DETERMINATION OF TRACE AMOUNTS OF LEAD BY ADSORPTIVE CATHODIC STRIPPING VOLTAMMETRY WITH L-3-(3,4-DIHYDROXYPHENYL)ALANINE

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A sensitive and selective procedure is presented for the voltammetric determination of lead. The procedure involves an adsorptive accumulation of lead L-3-(3,4-dihydroxyphenyl)-alanine (LDOPA) on a hanging mercury drop electrode, followed by a stripping voltammetric measurement of reduction current of an adsorbed complex at –0.15 V (vs Ag|AgCl). Optimum conditions for lead analysis include pH 8.5, 80 μM LDOPA and accumulation potential –0.15 V (vs Ag|AgCl). The peak currents are proportional to the lead concentration 1–300 nmol l^{-1} with a detection limit of 0.6 nmol l^{-1} and accumulation time 60 s. The method was used for the determination of lead in blood, dry tea and also in waters.

Keywords: Adsorptive stripping voltammetry; Lead; Levodopa; Amino acids; Pollutants determination; Waste water.

The lead pollution is one of the most serious environmental problems because of its stability at the contaminated sites and complex mechanisms of biological toxicity. Once absorbed, lead can be accumulated in the body and be a threat for human health[1–3]. Sensitive methods for determination of trace amounts of lead have received much attention and many techniques have been employed for the purpose. The most commonly used methods for determination of various metal ions are atomic absorption spectrometry (AAS)[4,5], atomic emission spectrometry (AES)[6] and mass spectrometry (MS). However, these techniques have some disadvantages, such as complicated operation, high maintenance cost, expensive apparatus and requiring well-controlled experimental conditions. Electrochemical methods are most favorable techniques for the determination of heavy metal ions, including lead(II), because of their low cost, high sensitivity, easy operation and the ability for analyze element speciation. In previous works

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the determination of heavy metal ions were mostly carried out by electrochemical methods at mercury electrodes[7–19] including stripping voltammetry. The techniques, particularly anodic stripping voltammetry (ASV) and adsorptive cathodic stripping voltammetry (AdCSV), have shown numerous advantages including the speed of analysis, good selectivity and sensitivity, good performance with saline matrices like sea water. Because of the great sensitivity enhancement obtained with adsorption cathodic stripping voltammetry, several complexing agents have been studied for the adsorptive collection of lead ion complexes on hanging mercury drop electrode (HMDE)[20]. Several organic compounds such Xylenol Orange[21,22] Calcein Blue[23], quinolin-8-ol[24], Pyrogallol Red[25], morin[26], carbamoylphosphonic acid[27] and carbidopa[28] have been used as complexing agents for the voltammetric determination of lead. In this work, a sensitive adsorptive stripping voltammetric method for the lead determination at trace levels is described. The procedure is based on reduction of lead complexes with LDOPA after accumulation at the surface of a hanging mercury drop electrode.

EXPERIMENTAL

Reagents

All solutions were prepared with deionized water. Nitrogen (99.99%) was used to remove dissolved oxygen. Stock standard solutions of Pb(II) were prepared by dissolving $Pb(NO_3)_2$ (reagent grade; Merck) in water. Solutions of the chelating agent were prepared by dissolving LDOPA (Sigma) in water. The support electrolyte chosen was a borate buffer solution obtained by dissolving boric acid (analytical reagent grade; Merck) and borax (sodium tetraborate) (analytical reagent grade; Merck) in water.

Apparatus

All polarographic measurements were performed using a Metrohm multifunction instrument Model 693 VA processor equipped with a 694 VA stand. Measurements were carried out with a hanging mercury drop electrode (HMDE), (size 9) in a three-electrode arrangement. The auxiliary electrode was a Pt wire with a considerably larger surface area than that of HMDE. An Ag|AgCl (3 м KCl) was used as a reference electrode. Stirring was carried out with a large Teflon stirrer of 2000 rpm. A Metrohm 692 digital pH-meter was used for pH measurement. Solutions were purged with high-purity nitrogen for 5 min prior to each experiment, and the experiments were performed under nitrogen atmosphere.

Procedure

Ten milliliters of a supporting electrolyte solution containing 0.05 м borate solution was pipetted into the cell and purged with nitrogen for 5 min. An accumulation potential of

–0.150 V was applied to a fresh mercury drop for 60 s, while the solution was stirred. After the accumulation the stirring was stopped after 5 s. The voltammogram was recorded by applying a differential pulse scan terminating at –0.514 V. All the measurements were obtained at room temperature under nitrogen atmosphere.

RESULTS AND DISCUSSION

Cyclic Voltammetry

Preliminary studies of the electrochemical behavior of Pb(II), and its complexes with LDOPA were performed by cyclic voltammetry. Figure 1 shows the cyclic voltammograms obtained with 10 μM Pb(II) in the absence (curve a) and presence (curve b) of LDOPA in a stirred 0.05 M borate buffer (pH 8.5). The forward potential scan began at an initial potential of –0.200 V, and its direction was reversed at –0.600 V. At experimental conditions, a weak reduction peak for Pb(II) was observed at –0.448 V and its oxidation peak was observed at –0.387 V. After addition of LDOPA, the cyclic voltammogram shows a new reduction peak in the forward scan at –0.493 V due to the reduction of the Pb(II)-LDOPA complex; an anodic peak was observed in reverse scan at a peak potential of –0.458 V. There is a 35 mV difference between the cathodic and anodic peak potentials. The peak separation (34 mV) was close to the theoretical value 30 mV for a two-electron reversible wave. A comparison of the anodic peak current of Pb(II) in the absence (curve a) and presence (curve b) of LDOPA with cathodic peak current of Pb(II) in the presence of LDOPA revealed that the use of the

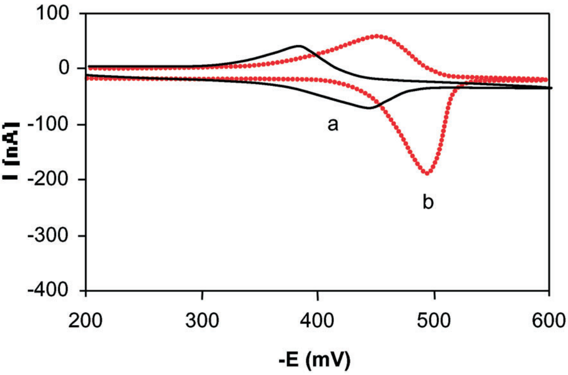

FIG. 1
Cyclic voltammograms of 10 μM Pb(II) (a), 10 μM Pb(II) and 80 μM LDOPA (b). Conditions: 0.05 M borate buffer, pH 8.5

cathodic adsorptive peak current enhanced the sensitivity of the proposed method for determination of Pb(II) ions.

Adsorptive Stripping Voltammetry

Figure 2 displays differential pulse voltammograms of the Pb(II)-LDOPA system on mercury electrode between –0.200 and –0.800 V (vs Ag|AgCl), in the absence of lead (curve a) after 0 s accumulation at –0.150 V. As it is seen, a reduction peak is appeared that my be due to reduction of oxidized product of LDOPA (e.g. oxygen). On addition of Pb(II) solution a well-defined peak at –0.514 V appears which is due to reduction of the adsorbed Pb-LDOPA complex. The voltammograms of lead in the presence of LDOPA after 0 (curve b) and 60 s (curve c) of accumulations at –0.150 V are also shown. A comparison of the voltammograms shows that the height of the Pb peak depends not only on the duration of the preconcentration step but also on the presence or absence of LDOPA and the stripping initial potential, which indicates the adsorptive nature of the response. Figure 3 displays the anodic stripping voltammograms of 0.1 μM Pb in the absence (curve a) and presence (curve b) of LDOPA after 60-s accumulation at –0.800 V and then stripped by scanning the potential toward more positive values. Curve c

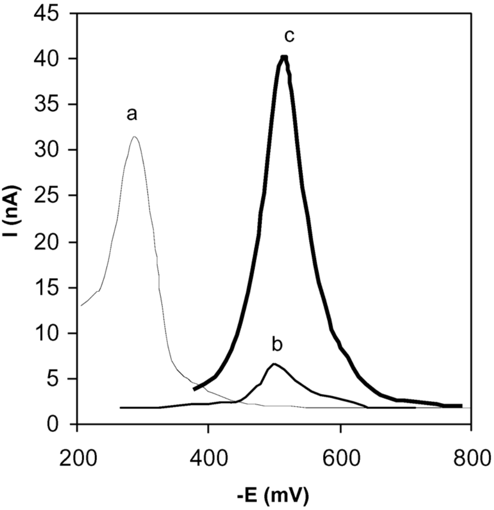

FIG. 2
Cathodic stripping voltammograms of 80 μM ligand (a), 80 μM ligand and 0.1 μM Pb(II) with accumulation time 0 s (b), 80 μM ligand and 0.1 μM Pb(II) with accumulation time 60 s (c)

shows a cathodic stripping voltammogram of the Pb-LDOPA system which was accumulated at –0.150 V for 60 s and then stripped by scanning the potential from –0.300 V toward more negative values.

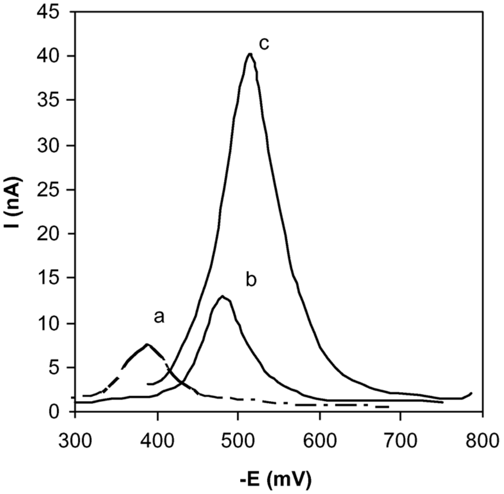

FIG. 3
Comparison of anodic and cathodic voltammogram of 0.1 μM Pb(II) in the Pb(II)-LDOPA system. ASV of Pb(II) (a); ASV of Pb(II) and 80 μM LDOPA, accumulation time t_{acc} = 60 s, accumulation potential E_{acc} = –0.800 V (b); AdCSV of Pb(II) and 80 μM LDOPA, t_{acc} = 60 s, E_{acc} = –0.150 V, pH 8.5 (c)

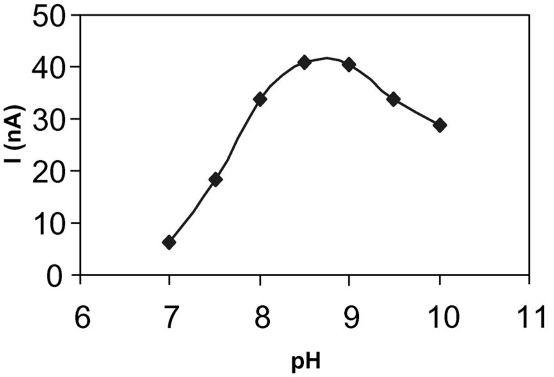

FIG. 4
Effect of pH on adsorptive cathodic stripping peak of 0.1 μM of Pb(II) in the presence of 80 μM LDOPA, t_{acc} = 60 s, E_{acc} = –0.150 V

OPTIMIZATION

Effects of Electrolytes and pH

Various supporting electrolytes, such as the ammonia–ammonium chloride buffer, Britton–Robinson buffer and borate buffer, were investigated. Of these, borate buffer (pH 8.5) gave the best response. The influence of pH was studied for the pH range of 7–11 in the presence of 0.1 μM Pb and 80 μM LDOPA (Fig. 4). It was found that at the pH 7.0–8.5, the peak current increases with increasing pH. At higher pH a decrease in the peak current was observed, probably due to the precipitation of lead hydroxide. Thus, pH 8.5 was adopted for further studies.

Effect of Ligand Concentration

As expected, concentration of LDOPA has a great influence on the sensitivity of lead determination. Figure 5 shows the dependence of peak currents on the LDOPA concentration. A linear increase in the peak current was observed when the ligand concentration increased from 10 to 80 μmol l^{-1}. No improvement was observed at concentrations greater than 80 μmol l^{-1}. Therefore, the LDOPA concentration 80 μmol l^{-1} was chosen as optimum value for further experiments.

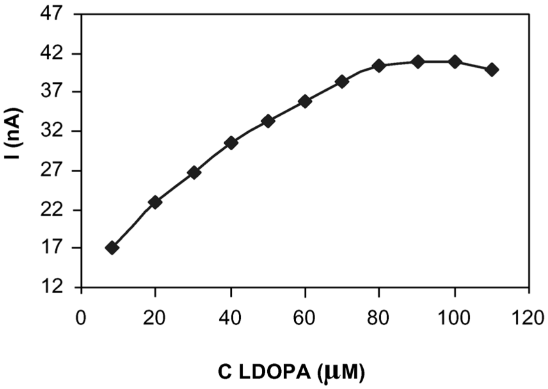

FIG. 5

Effect of the ligand concentration on the adsorptive cathodic stripping peak of 0.1 μM Pb(II). For other conditions, see Fig. 4

Effect of Accumulation Potential and Accumulation Time

The effect of varying the adsorption potential on the peak height of lead is shown in Fig. 6. The adsorption potential was varied between 0.100 and –0.400 V. The peak current increased with changing the potential from 0.100 to –0.150 V, probably due to increased accumulation of the Pb-LDOPA complex on the electrode surface, its height decreased at poten-

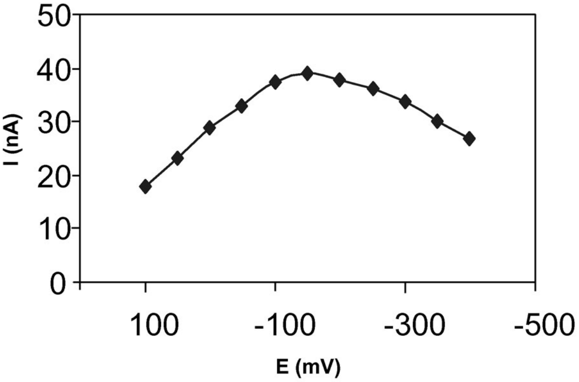

FIG. 6
Effect of the accumulation potential on the peak current of 0.1 μM Pb(II) in the presence of 80 μM LDOPA, t_{acc} = 60 s

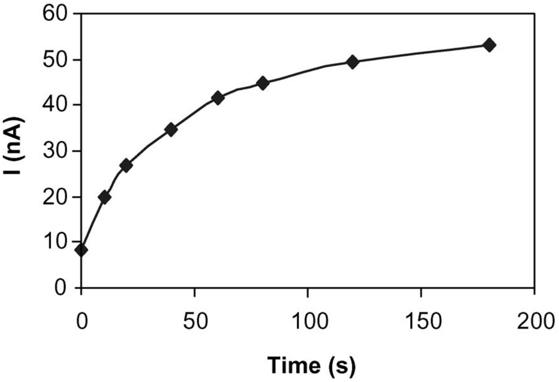

FIG. 7
Effect of the accumulation time on the peak current of 0.1 μM Pb(II). For other conditions, see Fig. 6

tials more negative than –0.15 V, which is due to the competition between ligand and complex for adsorption on the electrode surface. Thus, the potential –0.15 V was selected for subsequent use. Figure 7 shows the plots of the cathodic peak current versus the accumulation time. At first, the peak current increased with the accumulation time, indicating that, before adsorption equilibrium is reached, the longer the accumulation time, the more Pb-LDOPA complex was adsorbed and thus the peak current became high. However, after a specific accumulation period, the peak current tended to level off, illustrating that adsorption equilibrium was achieved. As a result of the surface-activity of the Pb-LDOPA complex, higher sensitivity could be achieved by extending the accumulation time. However, the use of a long accumulation time is inconvenient. An accumulation time of 60 s was used as a compromise between sensitivity and analysis speed.

LINEAR RANGE, DETECTION LIMIT, AND REPRODUCIBILITY OF THE METHOD

Under the selected conditions (borate buffer, pH 8.5, accumulation potential –0.150 V, accumulation time 60 s), the reduction peak current of Pb(II) complexes yields a well-defined concentration dependence. The linear range for lead was evaluated by increasing the lead concentration up to 500 nmol l^{-1}. The calibration plot obtained under the optimized conditions was linear over the range 1–300 nmol l^{-1} with a correlation coefficient of 0.9991. The calibration equation obtained by the least-squares method is $I = 0.3797\,C + 0.067$, where I (nA) is the peak current and C (nmol l^{-1}) is the lead concentration. The detection limit calculated as 3 S/N of seven replicate determination of blank solution after 60-s accumulation is 0.6 nmol l^{-1} (ref.[29]). Ten successive measurements of 0.1 μM Pb after 60-s accumulation showed a relative standard deviation of 2.8%.

EFFECT OF INTERFERENCES

In order to assess possible analytical application of the proposed method, the effects of some alkali, alkaline-earth and heavy-metal ions as well as some anions (more than 25) on the determination of 0.1 μM Pb was studied. The tolerance limit was defined as the concentration, which gave an error less than 3.0% of Pb(II). The results are shown in Table I. It is concluded that the method is free from interferences of foreign ions, except for UO_2^{2+}. However, the uranium interference could be easily reduced by adding 0.003 M NaF to the test solution.

TABLE I
Effect of diverse ions on the Pb determination (0.1 μM Pb(II))

Ion	Tolerance limit $C_{ion}/C_{Pb(II)}$
Na^+, K^+, ClO_4^-, Li^+, Ba^{2+}, F^-, Cl^-, CO_3^{2-}	10^4
Mn(II), Sr(II), V(III), Cr(III), Cr(IV), Al(III), Fe(III), W(IV), NO_3^-, Zn(II)	1000
Cu(II), Fe(II)	100
Co(II)	50
Ni(II), Cd(II)	20
UO_2(II)	1, 10[a]

[a] After addition of 0.003 M NaF.

ANALYSIS OF REAL SAMPLES

In order to examine the performance of adsorptive stripping voltammetry in practical situations, the method was used for determination of trace amounts of lead in natural water, human blood and dry tea samples. The data obtained for samples spiked with Pb(II) showed good recoveries. Sea water and spring water samples were filtered and subjected to ultraviolet (UV) digestion for 2 h before determination. Then the pH of samples was adjusted with a buffer to 8.5 and the samples were stored in a cool place. The results are shown in Table II. The blood sample preparation was carried out according to literature[30] as follows: 2.0 ml of blood in a beaker, 4 ml of acid mixture (2 ml concentrated HNO_3 + 2 ml concentrated $HClO_4$) were added. After 10 min, the sample was heated until half of the mixture evaporated. Before subsequent warming, 2 ml of concentrated nitric acid were added (to avoid explosion) and the mixture was evaporated almost to dryness. After that, 2 ml of concentrated $HClO_4$ were added and the mixture was heated again to dryness. After cooling, 2 ml of concentrated HCl were added and the evaporation was repeated. The sample was diluted to 10 ml in a calibrated flask and the solution was stored as the digested blood sample solution. For measurement, 1 ml of the sample was added to a voltammetric cell and the procedure was followed. The result is shown in Table III.

The procedure used for the extraction of zinc from a tea sample was similar to that reported in the literature[31]. For measurement, 1 mg of a dry tea sample was placed in a beaker, followed by the addition of 7 ml of concentrated nitric acid, and the beaker was covered with a watch glass. The mixture was allowed to stand overnight, and the content was heated on a hot plate (150 °C) for 15 min. Then the sample was cooled until the solution became clear (ca. 1 h). The acid was evaporated to dryness at 150 °C. The residue was dissolved in 5 ml of 1 M nitric acid and the solution was transferred into a 100-ml calibrated flask. Then, the solution was neutralized

TABLE II
Determination of lead in water samples by AdCSV

Sample	Pb(II) added, M	Pb(II) found, M	Recovery, %
Sea water	–	10.1 ± 0.2	–
	10	20.9 ± 0.3	96.1
Tap water	–	7.8 ± 0.2	–
	10	17.3 ± 0.3	97.2
Spring water	–	5.2 ± 0.1	–
	10	15.9 ± 0.2	104.6

TABLE III
Determination of Pb^{2+} in blood ($n = 3$)

Sample	AdCSV	AAS
1	$1.1(\pm 0.1) \times 10^{-7}$ M	$1.4(\pm 0.2) \times 10^{-7}$ M
2	$1.6(\pm 0.3) \times 10^{-7}$ M	$1.2(\pm 0.1) \times 10^{-7}$ M
3	$2.1(\pm 0.3) \times 10^{-7}$ M	$2.6(\pm 0.2) \times 10^{-7}$ M

TABLE IV
Determination of Pb^{2+} in tea samples by AdCSV

Lead added, M	Lead, M	Recovery, %
–	$3.24(\pm 0.31) \times 10^{-8}$[a]	–
2×10^{-8}	$5.59(\pm 0.24) \times 10^{-8}$	106.6
4×10^{-8}	$7.06(\pm 0.15) \times 10^{-8}$	97.6
6×10^{-8}	$9.69(\pm 0.22) \times 10^{-8}$	104.8

[a] 3.88×10^{-8} by electrothermal atomic absorption spectrophotometry.

with a NaOH solution and diluted to the mark. At least, 100 μl of this solution were pipetted to 10 ml of supporting electrolyte. The sample was also analyzed for the Pb(II) content by AAS. The results are shown in Table IV. A comparison of the results obtained by the proposed method and AAS reveals the suitability of the method for determination of lead.

CONCLUSION

The present study demonstrates that stripping voltammetry of lead based on accumulation of the Pb-LDOPA complex can be used for determination of trace amounts of this element. A comparison of this method with the previously reported methods[21–28] is shown in Table V. The method offers a practical potential for trace determination of lead. It shows a high selectivity and sensitivity, simplicity, speed and a suitable linear range which are not present together in the previously reported methods.

TABLE V
Complex-forming agents for determination of lead

Complexing reagent	Detection limit mmol l^{-1}	Linear range mmol l^{-1}	Ref.
Xylenol Orange	29	–	21
Calcein Blue	0.008	10–100	23
Quinolin-8-ol	0.2	–	24
Pyrogallol Red	0.3	5–150	25
Morin	0.4	1.5–385	26
Carbamoylphosphonic acid	25	50–1000	27
Xylenol Orange	5	27–724	22
Carbidopa	0.05	0.2–480	28
Levodopa	0.6	1–300	this work

REFERENCES

1. Mesgar M. J., Miguez B., Perez M., Garcia M. A., Fernandez M. I., Vidal M.: *J. Environ. Sci. Health* **1997**, *32*, 687.
2. Patriarca M., Menditto A., Rossi B., Lyon T. D. B., Fell G. S.: *Microchem. J.* **2000**, *67*, 351.
3. Darwish I. A., Blake D. A.: *Anal. Chem.* **2002**, *74*, 52.
4. Krug F. J., Lima E. C.: *Spectrochim. Acta, Part B* **1999**, *54*, 1155.
5. Bulska E. B., Walcerz M., Jedral W., Hulanick A.: *Anal. Chim. Acta* **1997**, *357*, 133.

6. Wensing M. W., Liu D. Y., Smith B. W., Winefordner J. D.: *Anal. Chim. Acta* **1994**, *299*, 1.
7. Fischer E., Van der Berg C. M. G.: *Anal. Chim. Acta* **1999**, *385*, 273.
8. Yang H. Y., Sun I. W.: *Anal. Chim. Acta* **1998**, *358*, 285.
9. Lu T. H., Yang H. Y., Sun I. W.: *Talanta* **1999**, *49*, 59.
10. Zen J. M., Ting Y. S.: *Anal. Chim. Acta* **1996**, *332*, 59.
11. Brett C. M. A., Brett A. M. O., Matysik F. M.: *Talanta* **1996**, *43*, 2015.
12. Yokoi K., Yamaguchi A., Mizumachi M., Koide T.: *Anal. Chim. Acta* **1995**, *316*, 363.
13. Pravda M., Vytras K.: *J. Pharm. Biomed. Anal.* **1996**, *14*, 765.
14. Korolezuk M.: *Talanta* **2000**, *53*, 679.
15. Ramirez S., Gordillo G. J., Posdas D.: *J. Electroanal. Chem.* **1997**, *431*, 171.
16. Mclian J. A. H., Brito J. H., Caballero M. D. G., Pena J. P.: *Anal. Chim. Acta* **1994**, *299*, 59.
17. Saito M. A., Moffett J. W.: *Mar. Chem.* **2001**, *75*, 49.
18. Cordon F., Ramirez S. A., Gordillo G. J.: *J. Electroanal. Chem.* **2002**, *534*, 131.
19. Sancho D., Deban L., Campos I., Pardo R., Vega M.: *Food Chem.* **2000**, *71*, 139.
20. Achterberg E. P., Braungardt C.: *Anal. Chim. Acta* **1999**, *400*, 381.
21. Qingguo W., Batley E.: *Anal. Chim. Acta* **1995**, *309*, 95.
22. Ensafi A. A., Khayamian T., Benvidi A., Mirmomtaz E.: *Anal. Chim. Acta* **2006**, *561*, 225.
23. Yokio K., Yamaguchi A., Mizumachi M., Koide T.: *Anal. Chim. Acta* **1995**, *316*, 363.
24. Collado C., Perez J., Cabbalero M., Hernandez J.: *Anal. Chim. Acta* **1996**, *320*, 19.
25. Ensafi A. A., Khayamian T., Atabati M.: *Talanta* **2003**, *59*, 727.
26. Shams E., Babaei A., Soltaninezhad M.: *Anal. Chim. Acta* **2004**, *501*, 119.
27. Yantasee W., Lin Y., Fryxell G. E., Busche B. J.: *Anal. Chim. Acta* **2004**, *502*, 207.
28. Hosseinzadeh L., Abbasi S., Ahmadi F.: *Anal. Lett.* **2007**, *40*, 2693.
29. Miller J. C., Miller J. N.: *Statistics for Analytical Chemistry*. Ellis Horwood, Chichester 1984.
30. Inam R., Somer G.: *Talanta* **1998**, *46*, 1347.
31. Ichinoki S., Yamazaki M.: *Anal. Chem.* **1985**, *57*, 2219.