IAU-ARAK

J. Iran. Chem. Res. 3 (2010) 271-278

Journal of the
Iranian
Chemical
Research
www.iau-jicr.com

Determination of trace amounts of lead by adsorptive cathodic stripping voltammetry in the presence of xylenol orange

Ali Niazi [*], Roya Tajik, Samira Kamel Foladi

Department of Chemistry, Faculty of Science, Islamic Azad University – Arak Branch, Arak, Iran

Received 16 February 2010; received in revised form 20 September 2010; accepted 25 September 2010

Abstract

Lead forms the complexes with xylenol orange in the basic solution. An adsorptive differential pulse stripping method for the determination of lead is proposed. The procedure involves an adsorptive accumulation of lead on a hanging mercury drop electrode (HMDE) in the presence of xylenol orange, followed by reduction of adsorbed lead by voltammetric scan using differential pulse modulation. The optimum experimental conditions are: xylenol orange concentration of 0.20 μg mL^{-1}, pH 10.5, accumulation potential of -900 mV versus Ag/AgCl, accumulation time of 200 s, scan rate of 10 mV s^{-1} and pulse height of 100 mV. The peak current is proportional to the concentration of lead over range of 0.03-0.65 μg mL^{-1}, and the detection limit is 0.01 μg mL^{-1}. The relative standard deviations (n=3) for 0.10 μg mL^{-1} lead is 0.86%, respectively. The proposed method was applied to the determination of lead in hair and water samples with satisfactory results.

Keywords: Lead; Determination; Stripping; Differential pulse voltammetry; Hair; Water.

---

1. Introduction

The pollution of lead is one of the most serious environmental problems because of their stability in contaminated site and complexity of mechanism in biological toxicity. Once absorbed, lead can be accumulated in body and greatly threaten the health of human [1, 2]. Sensitive methods for the determination of trace amount of lead have received much attention and many techniques have been employed for the determination of lead. The most commonly used methods for determination of various metal ions are atomic absorption spectrometry (AAS), atomic emission spectrometry (AES) and mass spectrometry (MS) [3, 4]. However, these techniques have some disadvantages, such as complicated operation, high cost of maintenance, expensive apparatus and requiring well-controlled experiment conditions.

In recent years, stripping voltammetry techniques, particularly anodic and adsorptive cathodic stripping voltammetry, have shown numerous advantages, including speed of analysis, good selectivity and sensitivity, and low costs of instrumentation compared with other techniques [5-12]. The present investigation was prompted by a desire to develop an alternative method for determination of lead based on adsorptive accumulation stripping voltammetry. The present scheme, based on the accumulation and reduction of lead-XO complex, offers both

---

[*] Corresponding author. Tel.: +98 8613663041, Fax: +98 8613670017
E-mail address: a-niazi@iau-arak.ac.ir & ali.niazi@gmail.com (A. Niazi)

sensitivity and selectivity, and represents an attractive alternative to conventional stripping measurements of lead. In particular, the present method is free from most interference of common interfering ions. The effect of various parameters including concentration of xylenol orange, pH, accumulation potential, accumulation time, scan rate and pulse amplitude in the standard solution on the sensitivity and accuracy of method were investigated. The propose methodology is fast, simple and does not generate hazardous chemical wastes, thus makes it easily possible to be used in control analysis of lead in human hair and water samples.

2. Experimental

2.1. Reagents and solutions

All chemical were reagent grade chemicals, doubly distilled water was used in preparation of all solutions. Stock standard solution of lead, 1000 μg mL^{-1}, was prepared by dissolving appropriate amounts of lead nitrate in water. More dilute solutions were prepared by diluting this solution with water. Britton-Robinson (B-R) buffer [13] was prepared by dissolving appropriate amounts of boric acid, orthophosphoric acid and glacial acetic acid in water and adjusting to the desired pH value with sodium hydroxide and hydrochloric acid solutions.

2.2. Instrumentation and software

Voltammograms were obtained by using an Autolab instrument (Eco Chemie, The Netherlands), Model PGSTAT12 processor, and a three electrodes system consisting of a HMDE (drop size of 3) as working electrode, an Ag/AgCl (3.0 M KCl) reference electrode and a carbon counter auxiliary electrode. All pH measurements were performed with a Horiba M-12 pH meter using a combined glass electrode. Solutions were deoxygenated with high-purity nitrogen for 3 min prior to each experiment.

2.3. General procedure

The general procedure used to obtain cathodic adsorptive stripping voltammograms was as follows. All experiments were performed at room temperature. A 5 mL aliquot of buffer (B-R) solution (pH 10.5) and appropriate volumes of the xylenol orange and sample solutions were pipetted into a 25 mL volumetric flask, diluted to the mark, and transferred to the electrochemical cell. The solution was purged with nitrogen first for 5 min and then for 50 s before each adsorptive stripping step. Then an accumulation potential of -900 mV versus Ag/AgCl was applied to a fresh HMDE during stirring the solution for a period of 200 s.

Following this preconcentration stirrer was stopped and after equilibrium of 10 s, the differential pulse voltammograms was recorded from -300 to -600 mV with a potential scan rate of 10 mV s^{-1} and pulse amplitude of 100 mV. The current was measured and recorded for the sample solution. Peak heights were evaluated as the difference between each voltammograms and the background electrolyte voltammograms. Between experiments, the cell was treated with concentrated HNO_3 and then washed with acetone and distilled water. All these determinations were performed in triplicate.

3. Results and discussion

3.1. Preliminary investigation

Preliminary experiments were carried out to identify the general features, which characterize the behavior of the metal ion-XO systems on hanging mercury drop electrode. Fig. 1 displays the stripping voltammograms of 0.10 μg mL^{-1} of lead in presence of xylenol orange at pH 10.5 after

200 s accumulation at -900 mV. As can be seen in Fig. 1, in the absence of xylenol orange the reduction current is rather small. Addition of 0.20 μg mL^{-1} xylenol orange causes an increases of the lead reduction current in comparison to the lead current (Fig. 1d).

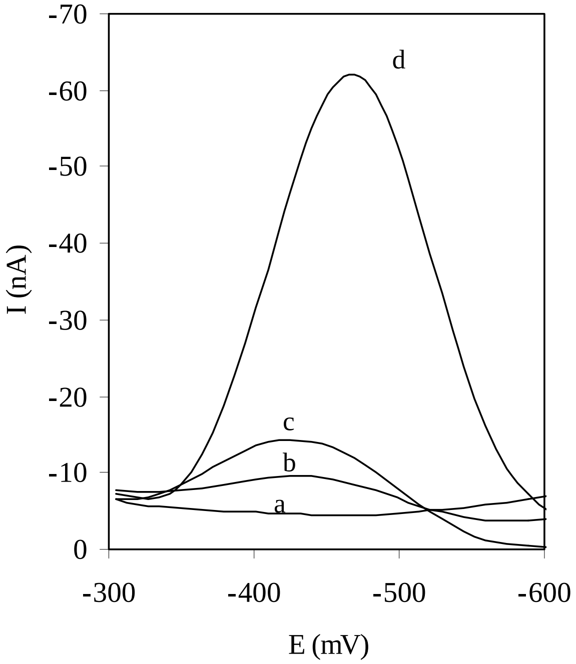

Fig. 1. Differential pulse voltammograms for (a) background, (b) 0.2 μg mL^{-1} of xylenol orange, (c) 0.04 μg mL^{-1} of lead and (d) 0.04 μg mL^{-1} of lead and 0.2 μg mL^{-1} xylenol orange in B-R buffer (pH 10.5). Other conditions were accumulation time 200 s, accumulation potential -900 mV, pulse amplitude of 100 mV and scan rate of 30 mV s^{-1}.

3.2. Effect of operational parameters

Taking into account that the differential pulse voltammetry technique was used to develop the method for quantitative determination of lead, and in order to choose the optimum conditions, some analytical and instrumental parameters were studied.

3.3. Effect of chemical variables

The influence of the pH on the stripping peak current of lead was studied in the pH range 7.0 to 11.5 (Fig. 2). In order to keep the composition of the buffer constant when studying the effect of the pH, Britton-Robinson buffers were used. It was found that at the pH range of 9.5 to 11.0, the peak current increases with an increase in the pH. At higher pH values there was a decrease in the peak current, probably due to the precipitation of lead hydroxide at such pH values. Thus, a pH of 10.5 was adopted for further studies. The concentration of xylenol orange has a significant effect on peak current. It can be seen from Fig. 3 that the peak current increases with an increase in the xylenol orange concentration up to 0.20 μg mL^{-1}, above which it starts to decline. Therefore, 0.20 μg mL^{-1} xylenol orange was selected.

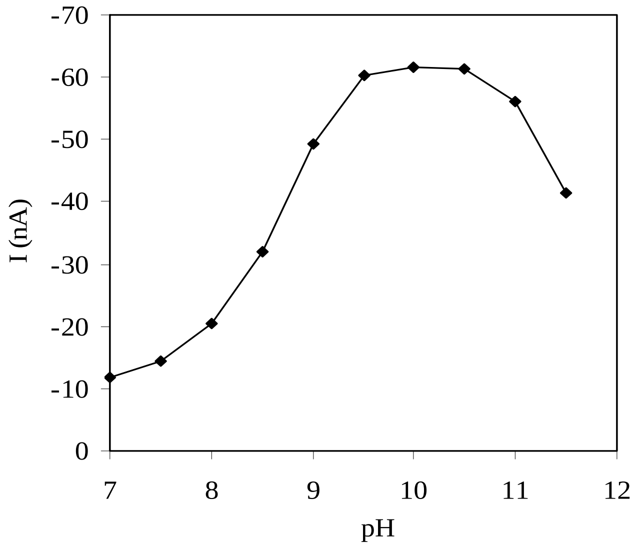

Fig. 2. Effect of the pH on the peak current of 0.04 μg mL^{-1} of lead in presence of 0.2 μg mL^{-1} of xylenol orange. All other conditions as in Fig. 1.

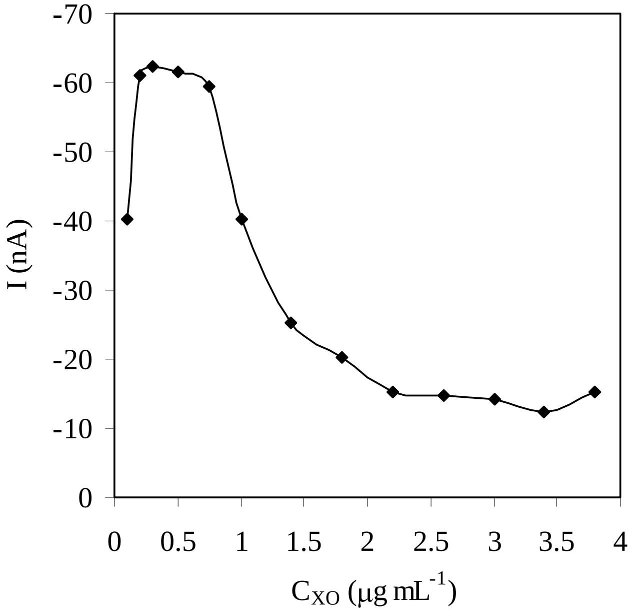

Fig. 3. Effect of xylenol orange concentration on the peak current at pH 10.5. All other conditions as in Fig. 1.

3.4. Effect of variation of accumulation potential and accumulation time

The accumulation potential was varied between 0 and -1.1 V during a constant accumulation time of 200 s. The cathodic voltammetric scan was started after an equilibrium time of 10 s without stirring to allow the electrode to equilibrate before performing the measurement process. Maximum peak currents were observed at accumulation potentials of -0.8 to -1.1 V for lead (Fig. 4). Generally, an accumulation potential of -900 mV vs. Ag/AgCl was used for further investigation. Variation of the accumulation time between 0 and 200 s at an accumulation potential of -900 mV was investigated. The influence of accumulation time on the stripping peaks of lead was investigated. The time required for accumulation of the lead complex onto the electrode depends on the concentration of the complex, less time required for higher concentrations.

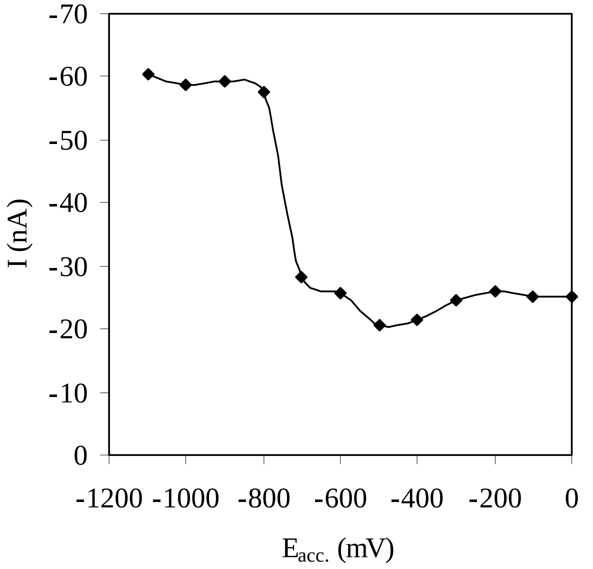

Fig. 4. Effect of the accumulation potential on the peak current. All other conditions as in Fig. 1.

As mentioned before ligand concentrations that are higher than required may cause inhibition of the chelate adsorption by competitive coverage by the free ligand. An increase in the stripping peaks current with accumulation time was observed for Pb(II)-XO complex. As is expected for adsorption processes, the dependence of the peak current on the accumulation time is limited by the saturation of the electrode, resulting in the current reaching a plateau at high accumulation time, as shown in Fig. 5. Thus, deposition time of 200 s was used throughout, as it combines good sensitivity and relatively short analysis time.

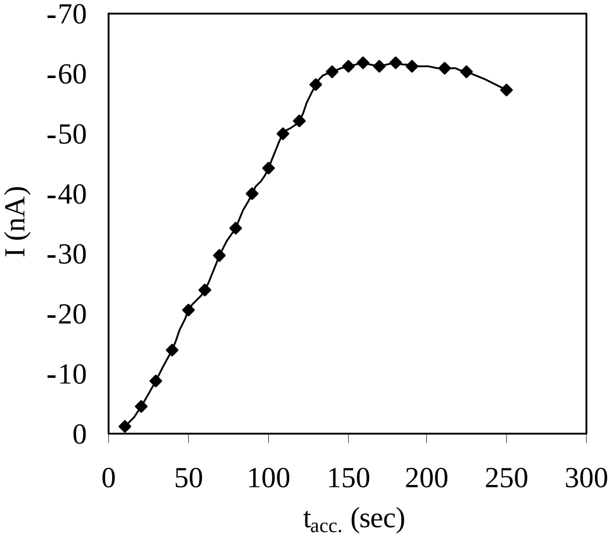

Fig. 5. Variation of the peak current with the accumulation time at the optimum conditions.

3.5. Effect of pulse height and scan rate

The effect of pulse height on the sensitivity of the reduction current peak was also checked using different pulse heights in the range of 10 and 100 mV with the optimum conditions. The results showed that the peaks current were increased by increasing pulse height to 100 mV, and then leveled off. This is due to the fact, after 100 mV, the peak current broadened. Thus, 100 mV pulse height was selected. The influence of potential scan rate on the peak current of lead was studied in the range of 10-120 mV s^{-1} with the optimum conditions. The results showed that by increasing scan rate from 10 to 30 mV s^{-1}, the peak currents increased linearly, whereas for higher scan rate the rate of increasing in peaks current decreased. This is due to the fact that at lower scan rate (30 mV s^{-1}) the adsorption processes is the main of phenomena at the electrode surface, whereas at higher scan rate diffusion of the lead from solution to the electrode surface added to the adsorption phenomena. Therefore, a scan rate of 30 mV s^{-1} was selected for study.

3.6. Effect of stirring speed, drop size and equilibrium time

Fig. 6 shows the influence of stirring rate on the voltammetric response and also on R.S.D. [6]. It was found that peak current increased with stirring rate in the range of 500 to 2000 rpm, and levels off at higher stirring rates. The R.S.D. value decreases rapidly from 500 to 2000 rpm and then rises after 2000 rpm. This is because at lower stirring rates the solution was stirred heterogeneously and at higher speed, the solution was stirred turbulently. A stirring rate of 2000 rpm, which gave the best reproducibility, was selected. The effects of drop size and equilibrium time on the voltammetric response were examined in developing a suitable analytical procedure for the determination of lead. The chosen working conditions were: drop size of 3 and equilibrium time of 10 s.

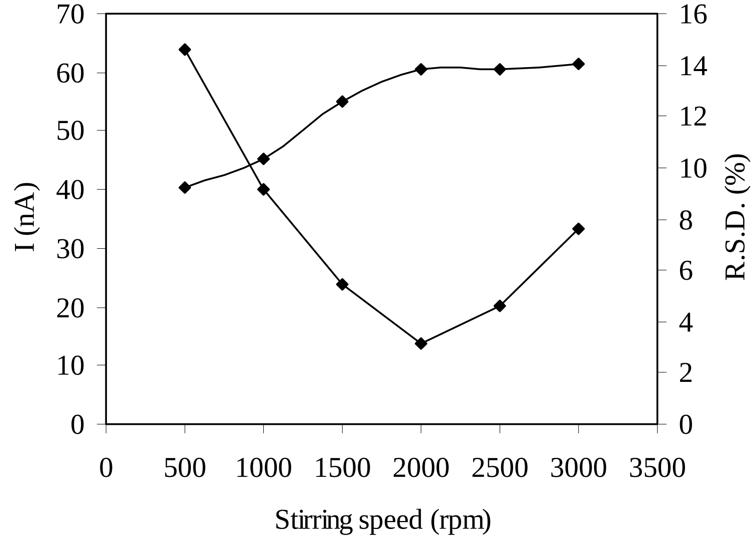

Fig. 6. The effect of stirring speed on the peak current and its R.S.D. (%) for 0.04 μg mL^{-1} of lead. All other conditions as Fig. 1.

3.7. Reproducibility, linear range and detection of the method

The reproducibility of repeating the determination of low concentration of lead was found under the optimum conditions. The R.S.D. for three determinations was calculated as 0.86% for lead concentrations of 0.10 μg mL^{-1}, respectively. Typical adsorptive cathodic differential pulse voltammetry and calibration graph are shown in Fig. 7. Under the optimized conditions the peak current of lead was found to be proportional to its concentration over the range 0.03–0.65 μg mL^{-1} and its equation was $[\text{current}]_{\text{nA}} = -3878.1 \times [\text{lead}] + 114.9$. The correlation coefficient (r) was 0.9984. The detection limit $(Y_{LOD} = \hat{X}_B + 3S_B)$, (where Y_{LOD} is the signal for detection limit,

$\hat{X}_B$ is the mean of blank signal, and S_B is the standard deviation of blank signal) was obtained as 10 ng mL^{-1} [14].

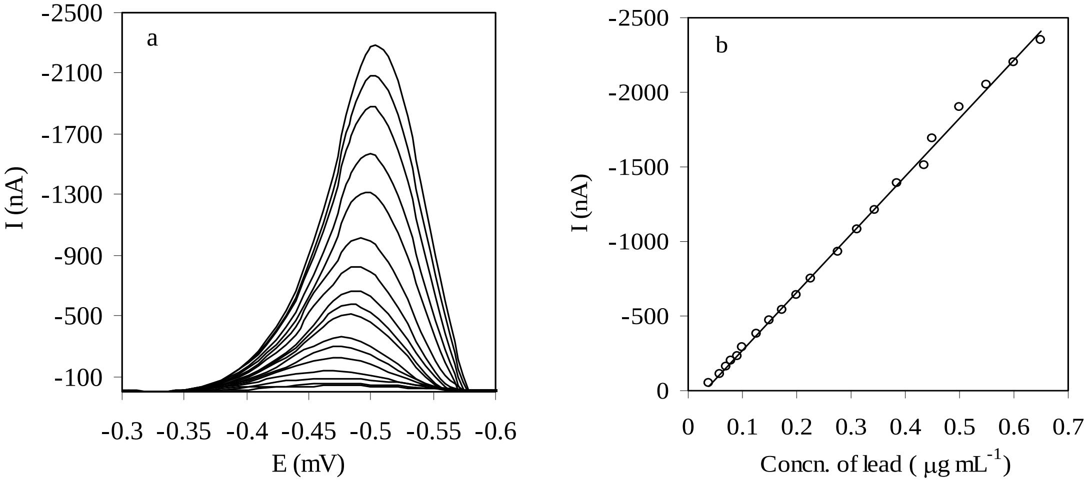

Fig. 7. (a) Typical voltammograms and (b) Calibration graph for determination of lead at pH 10.5. All other conditions as Fig. 1.

3.8. Interferences studies

To check the selectivity of the proposed stripping voltammetric method for determination of lead, various cationic and ionic ions, as potential interferents, were tested. Interference was taken as the level causing an error in excess of 3%. The results show that less than 500-fold excess of alkaline and alkaline earth metal, Cr^{6+}, Mo^{6+}, Th^{4+}, Sn^{4+}, Al^{3+}, Ga^{3+}, Bi^{3+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, SO_4^{2-}, SO_3^{2-}, NO_2^-, Br^-, Cl^-, CO_3^{2-}, CN^-; 200-fold excess of As^{3+}, Cr^{3+}, Fe^{3+}, Fe^{2+}, Cd^{2+}, Hg^{2+}, ClO_3^-, ClO_4^-, $C_2O_4^{2-}$; 50-fold excess of Cd^{2+} and 10-fold excess of Tl^+ did not interfere the determination of 0.10 μg mL^{-1} of lead. Thus, the method is highly selective and therefore, has been successfully applied to trace determinations of lead in various synthetic and real samples without any prior separation.

3.9. Real sample analysis

The developed method was applied to the determination of lead in human hair and natural waters. The procedure of wet ashing of human hair is described by Sabermahani and Taher [15]. The hair sample was rinsed with acetone and 4.20 g of dried sample was accurately weighted and burned in a furnace at 700 °C until a white powder was obtained. The obtained ash was dissolved in a minimum volume of concentrated nitric acid with heating. The solution boiled to expel brown fumes, cooled and diluted with distilled water to 25 mL in a calibration flask. A 500 μL of this solution added t 25 mL of Britton-Robinson buffer with pH 10.5, and the generate procedure was used on the resultant solution. For waster samples, these water were exchanged with distilled water used fro the preparation of a Britton-Robinson buffer (pH 10.5) and the general procedure was used on these resultant solutions. As can be seen from Table 1, the results obtained in the determination of lead in human hair and water (tap, river and waste) samples were quit well. In fact, the recoveries ranged from 90.0% to 110.0% for lead. Therefore, the proposed method is able to predict the concentration of lead in the real matrix samples.

Table 1
Determination of lead in human hair and water samples.

Samples	Added	Determined [a]	S.D. [b]	Recovery (%)
Tap	-	0.03	0.12	-
	0.03	0.06	0.21	100.0
River	-	0.04	0.14	-
	0.20	0.25	0.19	105.0
Waste	-	0.16	0.11	-
	0.50	0.65	0.23	98.0
Human Hair	-	0.04	0.09	-
	0.10	0.13	0.18	90.0
Human Hair	-	no detect	-	-
	0.10	0.11	0.21	110.0

[a] determination according standard addition method
[b] standard deviation (n = 3)

4. Conclusion

The present study demonstrated that the use of a HMDE for determination of trace amount of lead by cathodic stripping voltammetry based on adsorptive accumulation and electrochemical reduction of lead-XO complex on the electrode surface is feasible. Therefore the presented system offers a practical method for determination of lead in human hair and water samples, which has advantages of high sensitivity, high selectivity, simplicity and speed.

References

[1] M. Patriarca, A. Menditto, B. Rossi, T.D.B. Lyon, G.S. Fell, Microchem. J. 67 (2000) 351-361.
[2] I.A. Darwish, D.A. Blake, Anal. Chem. 74 (2002) 52-58.
[3] E.B. Bulska, M. Walcerz, W. Jedral, A. Hulanick, Anal. Chim. Acta 357 (1997) 133-140.
[4] M.W. Wensing, D.Y. Liu, B.W. Smith, J.D. Wienefordner, Anal. Chim. Acta 299 (1994) 1-7.
[5] A. Niazi, J. Ghasemi, M. Zendehdel, Talanta 74 (2007) 247-254.
[6] J. Ghasemi, A. Niazi, R. Ghorbani, Anal. Lett. 39 (2006) 1159-1169.
[7] A. Niazi, J. Chin. Chem. Soc. 54 (2007) 1195-1200.
[8] T.H. Li, Q.L. Zhao, M.H. Huang, Microchim. Acta 157 (2007) 245-249.
[9] A. Babaei, E. Shams, A. Samadzadeh, Anal. Sci. 22 (2006) 955-959.
[10] K. Zarei, M. Atabati, H. Ilkhani, Talanta 69 (2006) 816-821.
[11] M.B. Gholivand, A.A. Romiani, Anal. Chim. Acta 571 (2006) 99-104.
[12] R. Pirch, W.W. Kubiak, J. Electroanal. Chem. 599 (2007) 59-64.
[13] J.J. Lurie, Handbook of Analytical Chemistry, Mir Publishers, Moscow, 1978, p. 263.
[14] J.C. Miller, J.N. Miller, Statistics for Analytical Chemistry, Ellis Harwood Ltd., Chichester, 1992.
[15] F. Sabermahani, M.A. Taher, Anal. Chim. Acta 565 (2006) 152-156.