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Flow-injection determination of iodide ion in nuclear emergency tablets, using boron-doped diamond thin film electrode☆

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Abstract

The electrochemical determination of iodide was studied at boron-doped diamond thin film electrodes (BDD) using cyclic voltammetry (CV) and flow-injection (FI) analysis, with amperometric detection. Cyclic voltammetry of iodide was conducted in a phosphate buffer pH 5. Experiments were performed using glassy carbon (GC) electrode as a comparison. Well-defined oxidation waves of the quasi-reversible cyclic voltammograms were observed at both electrodes. Voltammetric signal-to-background ratios (S/B) were comparable. However, the GC electrode gives much greater in the background current as usual. The potential sweep rate dependence exhibited that the peak current of iodide oxidation at 1 mM varied linearly ($r^2 = 0.998$) with the square root of the scan rate, from 0.01 to 0.30 V s^{-1}. This result indicates that the reaction is a diffusion-controlled process with negligible adsorption on BDD surface, at this iodide concentration. Results of the flow-injection analysis show a highly reproducible amperometric response. The linear working range was observed up to 200 μM ($r^2 = 0.999$). The detection limit, as low as 0.01 μM (3σ of blank), was obtained. This method was successfully applied for quantification of iodide contents in nuclear emergency tablets.

Keywords: Boron-doped diamond thin film electrode (BDD); Iodide; Flow-injection analysis

1. Introduction

Diamond itself does not have electrical properties in terms of being conductive or semiconductive. However, with the technology of a so-called chemically vapor deposition (CVD), film of diamond with specific dopants, such as boron, can be conveniently grown on a substrate [1–3]. This diamond film offers remarkable properties of being such an electrochemical sensor.

For electrochemical measurements, thin film of boron-doped diamond on Si wafer (BDD), has benefits over other electrodes especially those sp^2-bonded carbon electrodes, e.g., carbon paste and glassy carbon [1]. Examples [1–3] of the superior properties of the BDD include (i) low and stable background current which results in improvement in signal-to-background; (ii) considerably wide working potential window in both aqueous and non-aqueous media; (iii) very low capacitance; (iv) low adsorption of polar molecules, due to the hydrogen termination during the film growth (unlike the GC surface which is usually quite polar with covered film of oxide) [4]; (v) remarkable reproducibility [5] and (vi) morphological and micro structural stability although at over potential condition.

With respect to the outstanding properties of BDD film, quite a number of applications, based on use of this new material for electrochemical quantitation, have been reported [6–19]. This synthetic type of diamond film has already been applied as amperometric detectors in flow-injection (FI) analysis [6–14,19] and in liquid chromatography [15–19]. However, there has been no report of use of BDD electrode for determination of iodide. There is only a recent report for quantitative analysis of iodide, but on diamond paste based electrodes [20].

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Presently, iodine is one of the supplements being widely publicized in our country. Campaigns have been raised against iodine deficiency disorder (IDD) in populations. Drinking water and/or table salt as well as foods are supplemented with iodide or iodate. Supplementation of iodine also comes in as multivitamins.

In the States, customers can purchase a pharmaceutical product used in the event of nuclear emergency. This product is basically potassium iodide, known as "potassium iodide tablet". The product is orally consumed to protect human thyroid from body absorption of radioactive iodine.

Since there are varieties of samples being the source of iodine, and somehow, intake of iodine should be concerned with extreme caution. Some people can be markedly sensitive to the element [21].

In the previous reports, determination of iodide can be made using several methods such as spectrometric analysis [22,23], catalytic spectrometric analysis [24,25] and by potentiometric detection [26]. Analysis of iodide using amperometric detection by other working electrodes has been well established especially for liquid chromatography [27–29]. Nevertheless, there is no report for detection on the BDD electrode.

This paper presents, for the first time, the electrochemical oxidation of iodide on thin film of boron-doped diamond. Cyclic voltammetric investigation was made for an iodide solution with comparison to the commercially known glassy carbon electrode. Amperometric determination of iodide on BDD was explored by applying the thin film for quantitative analysis in some pharmaceutical products.

2. Experimental

2.1. Chemicals

All chemicals used were of analytical reagent grade and deionized-distilled water was used throughout. A stock solution of iodide standard (0.1 M) was prepared by dissolving approximately 1.66 g (accurate weight) of potassium iodide crystals (Merck, Germany) in 100.0 ml of water. Working solutions of iodide were obtained by appropriate dilution with water. A phosphate buffer 60 mM, pH 5, was prepared by dissolving 8.9056 g of sodium dihydrogen phosphate (Fluka, Switzerland) and 0.4914 g of disodium hydrogen phosphate (Fluka) in water and making up to the mark in a 1-l volumetric flask. Phosphate buffers 60 mM, pH 4–9, were prepared similarly with pH adjustment using 1 M sodium hydroxide and 1 M hydrochloric acid solutions.

2.2. Sample preparation

Four commercial products of potassium iodide tablets, for radiation emergency, were employed in validation of the method. IOSAT^{TM} (distributed by ANBEX, USA) and Thyro-Block^{TM} (Wallace Pharmaceuticals, USA) are the samples, which contain 130 mg KI/tablet. NO-RAD^{TM} (Body Gold, USA) and RAD BLOCK KI^{TM} (distributed by USDPI, USA) both contain 65 mg KI/tablet. In the analysis, tablets were accurately weighed and dissolved in 500.0 ml of water. Suspension was removed by filtration through 0.25 μM pore of cellulose acetate membrane before analyses.

2.3. Cyclic voltammetry

Similarly to the former reports [6,11–15], an Autolab potentiostat 100 (Eco-Chemie, the Netherlands) with a single compartment three electrode glass cell, was used for all the cyclic voltammetric studies. A BDD electrode was pressed against the smooth ground joint at the bottom of the cell and was isolated by an o-ring, which resulted in 0.07 cm^2 of electrode area. Electric contact was carried out by placing the backside of electrode (Si substrate) on a brass plate. The electrochemical cell was housed in a faradaic cage to reduce electronic noise. A platinum wire and a Ag/AgCl with a salt bridge were used as the auxiliary and reference electrodes, respectively.

Cyclic voltammetric study was also carried out, in the same way, using glassy carbon as the working electrode.

2.4. Amperometric determination on BDD electrode by flow-injection

For routine analysis, we propose use of the BDD detection of iodide by flow-injection technique [30]. The system is displayed schematically in Fig. 1. An Ismatec peristaltic pump (model IS7610, Switzerland) was used for propelling the carrier stream (phosphate buffer). Arrangement of the amperometric detection with a BDD working electrode was the same as that described in previous works [6,11–15]. Again in this present work, the electrode area was utilized at 0.36 cm^2.

The final sample solutions were diluted (25 or 50 times) before injections. External calibrations with aqueous solutions of potassium iodide were adopted.

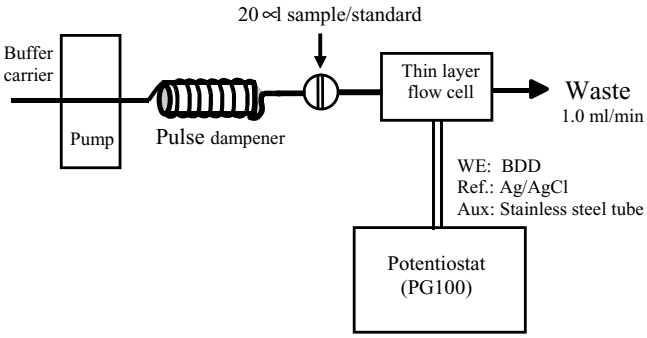

Fig. 1. The FI manifold with amperometric detection using BDD as the working (WE) electrode. Optimal condition: potential, 1.0 V; carrier, 60 mM phosphate buffer at pH 5.

2.5. Potentiometric analysis by ion selective electrode (ISE)

Accurate 10.00 ml of a sample solution was transferred into a 50 ml volumetric flask. To the flask, a 1.0 ml of 5 M $NaNO_3$ solution was added as an ionic strength adjuster. The mixture was made up to the level with water. The solution was measured for the potential developed across the employed iodide-ISE (Orion, USA) and the saturated calomel electrode (Orion). A digital Orion Ionanalyzer (model 601A) was used for the measurement.

2.6. The colorimetric method employed for comparison

Our colorimetric flow-injection method [23] which utilizes gas diffusion for selective determination of iodide was adopted for the validation. The detection is based on complex formation of I_3^-–starch. This method was previously validated against another technique.

3. Results and discussion

3.1. Cyclic voltammetry: BDD and GC electrodes

Fig. 2 shows the cyclic voltammograms that are obtained form an iodide solution together with the corresponding background voltammograms for BDD and GC electrodes. Peak-shaped oxidation responses are observed for both electrodes, but the background currents are dramatically different. The background current of the GC electrode is approximately 10 times greater than the background of BDD electrode. The BDD exhibits well-defined quasi-reversible oxidation peaks at 0.57 and 0.79 V versus Ag/AgCl, whereas the GC electrode provides the oxidation peaks at 0.48 and 0.74 V. To avoid using the high potential position, therefore, the first redox couple was considered. The potential differences between the first reduction peaks and the corresponding anodic peaks are at the order of 90 mV at GC electrode and 220 mV at BDD electrode. The peak separation suggested that the voltammetry is distorted by quasi-reversible behavior. The first anodic peak current, subtracted from background current, is 0.86 μA at BDD electrode and is 0.67 μA at GC electrode. We then expect that BDD electrode would provide a better sensitivity.

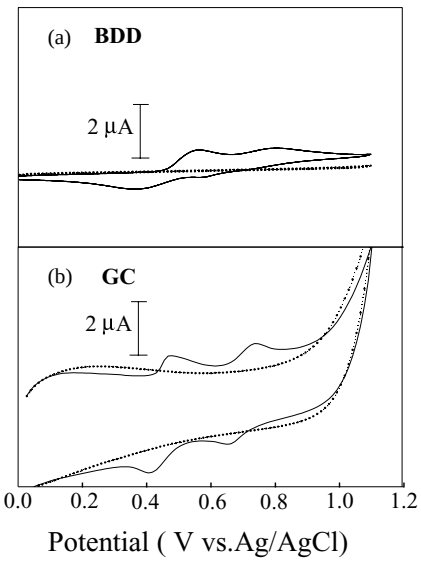

Fig. 2. Solid lines are the cyclic voltammograms that were obtained from batch experiment for 0.50 mM iodide in 60 mM phosphate buffer (pH 5). Background voltammograms (60 mM phosphate buffer, pH 5) are also shown as dotted lines for both electrodes. The scan rate was fixed at 0.02 V s^{-1}.

There have been some reports of cyclic voltammograms of iodide on platinum [31], gold and glassy carbon [32] electrodes. In these works, the authors also observed sequential oxidation of iodide, similarly to what we have seen in Fig. 2. Thus it is likely that the oxidation behaviors of iodide for both BDD and GC are the same as that reported in the systems studied by Hanson and Tobias [31] and by Qi and Hiskey [32]. These authors investigated and suggested that the oxidation sequence of iodide at the working electrodes can be represented by the following reactions:

$$3I^- \rightarrow I_3^- + 2e^- \quad (1)$$

$$2I_3^- \rightarrow 3I_2 + 2e^- \quad (2)$$

Our results also exhibit that the oxidation sequence is reversible for BDD and GC electrodes. For our work, we employed only the first oxidation peak current.

Buffer pH was also investigated from pH 4–9. The BDD and GC electrodes exhibit well-defined cyclic voltammograms of iodide in all pHs. It was observed that the oxidation peak currents slightly shift to positive potentials with increasing pH. The current background was enlarged when approaching the higher pHs. We chose pH 5 as the optimal pH for further studies on the BDD electrode.

3.2. Scan rate and concentration dependence study

Cyclic voltammograms of an iodide solution on BDD were investigated at different scan rates, the results are displayed in Fig. 3. As seen in the inset of Fig. 3, peak current varies linearly with the square root of scan rate. This indicates that the current is limited by semifinite linear diffusion of iodide to the BDD electrode.

The relationship between oxidation peak current (μA) and iodide concentration was examined from 0.50 to 10 mM. Linear calibration ($r^2 = 0.999$) was obtained with the slope of 6.07 μA mM^{-1}. These results have demonstrated that the BDD electrode is appropriate for the quantitation of iodide.

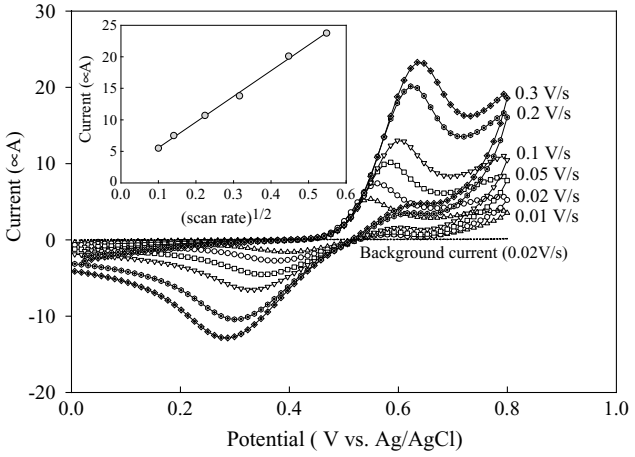

Fig. 3. Cyclic voltammograms, obtained at various potential scan rates for 1 mM iodide in 60 mM phosphate buffer (pH 5) at BDD electrode. The inserting figure shows the relationship between the oxidation current and the square root of the scan rate with regression figures of 40.74 μA $(s/V)^{1/2}$ (slope) and 0.998 (r^2).

3.3. Flow-injection analysis with amperometric detection

3.3.1. Optimal potential

For routine analysis, it is often more convenient than the potentiometric mode to use hydrodynamic injection of samples with amperometric detection. Optimization was first carried out using the FI manifold in Fig. 1 to find the most sensitive oxidation potential. The results are presented in Fig. 4. According to the results, the maxima S/B ratio was observed at 1.0 V. Therefore, this potential was chosen for amperometric detection in all FI experiments.

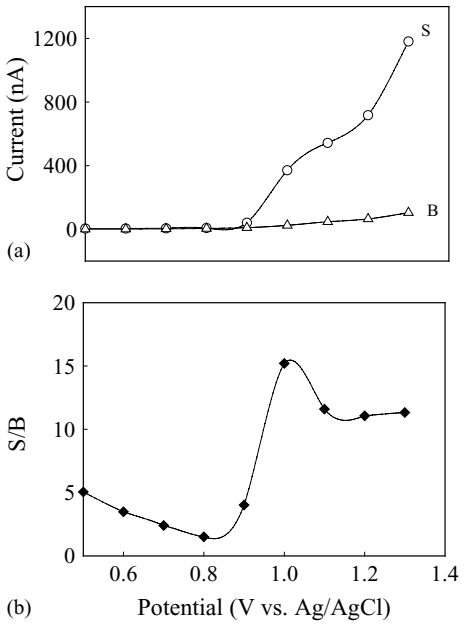

Fig. 4. Results obtained from the system of amperometric-FI (Fig. 1): (a) hydrodynamic signal of the carrier, 60 mM phosphate buffer or the background current (B) and peak current from injections ($n = 5$) of 10 μM of iodide into the carrier stream (S) and (b) plot of the signal-to-background ratio (S/B) and the applied potential.

3.3.2. Analytical features

We examined analytical performance of the manifold shown in Fig. 1. The system was operated at 1.0 V. Linear calibration was observed between 0.8 and 200 μM. The regression equation is $y = 37.41x - 2.28$ ($r^2 = 0.999$), where y and x are the area of peak current (nA s) and iodide concentration (μM), respectively. The detection limit (3σ) is as low as 0.01 μM. The system provides an impressively good precision (%R.S.D. = 2.2) for 20 μl injections ($n = 30$) of 0.1 mM iodide. Throughput of sample is 85 samples h^{-1}.

3.3.3. Performance on pharmaceutical applications

3.3.3.1. Nuclear emergency tablets. Samples of potassium iodide tablets were determined using our electrochemical method (Fig. 1). The results were compared with the values obtained from an ISE method and a colorimetric flow-injection method [23] as shown in Fig. 5. According to the ANOVA test [33], the results for IOSAT™, Thyro-Block™ and NO-RAD™ are not significantly different at 95% confidence [$F_{observed}$ are 0.1037 (IOSAT™), 0.7862 (Thyro-Block™) and 3.493 (NO-RAD™) where $F_{critical} = 4.256$]. The results of RAD BLOCK™ determined by all the method are not significantly different at 99% confidence ($F_{observed} = 6.667$, $F_{critical} = 8.022$). It can also be observed in Fig. 5 that all of our results, with three different analytical methods, agree well with the manufacture's contents.

For these samples, there is no evidence of interferents from sample matrices. Recovery studies made for all the samples have shown that the extracts' matrices do not have influence on electrochemical oxidation of iodide (86–103% recovery). For our method, the samples can be directly analysed after the following steps: water extraction, filtration, dilution and finally injection.

3.3.3.2. Multivitamin tablets. Multivitamins have always been our sample of interest. Usually these samples contain iodine at much lower levels (e.g., 150 μg I/tablet) than the raidoactive protection tablets (e.g., 49 mg I/tablet). With appropriate extraction (for example, one vitamin tablet is extracted with 100.0 ml of water, (approximately 1 mg I L^{-1})) we should be able to get reasonable signal currents from this type of sample.

Our results demonstrated that, although with C-18 clean up, the extracts still contain other electroactive species that cause positively erratic results (can be up to 500 times greater in signal current). An experiment was then carried out to study effects of foreign ions, including compounds that are likely to exist in aqueous vitamin extracts. The results are summarized in Table 1. According to these results, at least two ingredients (Vitamin B_6 and ascorbic acid) interfere the quantitative analysis of iodide.

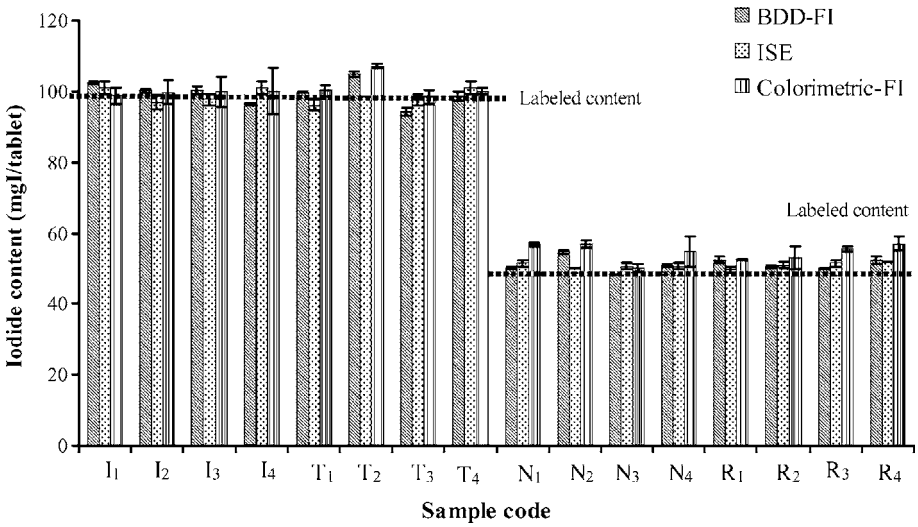

Fig. 5. Comparison of the iodide contents found in potassium iodide tablets, which were, obtained by the proposed method (BDD-FI), ISE method and colorimetric-FI method [20]. Determination by each method was carried out in triplicate for a sample. I: IOSAT, T: Thyro-Block, N: NO-RAD and R: RAD BLOCK KI.

Table 1
Effect of foreign ions on the alteration of FI signals obtained from replicate injections ($n = 5$) of standard potassium iodide 0.01 mM

Foreign species/added as	Investigated concentration ($mg\,L^{-1}$)[a]	Results[b]
1. Vitamin B_1 or aneurine hydrochloride/ $C_{12}H_{17}ClN_4OS{\cdot}HCl$	21–42	Does not interfere
2. Vitamin $B_2/C_{17}H_{20}N_4O_6$	24–48	Does not interfere
3. Vitamin B_6 or adermine hydrochloride/ $C_8H_{11}NO_3{\cdot}HCl$	30–60	Strongly interfere (e.g. 22% alteration even at $2\,mg\,L^{-1}$)
4. Vitamin C or L(+)ascorbic acid/$C_8H_8O_6$	900–1200	Strongly interfere (e.g. 19% alteration even at $1.6\,mg\,L^{-1}$)
5. Cl^-/NaCl	180–363	Does not interfere (studied up to $200\,mg\,L^{-1}$)
6. F^-/NaF	–	Does not interfere (studied up to $800\,mg\,L^{-1}$)
7. Br^-/NaBr	–	Does not interfere (studied up $200\,mg\,L^{-1}$)

[a] Likely concentrations of the foreign species, no. 1–5, in vitamin extracts.
[b] Greater than ±5% signal alteration is classified as interfering condition.

4. Conclusions

This work presents, for the first time, application of the BDD for quantitative analysis of iodide. For routine, we recommend amperometric detection in flow-injection mode. The flow-injection system is simply a single channel manifold with flow-through electrochemical cell of the working diamond electrode. With this construction, analysis of samples is very rapid (85 samples h^{-1}). Wide dynamic range (0.8–200 μM) was obtained, with good precision (R.S.D. = 2.2%).

The method is suitable for determination of iodide in nuclear emergency tablets. The BDD-FI method was proved to be valid for this type of samples. However, for multivitamins, separation prior the amperometric detection is required, since some of the ingredients have shown to interfere quite strongly. Utilization of the amperometric BDD as the detector for liquid chromatography is at present being investigated for multivitamins.

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References

[1] M. Hupert, A. Muck, J. Wang, J. Stotter, Z. Cvackova, S. Haymond, Y. Show, G.M. Swain, Diamond Relat. Mater. 12 (2003) 1940.
[2] T.N. Rao, A. Fujishima, Diamond Relat. Mater. 9 (2000) 384.
[3] S.G. Bairu, R.I. Stefan, J.F. van Staden, Crit. Rev. Anal. Chem. 33 (2) (2003) 145.
[4] J. Xu, Q. Chen, G.M. Swain, Anal. Chem. 70 (1998) 3146.

[5] T.N. Rao, I. Yagi, T. Miwa, D.A. Tryk, A. Fujishima, Anal. Chem. 71 (1999) 2506.
[6] O. Chailapakul, E. Popa, H. Tai, B.V. Sarada, D.A. Tryk, A. Fujishima, Electrochem. Commun. 2 (2000) 422.
[7] J. Xu, G.M. Swain, Anal. Chem. 70 (1998) 1502.
[8] M.D. Kappang, M. Witek, J. Blau, G.M. Swain, Anal. Chem. 71 (1999) 1188.
[9] M.A. Witek, G.M. Swain, Anal. Chim. Acta 440 (2001) 119.
[10] H. Notsu, T. Tatsuma, A. Fujishima, J. Electroanal. Chem. 523 (2002) 86.
[11] N. Wangfuengkanagul, O. Chailapakul, J. Pharm. Biomed. Anal. 28 (2002) 841.
[12] W. Siangproh, P. Ngamukot, O. Chailapakul, Sens. Actuators B 91 (2003) 60.
[13] N. Wangfuengkanagul, O. Chailapakul, Talanta 58 (2002) 1213.
[14] W. Siangproh, N. Wangfuengkanagul, O. Chailapakul, Anal. Chim. Acta 449 (2003) 183.
[15] O. Chailapakul, W. Siangproh, B.V. Sarada, C. Terashima, T.N. Rao, D.A. Tryk, A. Fujishima, Analyst 127 (2002) 1164.
[16] T.A. Ivandini, B.V. Sarada, C. Terashima, T.N. Rao, D.A. Tryk, H. Ishiguro, Y. Kubota, A. Fujishima, J. Electroanal. Chem. 521 (2002) 117.
[17] C. Terashima, T.N. Rao, B.V. Sarada, D.A. Tryk, A. Fujishima, Anal. Chem. 74 (2002) 895.
[18] C. Terashima, T.N. Rao, B.V. Sarada, Y. Kubota, A. Fujishima, Anal. Chem. 75 (2003) 1564.
[19] M.C. Granger, J. Xu, J.W. Strojek, G.M. Swain, Anal. Chim. Acta 397 (1999) 145.
[20] R.I. Stefan, S.G. Bairu, J.F. van Staden, Anal. Lett. 36 (8) (2003) 1493.
[21] USP, DI Drug Information for the Health Care Provider, Kingsport Press, Maryland.
[22] D. Nacapricha, C.G. Taylor, Analyst 118 (1993) 623.
[23] D. Nacapricha, K. Uraisin, N. Ratanawimarnwong, K. Grudpan, Anal. Bioanal. Chem. 378 (2004) 816.
[24] W. Chantore, S. Muangkaew, J. Shiowatana, D. Nacapricha, Lab. Robotics Automat. 11 (1999) 37.
[25] N. Choengchan, K. Lukkanakul, N. Ratanawimarnwong, W. Waiyawat, P. Wilairat, D. Nacapricha, Anal. Chim. Acta 499 (2003) 115.
[26] D. Devey, D.E. Malcahy, G.R. O'Connel, Talanta 37 (1990) 313.
[27] J. Xu, M. Xin, Anal. Chim. Acta 276 (1993) 261.
[28] J. Rendi, S. Seybold, W. Borner, Clin. Chem. 40 (6) (1994) 908.
[29] K. Han, W.F. Koch, K.W. Pratt, Anal. Chem. 59 (1987) 731.
[30] J. Ruzicka, E.H. Hansen, Flow Injection Analysis, second ed., Wiley, New York, 1998.
[31] K.J. Hanson, C.W. Tobias, J. Electrochem. Soc. 134 (1987) 2204.
[32] P.H. Qi, J.B. Hiskey, Hydrometallurgy 32 (1993) 161.
[33] J.H. Miller, J.C. Miller, Statistics and Chemometrics for Analytical Chemistry, fourth ed., Pearson Education Ltd., Essex, 2000 (Chapter3).