Full Paper

Fabrication of Bismuth/Multi-walled Carbon Nanotube Composite Modified Glassy Carbon Electrode for Determination of Cobalt

WANG, Yuane^{a,b,c}(王元娥) PAN, Dawei^a(潘大为) LI, Xinmin^a(李新民) QIN, Wei^{*,a,d}(秦伟)

^a Laboratory of Environmental Chemistry, Yantai Institute of Coastal Zone Research for Sustainable Development, Chinese Academy of Sciences, Yantai, Shandong 264003, China

^b Institute of Oceanology, Chinese Academy of Sciences, Qingdao, Shandong 266071, China

^c Graduate University of Chinese Academy of Sciences, Beijing 100049, China

^d School of Oceanology, Yantai University, Yantai, Shandong 264005, China

A bismuth/multi-walled carbon nanotube (Bi/MWNT) composite modified electrode for determination of cobalt by differential pulse adsorptive cathodic stripping voltammetry is described. The electrode is fabricated by potentiostatic pre-plating bismuth film on an MWNT modified glassy carbon (GC) electrode. The Bi/MWNT composite modified electrode exhibits enhanced sensitivity for cobalt detection as compared with the bare GC, MWNT modified and bismuth film electrodes. Numerous key experimental parameters have been examined for optimum analytical performance of the proposed electrode. With an adsorptive accumulation of the Co(II)-dimethylglyoxime complex at -0.8 V for 200 s, the reduction peak current is proportional to the concentration of cobalt in the range of 4.0×10^{-10} — 1.0×10^{-7} mol/L with a lower detection limit of 8.1×10^{-11} mol/L. The proposed method has been applied successfully to cobalt determination in seawater and lake water samples.

Keywords multi-walled carbon nanotube, bismuth film electrode, composite electrode, cobalt, adsorptive stripping analysis, voltammetry

Introduction

Mercury electrodes have been widely used in electrochemical analysis for the past forty years. However, the well-known toxicity restricts their applications. Bismuth is an environmentally friendly and non-toxic green element. Since 2000, bismuth film electrodes (BiFE) have received much attention in stripping analysis because the performance of the bismuth film electrode compares favorably to or even surpasses that of mercury electrode.^{1,2} The BiFE shows high sensitivity, low background, wide potential window, insensitivity to dissolved oxygen, well-defined and undistorted stripping signals and simple surface renewal.²⁻⁵ Due to these attractive electrochemical characteristics, nowadays various kinds of bismuth film electrodes have been prepared by in situ or ex situ plating bismuth onto substrates including glassy carbon (GC),³ carbon paste⁶ and silicon.⁷ These electrodes have been applied to determination of many heavy metals such as cadmium,⁸ lead,⁸ tin,⁹ nickel^{3,4} and cobalt.^{3,4,10,11}

Carbon nanotubes (CNT) have attracted much attention in electroanalysis due to the unique mechanical. electronic, geometrical and chemical properties.¹²⁻¹⁴ In recently years, it has been found that combining metal particles, such as platinum,¹⁵ nickel,¹⁶ copper¹⁷ and palladium,¹⁸ with CNT-modified electrodes can provide a promising way for fabrication of novel electrodes with largely improved performances.^{14,19} Although bismuth film electrodes have been extensively studied, the bismuth/CNT-modified electrodes are relatively rare and have only been employed for anodic stripping measurements of cadmium and lead.²⁰⁻²² Here we fabricate a bismuth/multi-walled carbon nanotube (MWNT) composite electrode for the determination of cobalt by differential pulse adsorptive cathodic stripping voltammetry. Cobalt is an important trace element in nature, which can be either essential or toxic to man, animals, and plants for a range of metabolic processes depending on its concentration levels. The monitoring of trace amounts of cobalt is of great importance not only in medical and clinical fields, but also for environmental

^{*} E-mail: wqin@yic.ac.cn

Received April 26, 2009; revised August 13, 2009; accepted September 1, 2009.

Project supported by the Chinese Academy of Sciences (No. KZCX2-YW-410), the National Natural Science Foundation of China (No. 40776058), the National 863 High Technology Project of the Ministry of Science and Technology of China (No. 2007AA09Z103), the Scientific Research Foundation for the Returned Overseas Chinese Scholars of the State Education Ministry, the Department of Science and Technology of Shandong Province (No. 2006GG2205033), the Outstanding Youth Natural Science Foundation of Shandong Province (No. JQ200814) and the Taishan Scholar Program of Shandong Province.

analysis and process control.²³ Most of the bismuth film electrodes developed for cobalt determination show a higher detection limit than mercury electrodes even when the catalytic processes are employed.^{3,4,10,11} This paper reports for the first time the adsorptive cathodic stripping behavior of a Bi/MWNT composite modified electrode, which shows a dramatically enhanced sensitivity to cobalt with a detection limit below 1×10^{-10} mol/L. Comparisons will be shown among the bare glassy carbon electrode, BiFE, MWNT and Bi/MWNT modified electrodes.

Experimental

Reagents

All the chemicals were supplied by Sinopharm Chemical Reagent and of analytical grade purity. The MWNT (30—70 nm) was purchased from Chengdu Organic Chemicals (Chengdu, China) with a purity of higher than 95%. Further purification was accomplished by stirring the MWNT in concentrated nitric acid for 6 h at 60 °C. Aqueous solutions were prepared with freshly deionized water (18.2 MQ•cm specific resistance) obtained with a Pall Cascada laboratory water system. 0.01 mol/L dimethylglyoxime (DMG) solution was prepared in 95% ethanol. 0.5 mg of MWNT was dispersed with the aid of ultrasonic agitation in 10.0 mL of deionized water to give a suspension of 0.05 mg/mL.

Apparatus

All the electrochemical measurements were performed on a CHI 660C electrochemical workstation (Chenhua Instruments, Shanghai, China) with a conventional three electrode configuration. A bare GC (3 mm diameter, Chenhua Instruments), an MWNT modified, a bismuth film or a Bi/MWNT composite modified electrode was employed as the working electrode. A saturated calomel electrode (SCE) and a platinum electrode were used as the reference and counter electrodes, respectively. All potential values refer to SCE. Experiments were performed in a 50 mL polytetrafluoroethylene beaker at room temperature.

Scanning electron microscopy (SEM) images were obtained from a JSM-6700F high resolution scanning electron microscope (JEOL). Seawater samples were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) using an Elan DRC II inductive coupling plasma-mass spectrometer (Perkin Elmer Sciex), while lake water samples were detected by atomic absorption spectrometry (AAS) with an AA6300 atomic absorption spectrophotometer (Shimadzu, Japan). Water samples were mineralized by using a 1000 W medium-pressure mercury lamp (Hanovia, UK).

Preparation of the Bi/MWNT composite modified electrode

The glassy carbon electrode was hand-polished with 0.3 and 0.05 μ m alumina slurries on a polishing pad, then rinsed with deionized water and sonicated for 2

min. The polished electrode was electrochemically treated in 0.5 mol/L H₂SO₄ by cyclic voltammetry from -0.2 to 1.5 V until a stable cyclic voltammogram was obtained. For fabrication of the MWNT modified electrode, 5 µL of 0.05 mg/mL MWNT suspension was transferred onto the GC electrode surface, followed by evaporating the solvent under an infrared lamp. The Bi/MWNT composite modified electrode was prepared by placing the MWNT modified electrode in a plating solution containing 0.1 mol/L acetate buffer (pH 4.4) and 100 mg/L Bi(III), and depositing at an applied potential of -1.0 V for 5 min while the solution was stirred at 300 r/min. The BiFE was prepared by plating bismuth onto the GC electrode surface in the same way as the Bi/MWNT composite modified electrode.

Electrochemical measurements

Electrochemical behavior of the Bi/MWNT composite modified electrode was studied in ammonia buffer solution (pH 9.0) by cyclic voltammetry from -0.3 to 0.5 V. Measurements of Co(II) were carried out in the presence of dissolved oxygen with 7.0×10^{-5} mol/L of DMG as complexing agent. A deposition potential of -0.8 V was applied to the working electrode under magnetic stirring (300 r/min) with an adsorption accumulation time of 200 s. After an equilibration period of 15 s, the differential pulse voltammetry was performed to scan from -0.8 to -1.4 V with a modulation amplitude of 50 mV, pulse duration time of 50 ms, interval time of 0.2 s and potential step of 4 mV. The height of the current peak corresponding with the reduction of the cobalt complex at -1.09 V was used as a measure of the reduction current. After each measurement, cobalt reduced at the surface of the modified electrode was removed by applying -0.3 V at the working electrode for 300 s with solution stirring.

Results and discussion

Characterization of the Bi/MWNT composite modified electrode

The SEM images of MWNT modified and Bi/MWNT composite modified electrodes are shown in Figure 1. It can be seen that the MWNTs with the diameters of 30—70 nm are randomly distributed on the GC electrode surface (Figure 1a). After electrolysis, bismuth was electro-deposited on the surface of each bundle of the MWNT with a brighter SEM image (Figure 1b), which indicates that the electron conductivity of the surface layers of the MWNT has increased dramatically due to bismuth coating. The thickness of the bismuth coating was estimated to be 30—50 nm.

Electrochemical behavior of the bare GC electrode, BiFE, MWNT modified and Bi/MWNT composite modified electrodes was studied in 0.01 mol/L ammonia buffer solution (pH 9.0) by linear sweep voltammetry from -0.3 to 0.5 V. As shown in Figure 2, the response obtained at the GC electrode (curve a) is almost



Figure 1 SEM images of MWNT modified (a) and Bi/MWNT composite modified (b) electrodes.



Figure 2 Linear sweep voltammograms of (a) bare GC electrode, (b) BiFE, (c) MWNT modified and (d) Bi/MWNT composite modified electrodes in 0.01 mol/L ammonia buffer solution (pH 9.0) with a scan rate of 100 mV/s.

a beeline, indicating no oxidation occurs. For the BiFE (curve b), a current peak was observed at -0.13 V, which is due to the oxidization of bismuth. There is a broad oxidation peak at the MWNT modified electrode (curve c), owing to the redox behavior of oxygen-containing functional groups attached to the surface of the MWNT.²⁴ For the Bi/MWNT composite modified electrode (curve d), a sharp oxidation peak of bismuth also occurred at -0.13 V, which suggests that the presence of MWNT support does not change the elec-

trochemical behavior of the bismuth film. The background current of Bi/MWNT composite modified electrode is larger than those of the other three electrodes, indicating that the Bi/MWNT composite modified electrode has a larger effective surface area. Figure 2 shows that the presence of MWNT amplifies the peak current of bismuth by about 20 times, which may be due to the greater amount of bismuth deposited by the larger surface area of the MWNT layer.

Differential pulse adsorptive cathodic stripping voltammetry of Bi/MWNT electrode in Co(II) solutions

Differential pulse voltammetry was used for comparison study of the bare GC, BiFE, MWNT modified and Bi/MWNT composite modified electrodes. As illustrated in Figure 3, there is no response at the bare GC electrode (curve a), while the BiFE (curve b) and MWNT (curve c) modified electrodes give well defined peak signals, which indicates that the presence of either bismuth or MWNT can improve the electroanalytical performance of GC electrode and enhance the sensitivity for cobalt detection. Figure 3 also shows that the electrode response can be further improved by modifying the electrode with both bismuth and MWNT. The peak current of cobalt reduction was dramatically increased by using the Bi/MWNT composite modified electrode (curve d), which is ca. 8- or 6-fold higher than that observed at the GC electrode modified by bismuth or MWNT alone. The significantly enhanced sensitivity of the Bi/MWNT modified electrode may be attributed to the larger surface area of MWNT which allows a greater amount of bismuth to be deposited.

Optimization for measurement of cobalt at Bi/MWNT electrode

Variation of the concentration of Bi(III) ions in the



Figure 3 Differential pulse adsorptive cathodic stripping voltammograms of (a) bare GC electrode, (b) BiFE, (c) MWNT modified and (d) Bi/MWNT composite modified electrodes for measuring 5.0×10^{-8} mol/L Co(II) in the presence of 0. 01 mol/L ammonia buffer (pH 9.0) and 7.0×10^{-5} mol/L DMG with an adsorptive accumulation at -0.8 V for 200 s.



Figure 4 Effect of varying (a) the bismuth concentration in the plating solution, (b) the DMG concentration, (c) sample pH and (d) adsorption potential on the reduction peak current for 5.0×10^{-9} mol/L cobalt. Experimental conditions are the same as those in Figure 3, unless indicated otherwise.

plating solution from 0.5 to 200 mg/L was found to have a dramatic influence on the reduction current response of Co(II). As shown in Figure 4a, the peak current of Co(II) increases as the concentration of Bi(III) ions increases to 100 mg/L, and then is stable to a concentration of at least 200 mg/L. Thus, 100 mg/L of Bi(III) ions was chosen for further studies.

The influence of DMG concentration on the reduction current of Co(II) at the Bi/MWNT nanocomposite modified electrode was examined in ammonia buffer solution (pH 9.0) containing 5.0×10^{-9} mol/L Co(II). The results are shown in Figure 4b. As DMG concentration increases from 2.0×10^{-5} to 5.0×10^{-5} mol/L, the peak current of Co(II) increases rapidly due to the more efficient complexation between DMG and Co(II). The Co(II) signal levels off at DMG concnetrations above 7.0×10^{-5} mol/L, indicating that the concentration of Co(II) complex reaches the maximal value. Therefore, 7.0×10^{-5} mol/L was employed for further experiments.

The influence of sample pH on the reduction current signal was investigated by changing pH values from 8.0 to 10.0 with 0.01 mol/L ammonia buffer solution. As shown in Figure 4c, the current response is strongly dependent on pH, with a maximum at pH 9.0. At lower pH, the reduction of DMG could interfere with that of the Co(II) complex;²⁵ while at higher pH, the decrease of

peak current was due to the formation of $Co(OH)_2$, which might compete with the electroactive complex.

Figure 4d illustrates the effect of adsorption potential upon the reduction peak current of Co(II). It can be seen that the peak current increases almost linearly as adsorption potential changes from -0.4 to -0.8 V; at more negative potentials, the signals gradually decrease, which is probably due to complex reduction during the adsorption process. Therefore, -0.8 V was chosen as the adsorption potential.

Experiments to optimize the adsorption time were conducted in the time range from 15 to 300 s. It was found that the reduction peak current for cobalt increased rapidly with the increment of adsorption time until 200 s and then leveled off due to the limited working area of the Bi/MWNT composite film on the electrode surface. Considering a compromise between sensitivity and analysis time, the adsorption time of 200 s was employed for subsequent experiments.

Performance of Bi/MWNT modified glassy carbon electrode for cobalt measurements

Under the selected conditions given above, the response of Bi/WMNT modified electrode to cobalt ranging from 4.0×10^{-10} to 3.0×10^{-7} mol/L is shown in Figure 5. A highly linear calibration curve (R^2 =0.998,

N=10) was obtained in the concentration range of 4.0 $\times 10^{-10}$ -1.0×10^{-7} mol/L with a regression equation of y = 19.68x - 0.35, where y and x are the peak current (nA) and Co(II) concentration (nmol/L), respectively. The detection limit is 8.1×10^{-11} mol/L, which gives a signal equal to the blank signal plus three times the standard deviation of the blank measurement. The relative standard deviation was 2.9% for 3.3×10^{-9} mol/L (N=7). The response characteristics of the proposed method were compared with those reported in the literature and the results are shown in Table 1. It can be seen that the proposed Bi/MWNT composite modified electrode has a wide linear dynamic range, lower detection limit and larger sensitivity than most of other methods for adsorptive determination of Co(II). Although the detection limit $(1.8 \times 10^{-11} \text{ mol/L})$ reported in Ref. 11 is a bit lower than that of the present sensor, a more complicated catalytic system was employed for that work in which cetyltrimethylammonia bromide and piperazine-N,N'-bis(2-ethanesufonic acid) were added simultaneously to the supporting electrolyte for cobalt determination in the presence of dimethyglyoxime.

Table 1 Comparison of the response characteristics of the pre-sent work with other studies^a

Detection limit/ $(nmol \bullet L^{-1})$	Linear range/ $(nmol \bullet L^{-1})$	Sensitivity/ $[nA/(nmol \cdot L^{-1})]$	Reference
1.2	3.4—34	0.5	3
1.2	33.7—337	NR	4
0.018	0.2—20	82.2	11
0.95	3.4—340	NR	26
1.3	NR	NR	27
1.2	3.4—340	0.49	28
1.2	3.4—30	0.56	29
1.5	33.9—271.5	2.16	30
0.081	0.4—300	19.7	Present work

^a NR means not reported.

Interference study

Possible interference by other metals with cobalt determination using the Bi/MWNT composite modified electrode under optimized conditions was tested by analyzing a standard solution of cobalt (5.0×10^{-1}) mol/L) to which increasing amounts of interfering metals were added. The tolerable concentration ratios with respect to 5.0×10^{-9} mol/L cobalt for interference at 5% level were over 1000 for Ca(II), Mg(II), Zn(II), Cd(II), Mn(II), Cu(II), Cr(III) and Al(III), 500 for Fe(III) and Mo(VI), and 100 for Pb(II) and V(V). The excellent selectivity toward Co(II) over those metal ions is probably due to the specific complexation between Co(II) and DMG. However, it is known that Ni can also form complex with DMG and may interfere with Co(II) determination. Experiments showed that in the presence of 10-fold excess of Ni(II), both yielded independently



Figure 5 Calibration curve for cobalt determination using the Bi/MWNT composite modified GC electrode. Inset shows the adsorptive stripping voltammograms for cobalt at different concentrations of 0, 5.0, 10.0 and 50.0 nmol/L (from top to bottom). Other conditions are the same as those in Figure 3.

well-resolved signals at the Bi/MWNT composite modified electrode with a peak potential difference of *ca*. 0.1 V. This implies that Co(II) and Ni(II) can be measured simultaneously with the present modified electrode.

Surface-active substances are known to lower the sensitivity due to competitive adsorption on the electrode surface. These kinds of interferences were tested using Triton X-100 (nonionic by surfactant), hyamine-1622 (cationic) and sodium dodecylbenzenesulfonate (SDS, anionic) as model compounds. As shown in Figure 6, addition of 0.7 mg• L^{-1} of Triton X-100 or 0.3 $mgetendleL^{-1}$ of hyamine-1622 caused a decrease of Co(II) peak to about 50% of its original value. A similar suppression was achieved with 2.0 mg•L⁻ SDS. The lower interference of anionic surfactant (SDS) is probably due to the negative surface charge at the adsorption potential of -0.8 V.



Figure 6 Effect of surfactants on the current response of 5.0×10^{-9} mol/L Co(II). (•), (•) and (•) denote hyamine-1622, SDS and Triton X-100, respectively. $i_{p,o}$ and i_p are peak currents before and after addition of surfactants, respectively. Experimental conditions are the same as those in Figure 3.

EDTA was chosen to study the influence of complexing agents on the reduction current signal of Co(II) and the results are presented in Figure 7. It can be seen that the DMG complex with Co(II) is very stable, as there was no decrease in the peak signal up to 1.0 mmol/L EDTA. However, the peak height could be suppressed by about 50% with EDTA at a high concentration of 0.01 mol/L.



Figure 7 Effect of EDTA concentration on the current response of 5.0×10^{-9} mol/L Co(II). Experimental conditions are the same as those in Figure 3.

Analytical applications

Prior to cobalt determination, water samples were filtrated through a 0.45- μ m membrane filter, acidified to pH *ca.* 2 with HNO₃, and then digested by UV irradiation for 1 h to eliminate the interference of organic matter. A standard addition method was employed for cobalt quantification. For comparison, AAS and ICP-MS were used for analyses of Co(II) in lake water and seawater samples, respectively. The corresponding results are shown in Table 2. It can be seen that the results obtained by the proposed electrode agree well with those obtained by AAS and ICP-MS.

 Table 2
 Results of Co(II) determination in seawater and lake water samples

Sample	Co(II) concentration/(nmol• L^{-1})		
	Proposed method ^a	Reference value	
Seawater 1	8.6±0.3	8.5 ± 0.4^b	
Seawater 2	6.5 ± 0.2	$5.6 {\pm} 0.3^{b}$	
Lake water 1	56.6 ± 1.5	50.0 ± 3.5^{c}	
Lake water 2	35.7 ± 1.0	33.3 ± 2.3^{c}	

^{*a*} Average value of 3 determinations \pm standard deviation. ^{*b*} Average value of 5 determinations \pm standard deviation by ICP-MS. ^{*c*} Average value of 7 determinations \pm standard deviation by AAS.

Conclusion

A bismuth/multi-wall carbon nanotube composite modified electrode has been described for determination of cobalt by differential pulse adsorptive cathodic stripping voltammetry. Compared with bare glassy carbon, MWNT modified and bismuth film electrodes, the Bi/MWNT composite modified electrode exhibits improved electroanalytical behavior which may be due to the larger surface area of MWNT allowing a greater amount of bismuth to be deposited. The proposed electrode shows high sensitivity with a detection limit of 8.1 $\times 10^{-11}$ mol/L, which is much lower than those obtained with bismuth film electrodes.^{3,4,26,27} The Bi/MWNT modified electrode can be applied to the determination of trace cobalt in real samples.

References

- 1 Wang, J. Electroanalysis 2005, 17, 1341.
- 2 Wang, J.; Lu, J. M.; Hočevar, S. B.; Farias, P. A. M. Anal. Chem. 2000, 72, 3218.
- 3 Hutton, E. A.; Hočevar, S. B.; Ogorevc, B. Anal. Chim. Acta 2005, 537, 285.
- 4 Morfobos, M.; Economou, A.; Voulgaropoulos, A. Anal. Chim. Acta 2004, 519, 57.
- 5 Economou, A.; Voulgaropoulos, A. Talanta 2007, 71, 758.
- 6 Baldrianova, L.; Svancara, I.; Sotiropoulos, S. Anal. Chim. Acta 2007, 599, 249
- 7 Kokkinos, C.; Economou, A.; Raptis, I.; Efstathiou, C. E.; Speliotis, T. *Electrochem. Commun.* 2007, 9, 2795.
- 8 Kefala, G.; Economou, A. Anal. Chim. Acta 2006, 576, 283.
- 9 Hutton, E. A.; Hočevar, S. B.; Mauko, L.; Ogorevc, B. Anal. Chim. Acta 2006, 580, 244.
- 10 Krolicka, A.; Bobrowski, A.; Kalcher, K.; Mocak, J.; Svancara, I.; Vytras, K. *Electroanalysis* 2003, 15, 1859.
- 11 Korolczuk, M.; Moroziewicz, A.; Grabarczyk, M. Anal. Bioanal. Chem. 2005, 382, 1678.
- Li, C.; Thostenson, E. T.; Chou, T. W. Compos. Sci. Tech. 2008, 68, 1227.
- 13 Yogeswaran, U.; Chen, S. M. Anal. Lett. 2008, 41, 210.
- Wildgoose, G. G.; Banks, C. E.; Leventis, H. C.; Compton, R. G. *Microchim. Acta* 2006, *152*, 187.
- 15 Hrapovic, S.; Liu, Y. L.; Male, K. B.; Luong, J. H. T. Anal. Chem. 2004, 76, 1083.
- 16 Deo, R. P.; Lawrence, N. S.; Wang, J. Analyst 2004, 129, 1076.
- 17 Wang, J.; Chen, G.; Wang, M.; Chatrathi, M. P. Analyst 2004, 129, 512.
- 18 Li, Y.; Wang, H.; Chen, Y.; Yang, M. Sens. Actuators B: Chem. 2008, 132, 155.
- 19 Khan, M. A. K.; Kerman, K.; Petryk, M.; Kraatz, H.-B. Anal. Chem. 2008, 80, 2574.
- 20 Liu, G. D.; Lin, Y. H.; Tu, Y.; Ren, Z. F. Analyst 2005, 130, 1098.
- 21 Wang, N.; Dong, X. Anal. Lett. 2008, 41, 1267.
- 22 Hwang, G. H.; Han, W. K.; Park, J. S.; Kang, S. G. *Talanta* 2008, 76, 301.
- 23 Kong, X.; Jia, Q.; Zhou, W. Microchem. J. 2007, 87, 132.
- 24 Barisci, J. N.; Wallace, G. G.; Baughman, R. H. J. *Electroanal. Chem.* **2000**, 488, 92.
- 25 Ni, Y. M.; Li, L.; Zhou, C.; Gao, X. X. Acta Chim. Sinica 1987, 45, 971.
- 26 Hutton, E. A.; Ogorevc, B.; Hocevar, S. B.; Smyth, M. R.

Determination of cobalt

Anal. Chim. Acta 2006, 557, 57.

- 27 Hutton, E. A.; Hocevar, S. B.; Ogorevc, B.; Smyth, M. R. *Electrochem. Commun.* **2003**, *5*, 765.
- 28 Hutton, E. A.; Hocevar, S. B.; Ogorevc, B. Anal. Chim. Acta 2005, 537, 285.

- 29 Hutton, E. A.; Ogorevc, B.; Hocevar, S. B.; Smyth, M. R. *Anal. Chim. Acta* **2006**, *557*, 57.
- 30 Kokkinos, C.; Economou, A.; Koupparis, M. *Talanta* 2009, 77, 1137.

(E0904261 Chen, J.; Lu, Z.)