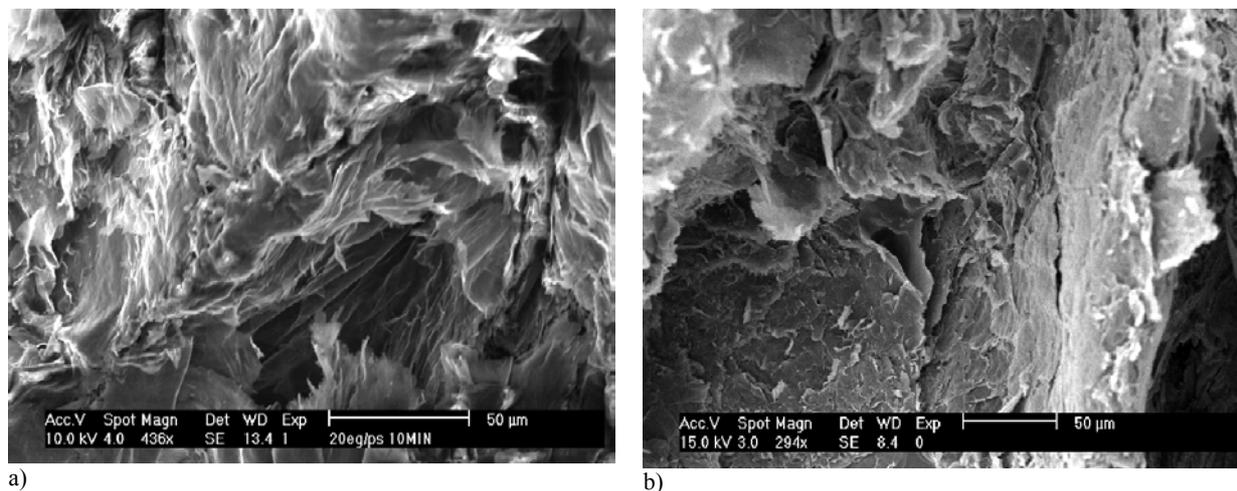


Fig. 1 – SEM image of a fractured surface of: a) EG-PS film and b) EG-Epoxy film.

The analytical utility for 4-CP detection of EG-PS and EG-Epoxy electrodes imposed their electrochemical characterization. The potential window of these graphite composite electrodes has an important effect upon the scope of their analytical utility. The EG-Epoxy electrode versus EG-PS electrode displayed a slight larger potential window and substantial lower background current, determined by the CVs of the EG-PS and EG-Epoxy electrodes in the presence of various concentrations of 4-CP in 0.1 M Na_2SO_4 (the results are not shown here). The dependence between the anodic peak current recorded at 0.8 V vs. SCE and 4-CP concentration was linear and the analytical parameters are shown in Table 1.

In Fig. 2 a) and b) linear scan voltammograms obtained under the same CV conditions on both EG-PS and EG-Epoxy are shown. The response of 4-CP on both electrodes recorded at 0.8 V is linear in the explored concentration range between 0.08 mM-0.5 mM with the good correlation coefficients, 0.982 and 0.998, respectively.

The analytical parameters for both electrodes using CV and LSV techniques of the amperometric detection of 4-CP are gathered in Table 1. It must be underlined that EG-Epoxy electrode exhibited better features suitable for the electrochemical detection of 4-CP in 0.1M Na_2SO_4 .

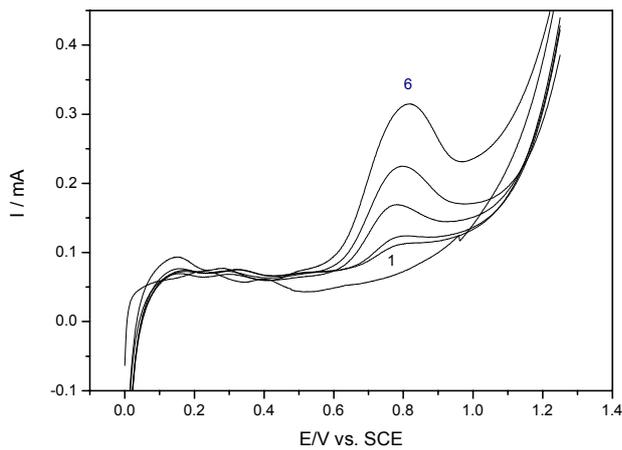


Fig. 2 – a) Linear-scan voltammograms of an EG-PS electrode in 0.1 M Na₂SO₄ supporting electrolyte and in the presence of various concentrations of 4-CP: 1 - 0; 2 - 0.08 mM; 3 - 0.1 mM; 4 - 0.2 mM; 5 - 0.3mM; 6 - 0.4 mM; scan rate: 0.05 V·s⁻¹.

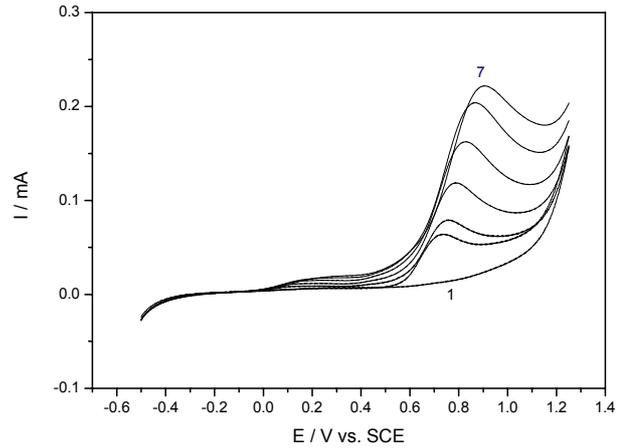


Fig. 2 – b) Linear-scan voltammograms of an EG-Epoxy electrode in 0.1 M Na₂SO₄ supporting electrolyte and in the presence of various concentrations of 4-CP: 1 - 0; 2 - 0.08 mM; 3 - 0.1 mM; 4 - 0.2 mM; 5 - 0.3 mM; 6 - 0.4 mM; 7 - 0.5 mM; scan rate: 0.05 V·s⁻¹.

Table 1

The analytical parameters of amperometric detection of 4-CP at EG-PS and EG-Epoxy electrodes using CV and LSV techniques

Type of composite electrode	Used technique	Electrode sensitivity (mA·mM ⁻¹)	Correlation coefficient (R ²)	LOD (mM)	RSD* (%)
EG-PS	CV	0.358	0.989	0.1	3.6
EG-Epoxy	CV	0.450	0.996	0.02	2.7
EG-PS	LSV	0.362	0.982	0.1	3.9
EG-Epoxy	LSV	0.440	0.994	0.02	2.9

*-three replicates

The LOD was determined using the equation:¹⁵

$$LOD = \frac{3S_d}{b} \quad (1)$$

where S_d is the standard deviation of the blank and b the slope of the calibration equation plots.

The better performance of the amperometric detection of 4-CP with EG-Epoxy electrode led to its analytical testing further using DPV and batch analysis system (BSA). DPV is used in order to establish the working conditions of the easiest method of the amperometric detection, *i.e.*, BSA.

Fig. 3 shows differential pulse voltammograms obtained for increasing concentrations of 4-CP ranging from 0.1 to 0.6 mM on the EG-Epoxy electrode recorded in 0.1 M Na₂SO₄. Electrode surface renewing between successive DPV determinations was performed.

The sharp and well-defined anodic peak appears at around of 0.69V vs SCE. As shown in the inset of Fig. 3 the response of the 4-CP on EG-Epoxy electrode is linear in this range with a correlation coefficient of 0.986 and with a sensitivity of 0.320 mA·mM⁻¹.

Although, it was expected that by using DPV should be obtained better LOD and sensitivity than those obtained by CV and LSV, the results showed the opposite results, which proved that electro-polymerization occurred with partial electrode fouling.¹⁸

The amperometric response of the EG-Epoxy electrode obtained for successive and continuous addition of 0.5 mM 4-CP to 0.1 M Na₂SO₄ solution (batch system analysis -BSA) at an applied potential of 0.69 V vs. SCE established by DPV is shown in Fig. 4. The response of the electrode is linear in the concentration range of 0.5 mM to 2.5 mM (Inset of Fig. 4).

Under the continuous adding of 4-CP, without electrode surface renewing during the measurement the sensitivity was about ten times smaller than one obtained using the other techniques, which allowed electrode surface renewal. This phenomenon could be explained by the electropolymerization secondary process that leads to a low rate of 4-CP oxidation, low permeability and strong adhesion on the electrode.²¹⁻²³

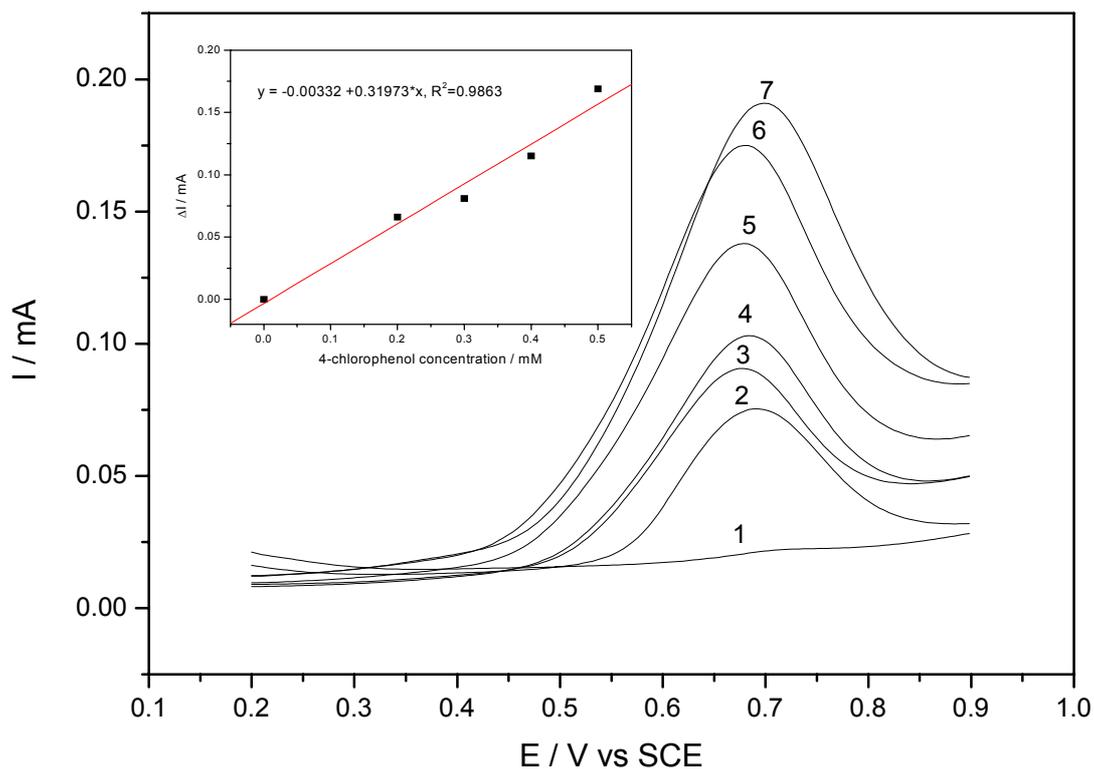


Fig. 3 – Differential pulse voltammograms of EG-Epoxy electrode in 0.1 M Na_2SO_4 supporting electrolyte and in the presence of various concentrations of 4-CP: 1 – 0 mM; 2 – 0.1 mM; 3 – 0.2 mM; 4 – 0.3 mM; 5 – 0.4 mM; 6 – 0.5 mM; 7 – 0.6 mM; scan rate: $0.05 \text{ V} \cdot \text{s}^{-1}$. Inset: calibration plots of current vs. 4-chlorophenol concentration, recorded at 0.69 V vs. SCE.

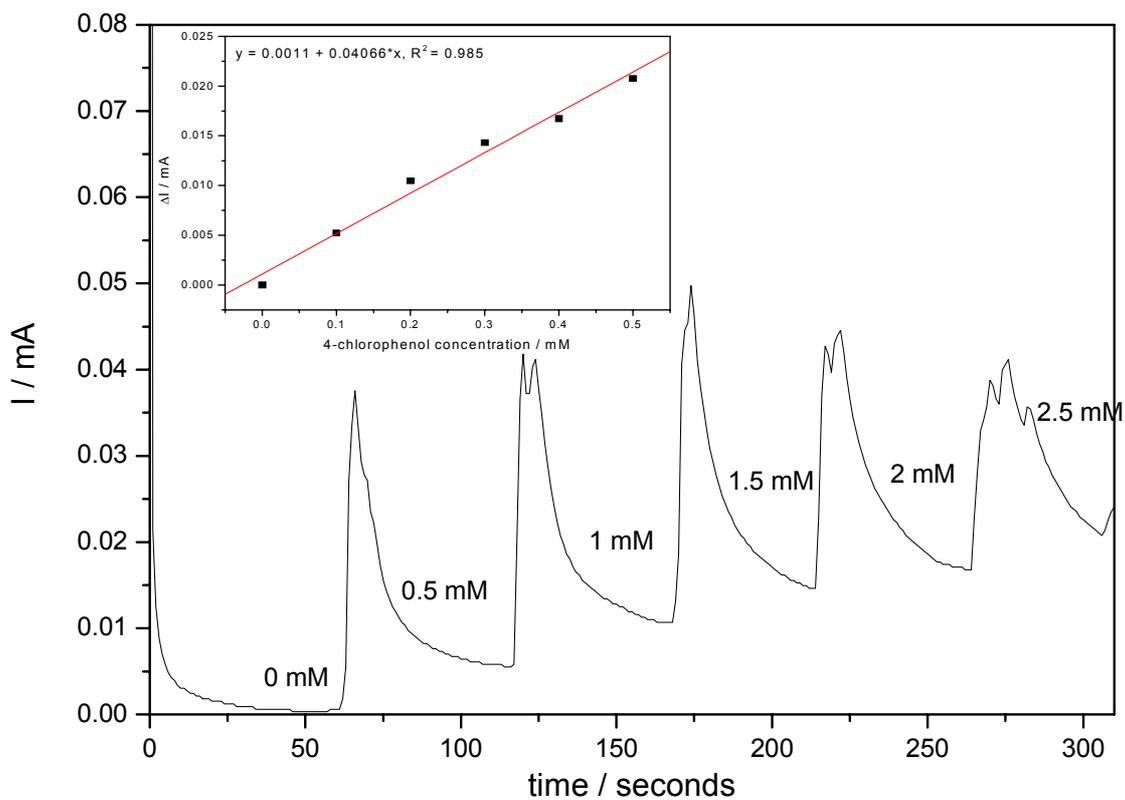


Fig. 4 – Amperometric response (BSA) of the EG-Epoxy electrode for the successive and continuous addition of 0.5 mM 4-CP; applied potential: 0.69 V vs. SCE. Inset: calibration plots of useful signal vs. 4-chlorophenol concentration.

A recovery test was also performed using EG-Epoxy electrode by analyzing three parallel tap water samples, which contain $128.56 \text{ mg}\cdot\text{dm}^{-3}$ 4-CP. This test was run in $0.1 \text{ M Na}_2\text{SO}_4$ as supporting electrolyte and a recovery of 95% was found with a RSD of 3.5 % using LSV. Finally, the results obtained by this method were compared with that obtained by means of a conventional dichromate titration method.²⁴ Using the titration method to evaluate the precision of this method, it can be concluded that the results obtained by the two methods are very close and the accuracy of the proposed voltammetric method is good.

EXPERIMENTAL

The composite electrodes were prepared from low viscosity polystyrene pellets (PS N2000, Shell) dissolved in toluene (Fluka) and mixed with expanded graphite powder (Conductograph, SGL Carbon) and epoxy resin (LY5052, Araldite) mixed with the same conductive filler. The ratios between the components were chosen to reach 20 % (wt.) of expanded graphite. The graphite filler in the EG-PS composite was added to the PS-toluene solution under constant stirring. The obtained viscous mixture was cast into a film using a teflon mold and the toluene was let to evaporate first at room temperature for 48 h and later in a vacuum oven at 50°C for 24 h. The final thickness of the obtained film was about 1 mm. In the case of the EG-Epoxy composite, it was not possible to add the full amount of EG to the matrix resin due to the high surface area of the graphite flakes, therefore, the mixing was performed in a roll-mill at room temperature. The two parts of the epoxy were mixed together and the full amount of the EG was added in steps forming a thick paste. Then the epoxy was cured in a hot press at 80°C for 40 minutes. Simultaneously the material was shaped in a plate of 1 mm thickness. The plate was slowly cooled down (for about 12 h) to room temperature without removing the applied pressure. Plates with a surface area of 81 mm^2 were cut from both composites and put on glass supports and electrical contacts were made using a silver paint. The electrodes were isolated on the one side and the edges by epoxy resin. The prepared EG-PS and EG-Epoxy electrodes showed good mechanical strength with low electrical resistance (3.2Ω and 5.25Ω , respectively). Prior to use, the working electrode was polished on a felt-polishing pad by using $0.3 \mu\text{m}$ alumina powder (Metrohm, Switzerland) in distilled water for 5 minutes and rinsed with distilled water. Subsequently, an electrochemical pretreatment by three repetitive cycling between -0.5 V to 1.25 V vs. SCE in $0.1 \text{ M Na}_2\text{SO}_4$ supporting electrolyte was performed. All measurements were carried out using a potentiostat/galvanostat PGSTAT 302 (Eco Chemie, The Netherlands) controlled with GPES 4.9 software and a three-electrode cell, with a saturated calomel electrode as reference, a platinum counter-electrode, and EG-PS, or EG-Epoxy as working electrode. The reagents of 4-chlorophenol and sodium sulphate were analytical grade from Merck, and freshly prepared with double-distilled water.

The electrochemical performances of these electrodes were studied by cyclic voltammetry (CV), linear-scan voltammetry (LSV), chronoamperometry (CA) and differential pulsed

voltammetry (DPV). DPV is a pulse technique, dependent on applied parameters, *i.e.*, a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$, a pulse modification of 50 mV in amplitude and 50 ms in duration at intervals of 200 ms. Electrode surface renewing between successive determinations was performed.

CONCLUSIONS

The EG-PS electrode comprised a random orientation of the conductive filler and a layering parallel to the surface of the electrode for the EG-Epoxy composite electrode.

Both electrodes exhibited useful features for the amperometric determination of 4-CP, related to its mechanical resistance, very low cost, simple preparation, and easy renewal of the active electrode surface, with better performance of EG-Epoxy composite electrode.

For the EG-Epoxy electrode at the potential value around $0.68\text{--}0.8 \text{ V}$ vs. SCE, linear relationships between the amperometric signal and 4-CP concentration were obtained in the range 0.08 to 1 mM using cyclic voltammetry, linear scan voltammetry, differential pulse voltammetry and chronoamperometry as batch system analysis (BSA). Under these experimental conditions, mechanical cleaning by polishing of the electrode between each addition of 4-CP was required. The reproducibility of the EG-Epoxy electrode using the above-mentioned techniques was evaluated for three replicate measurements of 4-CP detection. The revealed standard deviations reveal the good reproducibility of the electrode.

The accuracy of the applied methods was good as compared to the detection results obtained using the conventional dichromate titration method.

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REFERENCES

1. D. Sun, L. Zhu and G. Zhu, *Anal. Chim. Acta*, **2006**, *564*, 243-247.
2. R. K Mendes, P. Cervini and E. T. G. Cavalheiro, *Talanta*, **2006**, *68*, 708-712.
3. D. O'Hare, J. V. Macpherson and A. Wilson, *Electrochem. Commun.*, **2002**, *4*, 245-250.
4. F. Marken, M. L. Gerrard, I. M. Mellor, R. J. Mortimer, C. E. Madden, S. Fletcher, K. Holt, J. S. Foord and R. H. Dahm, *Electrochem. Commun.*, **2001**, *3*, 177-180.

5. Y. Tu, Y. Lin, W. Yantasee and Z. Ren, *Electroanalysis*, **2005**, *17*, 79-84.
6. M. Luque, A. Rios and M. Valcarcel, *Anal. Chim. Acta.*, **1999**, *395*, 217-223.
7. C. Fernandez, A. J. Reviejo, L. M. Polo and J. M. Pingarron, *Talanta*, **1996**, *43*, 1341-1348.
8. L. Moreno-Baron, A. Merkoci and S. Alegret, *Electrochim. Acta*, **2003**, *48*, 2599-2605.
9. D. Sun and H. Zhang, *Wat. Res.*, **2006**, *40*, 3069-3074.
10. M. Pumera, A. Merkoci and S. Alegret, *Sens. Actuators B.*, **2006**, *113*, 617-622.
11. P. Mailley, E. A. Cummings, S. Mailley, S. Cosnier, B. R. Egdins and E. McAdams, *Bioelectrochem.*, **2004**, *63*, 291-296.
12. P. Ramesh, P. Sivakumar and S. Sampath, *J. Electroanal. Chem.*, **2002**, *528*, 82-92.
13. M. P. Somashekarappa and S. Sampath, *Anal. Chim. Acta.*, **2004**, *503*, 195-201.
14. D. R. Shankaran, N. Uehara and T. Kato, *Anal. Chim. Acta.*, **2003**, *478*, 321-327.
15. P. Cervini, A. Ramos and E. T. G. Cavalheiro, *Talanta*, **2007**, *72*, 206-209.
16. A. Salimi, H. MamKhezri and R. Hallaj, *Talanta*, **2006**, *70*, 823-832.
17. U. A. Kirgoz, D. Odaci, S. Timur, A. Merkoci, S. Alegret, N. Besun and A. A. Telefoncu, *Anal. Chim. Acta.*, **2006**, *570*, 165-169.
18. S. Ramirez-Garcia, S. Alegret, F. Cespedes and R. J. Forster, *Analyst.*, **2002**, *127*, 1512-1519.
19. R. Aquilar, M.M. Davila, M.P. Elizalde, J. Mattusch and R. Wennrich *Electrochim. Acta*, **2004**, *49*, 851-859.
20. F. Manea, C. Radovan, I. Corb, A. Pop, G. Burtica, P. Malchev, S. Pichen, J. Schoonman, *Proc. of Int. Conf. on Mater. Sci. and Eng. BRAMAT 2007*, Roumania, February 22-24, 2007, CD-ROM
21. M. S. Ureta-Zañartu, P. Bustos, C. Berrios, M.C. Diez, M.L. Mora and C. Gutierrez, *Electrochim. Acta*, **2002**, *47*, 2399-2406.
22. F. Gherardini, P.A. Michaud, M. Panizza, Ch. Cominellis and N. Vatistas, *J. Electrochem. Soc.*, **2001**, *148*, 6, D72-D82.
23. J. M. Skowronski and P. Krawczyk, *J. Solid State Electrochem*, **2007**, *11*, 223-230.
24. M. A. H. Franson, "Standard Methods for the Examination of Water and Wastewater", 19th Edition A.P.H.A., Washington, D.C., 1995, 5220D, p.5-15.