Int. J. Electrochem. Sci., 2 (**2007**) 778 - 787

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

A Simple and Selective Flow-Injection Potentiometric Method for Determination of Iodide Based on a Coated Glassy Carbon Electrode Sensor

Saeed S. Beheshti, Mohammad K. Amini[*]

Department of Chemistry, University of Isfahan, Isfahan, 81746–73441, I. R. Iran
[*]E-mail: mkamini@chem.ui.ac.ir

Received: 5 August 2007 / *Accepted:* 18 August 2007 / *Published:* 1 October 2007

A flow-injection (FI) method is reported for the determination of iodide based on potentiometric detection, using a membrane electrode containing bis(4-chlorothiophenolato)mercury(II) [$Hg(CTP)_2$] as the active component. The response of the system was evaluated with regard to the parameters of the membrane electrode and the FI system. The calibration curve for iodide at the optimized conditions including 0.01 M sodium sulfate (pH 6.0) carrier solution with a flow rate of 1 mL min^{-1} and an injection volume of 100 µL was linear over the range 1.0×10^{-6}-7.6×10^{-2} M with a Nernstian slope of -59.4 mV per decade of iodide activity. The influence of several common inorganic and organic anions on the response of the FI system was investigated and selectivity coefficients were evaluated. The sensor shows high selectivity towards iodide, which can be related to the selective interaction of iodide as a soft anion with mercury atom in $Hg(CTP)_2$ as a soft metal center. This is certified by the very low tendency of the sensor towards chloride, bromide, and the highly lipophilic anions such as perchlorate, salicylate, nitrate, nitrite, and thiocyanate. The system exhibited a fast response time of less than 5 s (in the batch mode), a detection limit of 5.0×10^{-7} M and a relative standard deviation of 0.6% at 0.1 mM iodide. The sampling frequency was between 40-120 h^{-1} depending on the concentration of iodide in the measuring solution. The proposed system was applied to the determination of iodide in a pharmaceutical preparation and the results were compared with a standard potentiometric method based on silver indicator electrode.

Keywords: Iodide; Flow-injection analysis; Bis(4-chlorothiophenolato)mercury(II); Membrane electrode; Potentiometry

1. INTRODUCTION

Iodine is an essential nutritional factor with important biochemical functions such as mental development, and basic metabolisms [1]. Iodine is required for maintenance of cell growth in human and animals. In some areas where waters and soils are deficient in the amount of iodine required by the

normal diet, iodine supplements are administered. Iodine compounds are also used in preparation of some pharmaceutical products used to compensate iodine deficiency or used as antiseptic and disinfectant agents. Therefore, the determination of iodine and its related compounds is important in a variety of samples such as food [2,3], fodder [4], waters [4], clinical and biological samples [4,5], pharmaceutical preparations [6,7] and environmental samples [8,9].

A survey of literature reveals that iodide and/or iodine may be determined by various methods, including chromatography [10,11], capillary electrophoresis [12], gas chromatography-mass spectrometry (MS) [13], inductively coupled plasma (ICP)-MS [14], ICP atomic emission spectrometry [15], diffuse reflectance spectroscopy [16], radiochemical neutron activation analysis [17], chemiluminescence [5,7], UV-Vis spectrophotometry [18-20], catalytic spectrophotometric methods [21-23], and atomic absorption spectrometry [24,25]. Most of these techniques either involve several manipulation steps or are very expensive to be used for routine analysis.

Electrochemical detection methods such as amperometry [3,4], biamperometry [20], stripping voltammetry [26], and potentiometry [27-29] have also been reported but have not been as widely used as the spectroscopic methods. Among these methods, potentiometric detection is fundamentally the simplest of all, as the response is directly in the electronic domain and no excitation signal has to be applied [30]. Potentiometric sensors based on ion-selective electrodes (ISEs) offer much better selectivity and wider dynamic range than either spectroscopy or amperometry because of the logarithmic response of ISEs, and simpler instrumentation. These sensors are widely applied owing to their simplicity, low cost and applicability to samples of various nature [31,32]. The remarkable progress in the application of ISEs can be attributed mainly to their widespread use as flow-through detectors in automatic analyzers, continuous monitoring systems and flow-injection potentiometry (FIP) [33-35]. Potentiometric measurement in the FI mode is generally more advantageous than the steady state mode, in terms of fast sample throughput rate, use of small sample volumes, continuous washing of the detector, high precision and the possibility of system automation [36]. The FIP is also known to possess several other advantages including rapid response, simple instrumentation, low cost, high selectivity and sensitivity. Further, the transient nature of the signal in FIP may help to overcome the effect of interfering ions if their response is slower than the analyte [37,38].

The present work describes a FI method for the determination of iodide based on a potentiometric sensor. The sensor was prepared by coating a glassy carbon electrode with plasticized PVC membrane containing $Hg(CTP)_2$ as the active ingredient. The performance characteristics of the FIP system and the influence of several operating parameters on its response properties were investigated. The proposed method was used in an assay to determine iodine in a pharmaceutical product.

2. EXPERIMENTAL PART

2.1. Reagents and chemicals

Poly(vinyl chloride) (PVC) of high molecular weight, dibutylphthalate (DBP), methyltrioctylammonium chloride (MTOAC) and tetrahydrofuran (THF) were purchased from Aldrich

and were used as received. The salts used for preparation of standard solutions including potassium salts of iodide, thiocyanate, chloride, bromide, and sodium salts of sulfate, nitrate, nitrite, perchlorate, acetate, oxalate, salicylate and fluoride, were analytical reagent grade received from Merck. Deionized-distilled water was used throughout all experiments. The $Hg(CTP)_2$ carrier was prepared according to a previously reported procedure [39].

2.2. Sample preparation

The iodide sample was prepared from a pharmaceutical preparation (Meglumine Compound Injection from Daro-Paksh Pharmaceutical Co.). To 1.0 g of the preparation was added 12.5 mL 5.0 M sodium hydroxide solution, 25 mL water and 2.0 g zinc powder and the mixture was refluxed for 30 min [40]. After cooling, the mixture was filtered, washed with ~50 mL water, acidified to pH 6.0 with sulfuric acid and diluted to a final volume of 1 L. The iodide content of the resulting sample was determined by the proposed method using the standard addition method.

2.3. Preparation of the iodide sensor

Glassy carbon disk electrode (3 mm^2) was polished with alumina (0.05 μm) then rinsed thoroughly with water and finally with THF. The formation of membrane film on the glassy carbon disk surface was obtained by immersing the electrode tip into the membrane solution and keeping it upward to dry. The coated electrode was allowed to set overnight. The coated electrode was rinsed with water and conditioned for ~18 h in 0.05 M potassium iodide solution. The general procedure to prepare the membrane solution has been described previously [41]. Briefly, 31.0 mg powdered PVC, 61.7 mg DBP, 5.0 mg $Hg(CTP)_2$ and 2.3 mg MTOAC were dissolved in 2 mL THF. The coating solution is stable for several weeks if it is kept in refrigerator and can be used for construction of new electrodes.

2.4. Flow- injection system

The FIP system (Fig. 1) utilized a carrier solution, CS, (0.01 M Na_2SO_4, pH 6.0) conducted by a model MCP-ISM 404B peristaltic pump (Ismatec, Switzerland), PP, to the flow-cell, FC. The pump was furnished with 0.5 mm i.d. Tygon and Teflon tubing. The sample, S, was introduced into the carrier solution by means of a Valco Model C2V sample injection valve, IV, equipped with a 100 μL injection loop. The flow-cell used for the FIP system was the recommended wall-jet configuration [42], supplied by Metrohm Model 653030. The cell equipped with a Metrohm Model 607270 Ag/AgCl/3M KCl reference electrode, RE, and the coated glassy carbon as the working electrode, WE. The cell also comprised of a Metrohm Model 603330 built in gold counter electrode, CE, which was grounded to minimize noise, according to Slanina et al. [43]. The potential measurements were made with a Metrohm Model 692 pH/Ion meter, P. The meter was connected to a Philips Model PM8272 X-Y recorder, R, to record the FIP signals. After the loop-based injection, the sample zone passes through

the cell where a transient voltage is recorded as a peak with height proportional to the iodide concentration in the sample. The type, concentration, flow rate and pH of the carrier solution, and sample (loop) volume were adjusted in order to optimize the system response.

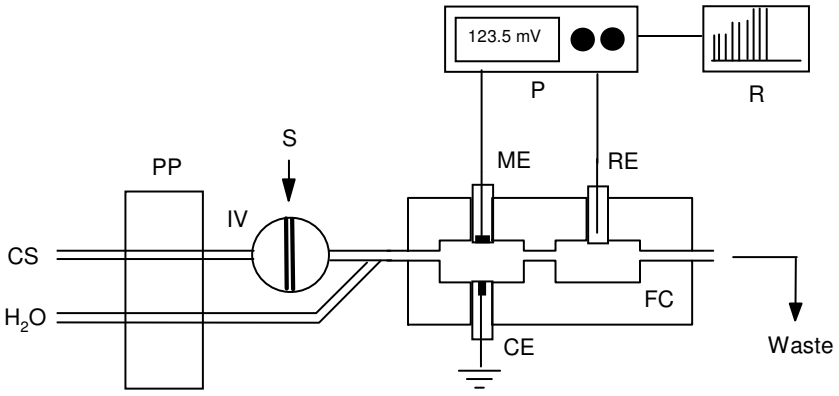

Figure 1. Flow-injection manifold for the determination of iodide. CS, carrier solution (0.01 M Na_2SO_4, pH 6); PP, peristaltic pump; IV, injection valve; S, sample; FC, flow-through cell; ME, membrane electrode; CE, counter electrode; RE, reference electrode (Ag/AgCl double junction); P, potentiometer; R, x-y recorder

3. RESULTS AND DISCUSSION

Ion sensors with high selectivity, high sensitivity, wide dynamic range and fast response are highly desirable for flow-injection analysis applications. One approach toward simple, cheap and reliable detector for this purpose is to prepare the potentiometric sensors. Our previous investigation on the use of mercury complexes for construction of ion selective sensors [41] indicated the suitability of these complexes for iodide detection. Mercury complexes such as $Hg(CTP)_2$ demonstrated high selectivity towards iodide. High selectivity is characteristic of recognition element in metal-ligand interactions. Therefore, we were prompted to use $Hg(CTP)_2$ for the preparation of a solid sensor in FIP determination of iodide ion.

3.1. Effect of type and concentration of the carrier solution

Several electrolytes were examined as the carrier solution, including potassium chloride, potassium nitrate, sodium acetate, sodium citrate, potassium dihydrogen phosphate and sodium sulfate. Among these, sodium sulfate was found to provide the best analytical performance with respect to linear dynamic range, detection limit, reproducibility and response time of the FIP sensor.

Before starting the measurement of iodide, it was necessary to condition the sensor in the FIP system by passing the carrier solution through the flow-cell for ~5 min. After this period, the baseline remained stable with a drift of less than 2 mV in 60 min. No other conditioning or pretreatment of the electrode was required before sample injection and for subsequent measurements.

The effect of concentration of Na_2SO_4 carrier solution on the potentiometric response of the FIP system was investigated in the range 5×10^{-3}-1×10^{-1} M. Three different concentrations of iodide were injected for each carrier concentration and the FIP responses recorded. Maximum sensitivity and lowest response time was observed with 1.0×10^{-2} M Na_2SO_4 solution. Therefore, this was used for further investigations.

3.2. Effect of pH

The pH dependence of the FIP response was tested by injecting 100 µL of 1.0×10^{-4} M iodide into the carrier solution with different pH in the range 2.5-12 (Fig. 2). The pH of 0.01 M Na_2SO_4 solution was adjusted by addition of dilute sulfuric acid or sodium hydroxide solution as appropriate. The response profile does not show a considerable difference in the observed potential over the pH range 3.5-11, which makes the proposed FIP system applicable to a wide variety of samples.

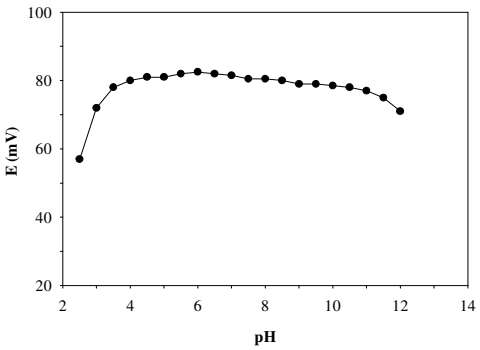

Figure 2. The influence of pH of the carrier solution on the FIP response obtained by injecting 100 µL of 1×10^{-4} M potassium iodide solution.

3.3. Effect of flow rate

An increase in peak height as well as a decrease in peak width was observed when the flow rate of the carrier, 0.01 M Na_2SO_4 solution of pH 6.0, was increased from 0.25 to 1.0 mL min^{-1}. The peak height is decreased and the reproducibility of the signal is deteriorated beyond carrier flow rates of 1.0 mL min^{-1}. A flow rate of 1.0 mL min^{-1} was chosen for further experiments, which allows analysis of 40 to 120 samples h^{-1} depending on the iodide concentration.

3.4. Injection volume study

The influence of the injection volume on the FIP response was studied with 20, 50 and 100 µL injection loops using 1.0×10^{-3}, 1.0×10^{-4} and 1.0×10^{-5} M iodide solutions. An increase in the peak height and peak width was observed by increasing injection volume. Generally, a sample volume of 100 µL was used for better sensitivity in the measurement.

3.5. Selectivity of the electrode in FIP system

The selectivity coefficients of the sensor system in the FIP mode were obtained by the separate solution method using 1.0×10^{-3} M iodide and the interfering ions. The selectivity coefficients obtained in the FIP mode are presented in Table 1, together with values obtained in the batch mode. The results indicate that the measuring system is highly selective towards iodide with respect to several anions that may be found together with iodide in real samples, such as acetate, oxalate, bromide, perchlorate, salicyalte, fluoride, chloride, nitrate and nitrite. Thiocyanate, $\log K^{pot}_{I^-,SCN^-}$ = -1.33, may show some interference in the determination if it is present at high concentration relative to iodide. The selectivities in the FIP mode are comparable to and in some instances better than those in the batch mode. This may be related in part to the transient nature of the signal in the FIP mode; i.e., the selectivities depend also on the relative response time of the electrode for different anions [37,38].

Table 1. Potentiometric selectivity coefficients, $\log K^{pot}_{I^-,J}$, for iodide in batch and flow-injection modes obtained by the separate solution method using 1×10^{-3} M iodide and interfering anions.

Ion	Batch mode	Flow-injection mode
Acetate	–4.86	–4.93
Oxalate	–4.78	–4.80
Bromide	–2.49	–2.99
Thiocyanate	–1.22	–1.33
Perchlorate	–2.85	–3.10
Salicylate	–4.36	–4.45
Fluoride	–3.96	–3.66
Chloride	–3.48	–3.55
Nitrate	–4.93	–4.84
Nitrite	–4.92	–4.87
Sulfate	–4.75	–[a]

[a] Sulfate was the carrier solution in the flow-injection mode

High selectivity of the sensor toward iodide can be related to the selective interaction of this anion with mercury atom in the $Hg(CTP)_2$ complex. This is certified by the very low tendency of the sensor towards chloride, bromide, and highly lipophilic anions such as perchlorate, salicylate, nitrate, and nitrite, and to some extent thiocyanate. In other words, high selectivity toward iodide with respect to these anions ($\log K^{pot}_{I^-,J^-}$ = -3.55, chloride; -2.99, bromide; -3.10, perchlorate; -4.45, salicylate; -4.84, nitrate; -4.87, nitrite; -1.33, thiocyanate;) is indicative of the relatively strong and selective interaction of iodide as a soft anion and mercury in the complex as a soft metal center.

3.6. Analytical characteristics

Figure 3 shows the recorder trace of the system to injections of 100 μL iodide solution at different concentrations. The proportionality between the FIP response and iodide concentration was

proven from the calibration plot obtained under the optimized conditions presented in Table 2. The calibration plot was linear over the concentration range 1.0×10^{-6}-1.0×10^{-1} M with a slope of -58.2±0.8 per decade of iodide concentration and a correlation coefficient, r, of 0.9995 (n=6), Fig. 4. The linear range in terms of iodide activity was 1.0×10^{-6}-7.6×10^{-2} M with a slope of 59.4±0.8 and r of 0.9996. The detection limit of the sensor in the FIP system was ~5×10^{-7} M iodide.

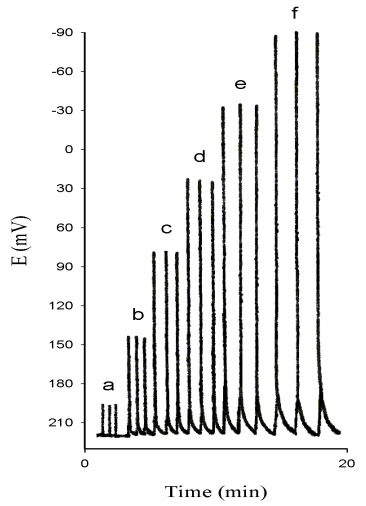

Figure 3. Recorder trace of FIP responses obtained at the optimum conditions by injecting 100 µL of iodide into the carrier solution at pH 6 and flow rate of 1 mL min^{-1}; (a) 1.0×10^{-6}, (b) 1.0×10^{-5}, (c) 1.0×10^{-4}, (d) 1.0×10^{-3}, (e) 1.0×10^{-2} and (f) 1.0×10^{-1} M I^-.

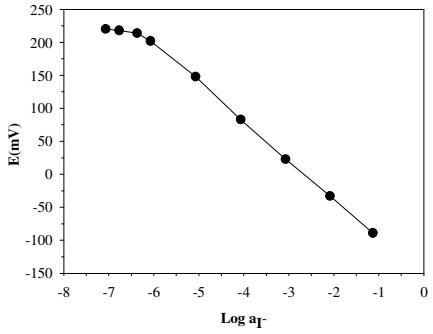

Figure 4. Calibration plot of FIP response vs. iodide activity. Conditions are given in Table 2.

The reproducibility of the measurement was obtained from ten repeated injections of 1.0×10^{-5} M and 1.0×10^{-4} M iodide solutions. The relative standard deviations were calculated to be 0.8% and 0.6%, respectively. The response time of the sensor in the batch mode is ≤ 5 s. The transient (baseline to baseline) time of the FIP signal, is 30 to 90 s, depending on the concentration of iodide in solution. The electrode is highly stable and no significant change in its response characteristics was observed during 1 month of continuous use. This can be in part related to insolubility of the carrier in aqueous solutions.

The FIP system was applied to the determination of iodine content of a pharmaceutical preparation. The sample preparation is described in the experimental section. The iodide content of the

sample was determined by the proposed FIP method using standard addition method and the results were compared with those obtained by potentiometric titration of the sample with standard silver nitrate solution using silver indicator electrode in conjunction with a double junction Ag/AgCl reference electrode. The results obtained by the FIP method, $(4.0 \pm 0.3) \times 10^{-3}$ M, were in close agreement with the potentiometric titration results $(3.8 \pm 0.2) \times 10^{-3}$ M (t_{calc} = 1.38, n = 5, $t_{0.05,4}$ = 2.78).

Table 2. Characteristics and response properties of the FIP system used for the determination of iodide ion.

Parameter	Characteristic, value or range
Sensor system:	
Electrode type	Coated glassy carbon electrode
Carrier	$Hg(CTP)_2$
Membrane composition (%)	PVC, 31.0; plasticizer (dibutyl phthalate), 61.7; Carrier, 5; cationic additive (MTOAC), 2.3.
Flow-injection system	
Carrier solution	Sodium sulfate, 0.01 M
Applicable pH range	3.5 – 11
Flow rate	1 mL min^{-1}
Injected volume	100 μL
Sampling rate	Max., 120 h^{-1} at 1×10^{-6} M; Min., 40 h^{-1} at 1×10^{-2} M iodide
Analytical parameters	
Reproducibility (as RSD%)	0.8% at 1×10^{-5} M iodide; 0.6% at 1×10^{-4} M iodide
Linear range	1×10^{-6} – 7.6×10^{-2} M iodide activity (r = 0.9995, n=6)
	1×10^{-6} – 1×10^{-1} M iodide concentration (r = 0.9996, n=6)
Slope	-59.4 ± 0.8 mV $decade^{-1}$ of iodide activity
	-58.2 ± 0.8 mV $decade^{-1}$ of iodide concentration
Detection limit	5×10^{-7} M

4. CONCLUSIONS

The results of this study demonstrate suitability of the iodide selective sensor based on $Hg(CTP)_2$ carrier for the flow-injection potentiometric detection of iodide. The proposed system provides a sensitive, fast and economic method for determination of iodide down to 1.0×10^{-6} M. High selectivity of the sensor with respect to chloride and bromide, and the highly lipophilic anions such as perchlorate, salicylate, nitrate, nitrite and thiocyanate, together with versatility, flexibility, high sample

throughput rate and ease of operation and maintenance of the FI method make the proposed FIP system promising for the analysis of iodide in a wide variety of samples and allow very fast and cheap methods to be developed.

ACKNOWLEDGEMENT
The authors gratefully acknowledge the support of this work by the Center of Excellence of Chemistry (Catalyst and Fuel Cell Division) and Office of Graduate Studies of the University of Isfahan.

References

1. N. N. Greenwood, and A. Eamshaw, "Chemistry of the Elements", Pergamon Press, Oxford, (1984).
2. Z. Xie, and J. Zhao, *Talanta*, 63 (2004) 339
3. L. Tian, L. Liu, L. Chen, N. Lu, and H. Xu, *Talanta*, 66 (2005) 130
4. S. D. Nikolic, J. J. Mutic, A. D. Lolic, and D. D. Manojlovic, *Anal. Sci*., 21 (2005) 525
5. T. Fujiwara, I. U. Mohammadzai, H. Inoue, and T. Kumamaru, *Analyst*, 125 (2000) 759
6. D. Nacapricha, K. Ratanawimarnwong, and K. Grudpan, *Anal. Bioanal. Chem*., 378 (2004) 816
7. N. Ratanawimarnwong, N. Amornthammarong, N. Choengchan, P. Chaisuwan, M. Amatatongchai, P. Wilairat, I. D. McKelvie, and D. Nacapricha, *Talanta*, 65 (2005) 756
8. O. Haase, and J. A. C. Broekaert, *Spectrochim. Acta* B, 57 (2002) 157
9. A. Kamavisdar, and R. M. Patel, *Microchim. Acta*, 140 (2002) 119
10. H. B. Li, F. Chen, and X. R. Xu, *J. Chromatogr.* A 918 (2001) 335
11. W. Hu, P. J. Yang, K. Hasebe, P. R. Haddad, and K. Tanaka, *J. Chromatogr*. A, 956 (2002) 103
12. K. Ito, T. Ichihara, H. Zhuo, K. Kumamoto, A. R. Timerbaev, and T. Hirokawa, *Anal. Chim. Acta*, 497 (2003) 67
13. H. S. Shin, Y. S. Oh-shin, J. H. Kim, and J. K. Ryu, *J. Chromatogr*. A, 732 (1996) 327
14. L. F. Sanchez, and J. Szpunar, *J. Anal. At. Spectrom*., 14 (1999) 1697
15. K. Krengel-Rothensee, U. Richter, and P. Heitland, *J. Anal. At. Spectrom*., 14 (1999) 699
16. M. P. Arena, M. D. Porter, and J. S. Fritz, *Anal. Chem*., 74 (2002) 185
17. X. Hou, H. Dahlgaard, B. Rietz, U. Jacobsen, S. P. Nielsen, and A. Aarkrog, *Anal. Chem*., 71 (1999) 2745
18. T. Yoshinaga, T. Shirakata, H. Dohtsu, H. Hiratsuka, M. Hasegawa, M. Kobayashi, and T. Hoshi, *Anal. Sci*., 17 (2001) 333
19. N. Choengchan, K. Uraisin, K. Choden, W. Veerasai, K. Grudpan, and D. Nacapricha, *Talanta*, 58 (2002) 1195
20. L. J. Li, H. Cheng, W. Y. Huang, H. X. Kong , J. L. Wu, J. P. Lu, W. Gao, and J. F. Song, *Chinese Chem. Lett*., 16 (2005) 1629
21. G. A. Milovanovic, F. T. Pastor, G. M. Petkovic, and M. Todorovic, *Microchim. Acta*, 144 (2004) 51
22. N. Choengchan, K. Lukkanakul, N. Ratanawimarnwong, W. Waiyawat, P. Wilairat, and D. Nacapricha, *Anal. Chim. Acta*, 499 (2003) 115
23. T. Tomiyasy, M. Nonaka, M. Uchikado, K. Anazawa, and H. Sakamoto, *Anal. Sci*., 20 (2004) 391
24. M. C. Yebra, and R. M. Cespón, Fresenius *J. Anal. Chem*., 367 (2000) 24
25. M. C. Yebra, and R. M. Cespon, *Anal. Chim. Acta*, 405 (2000) 191
26. Q. He, J. Fei, and S. Hu, *Anal. Sci*., 19 (2003) 681
27. F. M. Najib, and S. Othman, *Talanta*, 39 (1992) 1259
28. T. Masadome, R. Sonoda, and Y. Asano, *Talanta*, 52 (2000) 1123

29. D. E. Davey, D. E. Mulcahy, and G. R. O'Connell, *Analyst*, 117 (1992) 761
30. P. Schnierle, T. Kappes, and P. C. Hauser, *Anal. Chem*., 70 (1998) 3585
31. D. E. Davey, D. E. Mulcahy, and G. R. O' Connell, *Talanta*, 37 (1990) 313
32. C. Sanchez-Pedreno, J. A. Ortuno, and M. C. Lopez, *Anal. Chim. Acta*, 315 (1995) 63
33. S. S. Badawy, A. F. Youssef, and A. A. Mutair, *Anal. Chim. Acta*, 511 (2004) 207
34. Y. M. Issa, M. T. Abdel-Ghani, A. F. Shoukry, and H. M. Ahmed, *Anal. Sci*., 21 (2005) 1037
35. H. Karami, M. F. Mousavi, and M. Shamsipur, *Talanta*, 60 (2003) 775
36. L. T. Dimitrakopoulos, and T. Dimitrakopoulos, *Electroanalysis*, 13 (2001) 161
37. K. Cammann, Fresenius *J. Anal. Chem*., 329 (1988) 691
38. P. W. Alexander, T. Dimitrakopoulos, and D. B. Hibbert, *Electroanalysis*, 10 (1998) 707
39. N. Ueyama, K. Taniuchi, T. Okamura, A. Nakamura, H. Maeda, and S. Emura, *Inorg. Chem*., 35 (1996) 1945
40. M. Ying, R. Yuan, X. M. Zhang, Y. Q. Song, Z. Q. Li, G. L. Shen, and R. Q. Yu, *Analyst*, 122 (1997) 1143
41. M. K. Amini, M. Ghaedi, A. Rafi, M. H. Habibi, and M. M. Zohory, *Sensors*, 3 (2003) 509
42. U. Lemke, K. Cammann, C. Kotter, C. Sundermeier, and M. Knoll, *Sensors and Actuators* B, 7 (1992) 488
43. J. Slanina, W. A. Lingerak, and F. Bakker, *Anal. Chim. Acta*, 117 (1980) 91