Electroanalysis of Trace Manganese via Cathodic Stripping Voltammetry: Exploration of Edge Plane Pyrolytic Graphite Electrodes for Environmental Analysis*

Christine M. Welch,[a] Craig E. Banks,[a] Šebojka Komorsky-Lovrić,[b] and Richard G. Compton[a,]**

[a]*Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom*

[b]*Division for Marine and Environmental Research, Ruđer Bošković Institute, P.O. Box 180, 10002 Zagreb, Croatia*

Keywords
• edge plane pyrolytic graphite electrodes
• manganese detection
• cathodic stripping voltammetry
• carbon paste electrode

The determination of trace levels of manganese via cathodic stripping voltammetry at an edge plane pyrolytic graphite electrode (eppge) was evaluated for use in environmental analysis. The response of the eppge is compared with boron-doped diamond electrodes under quiescent conditions where the former is observed to have a three times higher sensitivity. Using this protocol with a stirred accumulation period, a detection limit of 14.2 nmol dm^{-3} and a sensitivity of 14.2 mol dm^{-3} A^{-1} is achieved with linearity from 25 to 250 nmol dm^{-3}, based on a 120 seconds accumulation period. The response at a carbon paste electrode is also compared under the same conditions with the eppge found to be superior in terms of sensitivity, detection limits and reproducibility. The efficacy of the protocol utilising the eppge was assessed in the determination of manganese in a certified seawater reference material, NASS-5, from the National Research Council Canada, which was found to be in excellent agreement with the independently verified sample.

INTRODUCTION

Manganese is an essential intake of the human body, playing a significant role in cellular metabolism at the trace level.[1–3] It is known that tea contains a high level of manganese (as high as 1800 µg per gram) with 30 % of the content in tea known to be in the form of manganese(II).[4] Although manganese is an essential micronutrient for plant and animals, it is also toxic at high levels. In man, chronic manganese poisoning affects the central nervous systems and can contribute to neurological disease.[1,2] Note that the maximum allowable concentration of manganese in domestic water supplies is 0.05 µg L^{-1} while the concentrations in excess of 1 mg g^{-1} in the diet are required before signs of toxicity are observed.[4,5] While the level of manganese in tea is monitored by the Ministry of Agriculture, Forestry and Fisheries, manganese can get into the body via the consumption of food, for example, molluscs in which the element is concentrated. Accordingly, there is a need for environmental

---

monitoring and we have reported[6,7] on sea water measurements made near a former ferromanganese industry in Šibenik bay, Croatia.

A plethora of techniques for manganese monitoring have been reported, such as atomic absorption spectroscopy and spectrophotometric detection.[8,9] The drawback is the requirement for sample pre-treatment steps, such as extraction to achieve the appropriate selectivity and sensitivity,[10] while the cost and portability limit further limit the application of such techniques for routine on-site environmental analysis. Electroanalytical methodologies are a highly attractive alternative due to their rapid, selective and portable nature.[11–13] The cathodic stripping voltammetry (CSV) of manganese is a favoured protocol owing to its specificity. The technique is based on first applying a pre-concentration step, where, employing a suitable electrode substrate, the electrode potential is held sufficiently positive to form insoluble manganese(IV) dioxide on the electrode surface:[4,6]

$$Mn^{2+} - 2e^- + 2H_2O \rightarrow MnO_2 + 4H^+$$

After a chosen pre-concentration time, the potential is then swept negative, producing a characteristic voltammetric stripping peak arising from the reduction of manganese(IV) dioxide back to manganese(II). Through careful choice of the deposition potential and time and with the possible application of convection during the pre-concentration period, the ultra trace level of manganese may be facilitated.

While electroanalytical techniques have been reported, the quantification of ultra trace levels of metal ions in seawater remains a challenging task due to surface contamination problems and matrix effects resulting in electrode passivation and inherent loss of sensitivity.[14] Recently we reported on a 'state of the art' electroanalytical technique for the quantification of ultra trace levels of manganese in seawater samples utilising sonelectroanalysis.[6] The protocol is based on applying power ultrasound during the CSV pre-concentration step at a boron-doped diamond (BDD) electrode. Ultrasound has two important effects: i) the increased mass transport arising from acoustic streaming increases the transport of manganese to the electrode surface, producing low detection limits and high sensitivities with short analysis times, and ii) acoustic cavitation also provides an *in-situ* electrode cleaning mechanism, keeping the electrode surface 'active' for manganese deposition from any surface passivating species that may be present in the environmental sample.[6]

The motivation for combining boron-doped diamond electrodes with ultrasound is two-fold. First, boron-doped diamond electrodes in comparison to other electrodes used for electroanalysis, such as glassy carbon, have very low levels of background interference allowing a wide potential window to be used, the combination of which means that high deposition potentials can be employed, producing low detection limits.[4,15] Second, applying ul-

trasound with electrode materials can result in pitting and ultimately electrode destruction, but due to the robustness of the BDD electrode, these electrodes are optimal for use in sonoelectroanalysis.[15,16]

Recently the edge plane pyrolytic graphite electrode has been reported as a new and attractive electrode substrate.[17–22] Highly ordered pyrolytic graphite is machined into a disc with the layers of graphite oriented and with the disc face parallel with the edge plane.[23,24] For a large variety of redox couples, the electron-transfer rate constants at basal-plane graphite have been found to be over 10^3 times slower than for edge-plane graphite (eppg).[24] We have shown that the advantageous properties of the eppg electrode lie in its excellent catalytic activity, sensitivity and low background currents. We have exemplified this in the electroanalytical detection of thiols,[17] NO_2,[18] ascorbic acid,[20] chlorine sensing[21] and halide detection.[22] In all cases low detection limits and high sensitivities were observed in comparison with other commonly used carbon based electrodes, representing the state-of-the-art sensing strategies. Given the wide range of important analytes that have been studied so far, eppg electrodes and their performance are yet to be explored for use in environmental analysis. It is this we address in this paper.

In this report we explore the possibility of using edge plane pyrolytic graphite electrodes for the cathodic stripping voltammetric detection of manganese in environmental samples. First, the responses of eppg electrodes are compared with boron-doped diamond electrodes under quiescent conditions where the former is observed to have a three times higher sensitivity. Second, differential pulse cathodic stripping voltammetry (DPCSV) with a stirred accumulation period is examined using eppg electrodes where a detection limit of 14.2 nmol dm^{-3} is shown to be possible with a high sensitivity of 14.2 mol dm^{-3} A^{-1} over the linear range from 25 to 250 nmol dm^{-3}. Third, the response at a carbon paste electrode is compared under the same conditions. While a nano-molar detection limit can be obtained, the eppg is found to be superior in terms of sensitivity, detection limit and reproducibility.

Last, the protocol utilising the efficiency of the protocol using eppg electrodes is assessed in the determination of manganese in a certified seawater reference material, NASS-5, from the National Research Council Canada. Excellent agreement with the independently determined value is found, suggesting that the monitoring of trace levels of manganese in environmental samples can be achieved using eppg electrodes employing a convection-assisted DPCSV protocol where sonoelectroanalysis may not be viable.

EXPERIMENTAL

All chemicals used were of analytical grade and used as received without any further purification. These were: manganese(II) perchlorate (Aldrich, 99 %), nitric acid (70 %,

Aldrich, ACS reagent) and ammonium nitrate (Aldrich, 99.9 %).

Solutions were prepared with deionised water of resistivity not less than 18.2 MΩ cm (Millipore water systems, UK). Voltammetric measurements were carried out using a μ-Autolab II potentiostat (Eco-Chemie, The Netherlands) with a three-electrode configuration.

Edge plane pyrolytic graphite (eppg, Le Carbone, Ltd. Sussex, UK) was used as a working electrode. Discs of pyrolytic graphite were machined into a 4 mm diameter, which was oriented with the disc face parallel with the edge plane. The counter electrode was a bright platinum wire, with a saturated calomel electrode completing the circuit. The working electrode was polished on alumina lapping compounds (BDH) of decreasing sizes (0.1–5 ìm) on soft lapping pads. All experiments were conducted at 20±2 °C. Convection was achieved by the use of a magnetic stir bar.

The carbon paste electrode was prepared by mixing carbon powder in a one to one (mass) ratio with mineral oil (light oil from Aldrich which is also used for preparation of nujol mulls for IR spectroscopy) in a beaker for 5 minutes. This was then packed into a plastic syringe (8 mm diameter) with a wire to make electrical contact. The electrode was allowed to partly dry for two hours at ambient temperature.[25]

A certified reference material, NASS-5, was obtained from the National Research Council Canada. This is a reference seawater material (salinity 30.4) collected from the North Atlantic at a depth of 10 m, 35 km southeast of Halifax, NS, Canada. The sample, as supplied, was acidified to pH = 1.6 with ultra trace nitric acid.

RESULTS AND DISCUSSION

Cathodic Stripping Voltammetry Utilising Edge Plane Pyrolytic Graphite Electrodes

The response of edge plane pyrolytic graphite electrodes for manganese(II) detection under stirred conditions was explored first. Using DPCSV with a deposition time of 120 seconds at +0.85 V (vs. SCE),[4] aliquots of manganese from 1 μmol dm^{-3} to 10 μmol dm^{-3} were added to a 0.5 mol dm^{-3} ammonium nitrate buffer (pH = 7) solution. The solution composition, deposition time and potential were chosen based on literature reports, allowing us to directly compare our results with the existing techniques.[4,6] Figure 1 shows the voltammetric responses from the manganese additions with a well-defined stripping peak corresponding to the reduction of manganese dioxide to manganese(II) observed at ca. +0.4 V, which is in close agreement with previous studies.[4,6] From the analysis of the peak height (I_H) versus added manganese concentration, a linear response was observed over the range studied (I_H / A = −26.5 ([Mn^{2+}] / mol dm^{-3}) − 2.35 × 10^{-5}; R^2 = 0.998). Note that the peak height is measured as the difference between the peak vertex and the baseline just before the onset of the stripping peak.
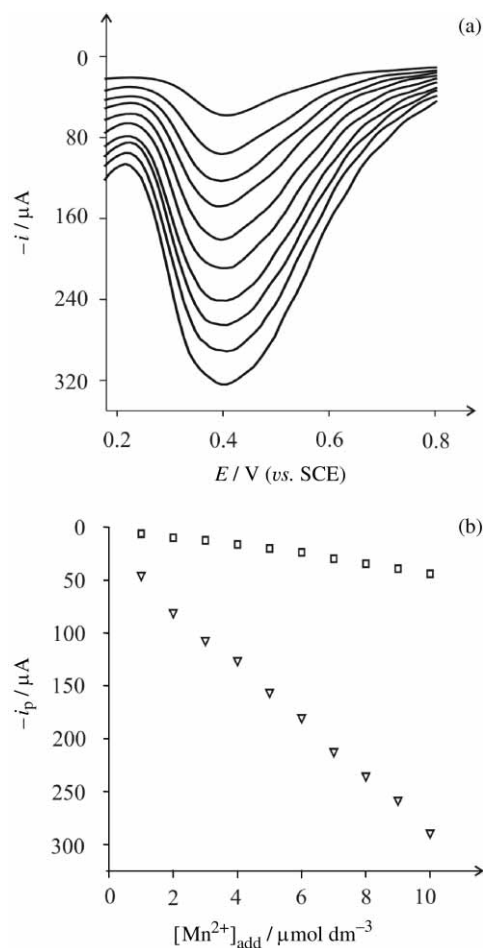

Figure 1. (a): Differential-pulse cathodic stripping voltamograms of 1 μmol dm^{-3} additions of manganese(II) into a 0.5 mol dm^{-3} ammonium nitrate buffer (pH = 7). Experimental parameters: 120 seconds stirred deposition at +0.85 V (vs. SCE); step potential = 10 mV, interval time = 0.1 s, modulation amplitude = 150 mV; modulation time = 0.02 s, standby potential = 0.0 V. (b): Plot of peak current (i_p) versus added manganese concentration ([Mn^{2+}]$_{add}$) for quiescent (squares) and stirred (triangles) deposition.

For comparison, the above procedure was repeated without the application of convection during the deposition step. Additions of manganese were made over the same range and analysis of the resulting peak height versus added manganese concentration produced the following linear regression: I_H / A = −4.3 ([Mn^{2+}] / mol dm^{-3}) − 2.87 × 10^{-7}; R^2 = 0.991). The effect of applying convection in the form of a gentle stirring can be observed in Figure 1, where the response in the absence (squares) and presence (triangles) of stirring increased the sensitivity by a factor of ca. 6. The response of a boron-doped diamond over the same concentration range using identical DPCSV (quiescent) conditions was previously examined for manganese detection by Goodwin et al.[6] From their paper, we can compare the response of the edge plane pyrolytic graphite electrode with that of a boron-doped diamond by calculating the current density in terms of electrode area. For the BDD electrode, we
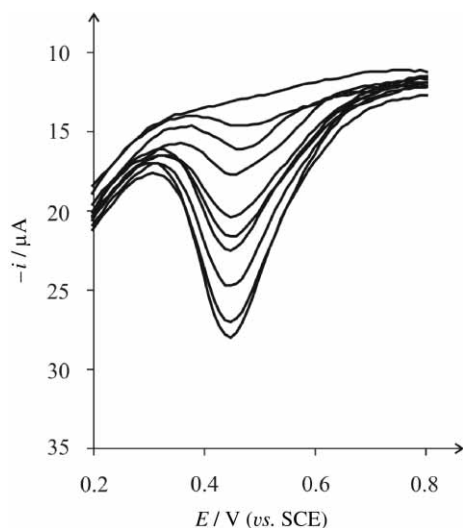
Figure 2. Differential-pulse cathodic stripping voltamograms arising from the addition of 25 nmol dm^{-3} of manganese(II) to a 0.5 mol dm^{-3} ammonium nitrate buffer (pH = 7). Experimental conditions same as in Figure 1.

found this to be 13.2 A mol^{-1} dm^3 cm^{-2} while in this study using an eppg electrode, this corresponds to 34.4 A mol^{-1} dm^3 cm^{-2}; clearly, the sensitivity is *ca.* three times higher on the eppg, suggesting that the BDD can be replaced in electroanalyical applications with an eppg electrode. This enhancement is likely to be due to the presence of a high proportion of edge plane sites which may act as nucleation centres for the growth of MnO$_2$.[23,24]

Next, the detection limit of using the above protocol utilising an eppge was assessed. Using the above convection-assisted procedure, lower concentrations of manganese(II) were made over the range 0 to 350 nmol dm^{-3}. Figure 2 shows the voltammetric responses from the manganese additions, with analysis of the peak height *versus* manganese additions revealing a linear dependence from 25 to 250 nmol dm^{-3} (I_H / A = –64.4 ([Mn^{2+}] / mol dm^{-3}) + 2.9 × 10^{-7}; R^2 = 0.992), with a limit of detection (3σ) found to correspond to 14.2 nmol dm^{-3}. The effect of increasing the deposition time on the sensitivity and detection limit was also explored.

Using DPCSV at an eppg electrode with a deposition potential of +0.85 V (*vs.* SCE), additions of manganese(II) were made to a 0.5 mol dm^{-3} ammonium nitrate buffer solution from 50 to 250 nmol dm^{-3} using convection assisted deposition times of 240 and 480 seconds. Analysis of the resulting peak heights *versus* manganese concentration produced sensitivities and detection limits of 122 A mol^{-1} dm^3 (I_H / A = –122 ([Mn^{2+}] / mol dm^{-3}) – 7.1 × 10^{-7}; R^2 = 0.998) and 6.2 nmol dm^{-3}, respectively, for the 240 seconds accumulation time, while for the 480 seconds deposition period, a sensitivity of 207 A mol^{-1} dm^3 (I_H / A = – 207 ([Mn^{2+}] / mol^{-1} dm^3) – 3.4 × 10^{-6}; R^2 = 0.999) with a detection limit of 3.7 nmol dm^{-3} was observed.

It can be observed that by applying the above protocol under quiescent conditions, micro-molar concentrations of manganese can be easily determined, while applying a convective accumulation period, the detection limit can be reduced to allow the quantification of ultra-trace manganese in samples with a high sensitivity through the choice of deposition time. This suggests that this protocol can be used as an effective substitute for sonoelectroanalysis[4,6] for the trace determination of manganese in water samples, such as seawater, where the concentration of manganese can lie between 10^{-6} to 10^{-10} mol dm^{-3};[26–28] we explore this aspect in depth.

Given the relative cost and performance of boron-doped diamond (*ca.* £ 140 for a 3 mm diameter) *versus* edge plane pyrolytic graphite (*ca.* £ 13 per electrode) with the latter having higher sensitivity, suggests that eppg can be used as a cheaper and superior substitute for BDD. In the area of electroanalysis, another alternative low cost carbon based electrode is the carbon paste electrode. We next consider the response of a carbon paste electrode for the detection of manganese.

Carbon Paste Electrodes for Manganese Detection

A carbon paste electrode was first fabricated as described in the Experimental. Additions of manganese(II) were made to a 0.5 mol dm^{-3} ammonium nitrate (pH = 7) solution over the range 25 to 250 nmol dm^{-3} using a convection-assisted deposition period of 120 seconds with the deposition potential maintained at +0.85 V (*vs.* SCE). The voltammetric responses are shown in Figure 3. From this data, a linear dependence of the stripping signal height was observed over the linear range explored (I_H / A = – 127 ([Mn^{2+}] / mol dm^{-3}) – 2.6 × 10^{-6} A; R^2 = 0.995) and the limit of detection based on 3σ was found to be 24 nmol dm^{-3}. Note that this is slightly higher than the detection limit of 14 nmol dm^{-3} observed using the edge plane pyrolytic graphite electrode. For direct comparison of the response of the carbon paste with the eppg electrode we consider the sensitivity in terms of the electrode area. This consequently becomes 254 A mol^{-1} dm^3 cm^{-2} for the carbon paste, which is less than found at the eppg electrode (510 A mol^{-1} dm^3 cm^{-2}) with both values obtained under identical conditions. Clearly the technique with higher sensitivity and a lower detection limit is favoured in electroanalysis. However, most importantly, the intra- and inter-reproducibility was found to be poor, with the sensitivity varying considerably from electrode-to-electrode.

The cathodic stripping procedure of manganese has already been explored for possible interferences.[4] Saterlay explored the possibility of potential interferences from metallic species and found that Zn^{2+}, Cu^{2+}, Pb^{2+} and Fe^{2+} had no effect on the stripping response of manganese in concentrations exceeding 100 fold that of manganese. The technique is also tolerant to Hg^{2+} and Al^{3+} at a 50-fold and 5-fold concentration excess, respectively.[4] In fact, the
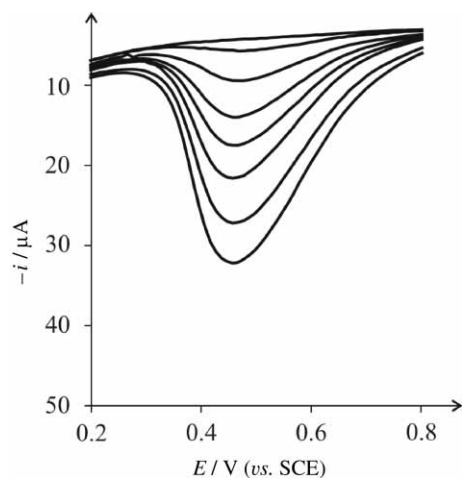
Figure 3. DPCSV of the additions of 25 nmol dm^{-3} of manganese(II) to a 0.5 mol dm^{-3} ammonium nitrate buffer (pH = 7) using a carbon paste (electrode area 0.5 cm^2). Experimental conditions same as in Figure 1

only interference was found to be Fe^{2+} when in equal amounts. However, if this is indeed present, through careful choice of the solution pH the voltammetric wave should be well positioned beyond the oxidation potential for Fe^{2+} to Fe^{3+}. This means that when the deposition step is initiated, iron(II) is oxidized to iron(III) by virtue of the high anodic potential employed to deposit manganese dioxide. The potential is never swept near the reduction potential to initiate the reduction of Fe^{3+} to Fe^{2+} due to the position of the manganese-stripping wave. Although Saterlay[4] explored a vast range of metallic species, no exploration was made of any other species that might be present in environmental samples such as biological species that are likely to cause electrode passivation. We therefore explore the efficiency of our analytical protocol in the determination of manganese in a certified seawater sample.

Validation of the Protocol for Manganese Determination in Environmental Samples

The analytical utility of the above protocol was assessed in the analysis of manganese in a certified seawater reference material. Full details of this sample are given in Experimental. The sample was used as received having been acidified to a pH of 1.1. Using the cathodic stripping protocol at an eppg electrode, with a stirred deposition period of 5 minutes at +1.1 V (*vs.* SCE), standard additions were made to the sample. Note that no treatment of the sample was required, with the natural salinity of the sample acting as a natural electrolyte. Typical voltamograms from the standard additions protocol are shown in Figure 4. Note that the manganese stripping peak is observed at *ca.* +0.89 V due to the different pH of the sample. Note that the deposition potential +1.1 V was selected rather than +0.85 V. This is due to the manganese stripping peak shifting in potential with pH in a
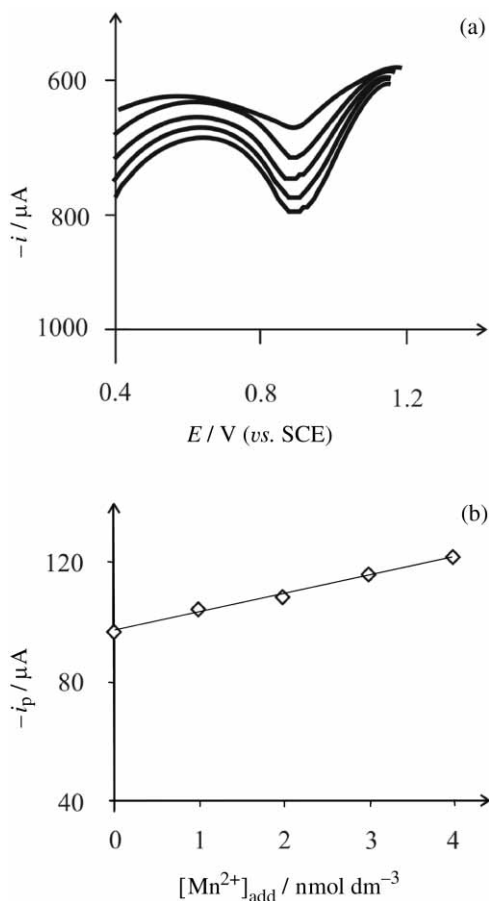

Figure 4. Typical voltamograms of standard additions to certified sea water reference materials using the cathodic stripping protocol technique at an eppg electrode. Parameters: stirred deposition time of 300 seconds with the potential maintained at + 1.1 V (vs. SCE). Also shown is a typical plot of concentration vs. peak current.

Nernstian fashion, such that the difference in the stripping peak potential and the deposition potential is kept similar. From the standard addition protocol, the manganese content was found to correspond to 15.8 ($\pm$ 0.05) nmol dm^{-3} ($N = 3$), which is in excellent agreement with the independently validated seawater reference standard value of 16.7 ($\pm$ 0.1) nmol dm^{-3}; this confirms the protocol to be specific, accurate and sensitive for quantifying manganese in seawater. This suggests that this protocol can be utilised for the routine sensing of manganese in environmental samples.

CONCLUSIONS

The determination of trace levels of manganese via cathodic stripping voltammetry at an edge plane pyrolytic graphite electrode (eppg) has been evaluated for use in environmental analyses. The response of the eppg under quiescent conditions has been shown to be superior for manganese sensing in comparison to boron-doped diamond electrodes, with a three times higher sensitivity observed in the former case. Using this protocol with a

stirred accumulation period allows nanomolar levels of manganese to be determined with high sensitivity, accurately and reproducibly in comparison to carbon paste electrodes under the same conditions.

The efficacy of the protocol utilising the eppg was finally assessed in the determination of manganese in a certified seawater reference material, NASS-5, from the National Research Council Canada, which was found to be in excellent agreement, suggesting that this protocol can be utilised for the routine sensing of manganese in environmental samples.

REFERENCES

1. R. Witholt, R. H. Gwiazda and D. R. Smith, *Neurotoxicol. Teratol.* **22** (2000) 851–861.
2. H. Frumkin and G. Solomon, *Am. J. Ind. Med.* **31** (1997) 107–115.
3. G. M. Gadd and A. J. Griffiths, *Microb. Ecol.* **4** (1978) 303–317.
4. A. J. Saterlay, J. S. Foord, and R. G. Compton, *Analyst* **124** (1999) 1791–1796.
5. S. B. Khoo, M. K. Soh, Q. Cai, M. R. Khan, and S. X. Guo, *Electroanalysis* **9** (1997) 45–51.
6. A. Goodwin, A. L. Lawrence, C. E. Banks, F. Wantz, D. Omanović, Š. Komorsky-Lovrić, and R. G. Compton, *Anal. Chim. Acta* **533** (2005) 141–145.
7. H. Bilinski, Ž. Kwokal, and M. Branica, *Water Res.* **30** (1996) 495–500.
8. C. Sarzanini, O. Abollino, and E. Mentasti, *Anal. Chim. Acta* **435** (2001) 343–350.
9. J. A. Resing and M. J. Mottl, *Anal. Chem.* **64** (1992) 2682–2687.
10. O. M. S. Filipe and C. M. A. Brett, *Talanta* **61** (2003) 643–650.
11. M. Branica, *Kem. Ind.* **50** (2001) 193–199.
12. M. Esteban and E. Casassas, *Trends Anal. Chem.* **13** (1994) 110–117.
13. G. E. Batley, *Mar. Chem.* **12** (1983) 107–117.
14. O. Abollino, M. Aceto, G. Sacchero, C. Sarzanini, and E. Mentasti, *Anal. Chim. Acta* **305** (1995) 200–206.
15. C. E. Banks and R. G. Compton, *Analyst* **129** (2004) 678–683.
16. C. E. Banks and R. G. Compton, *Chem. Anal.* **48** (2003) 159–180.
17. R. R. Moore, C. E. Banks, and R. G. Compton, *Analyst* **129** (2004) 755–758.
18. C. E. Banks, A. Goodwin, C. G. R. Heald, and R. G. Compton, *Analyst* **130** (2005) 280–282.
19. F. Wantz, C. E. Banks, and R. G. Compton, *Electroanalysis* **17** (2005) 655–661.
20. F. Wantz, C. E. Banks, and R. G. Compton, *Electroanalysis,* in press.
21. E. R. Lowe, C. E. Banks, and R. G. Compton, *Anal. Bioanal. Chem.*, in press.
22. E. R. Lowe, C. E. Banks, and R. G. Compton, *Electroanalysis*, in press.
23. C. E. Banks, R. R. Moore, T. J. Davies, and R. G. Compton, *Chem. Commun.* **6** (2004) 1804–1805.
24. C. E. Banks, T. J. Davies, G. G. Wildgoose, and R. G. Compton, *Chem. Commun.* **7** (2005) 829–841.
25. P. Tomčik, C. E. Banks, T. J. Davies, and R. G. Compton, *Anal. Chem.* **76** (2004) 161–165.
26. M.-L. Tercier-Waeber, C. Belmont-Hebert, and J. Buffle, *Environ. Sci. Technol.* **32** (1998) 1515–1521.
27. D. Schmidt, W. Gerwinski, and I. Radke, *Spectrochim. Acta, Part B* **48** (1993) 171–181.
28. J. S. Roitz and K. W. Bruland, *Anal. Chim. Acta* **344** (1997) 175–180.

SAŽETAK

Kvantitativna analiza tragova manganovih iona korištenjem voltametrijske redukcije manganova dioksida akumuliranog na površini radne elektrode: ispitivanje svojstava grafitne elektrode s radnom površinom okomitom na slojeve grafita i mogućnosti njene primjene u analizi prirodnih voda

Christine M. Welch, Craig E. Banks, Šebojka Komorsky-Lovrić i Richard G. Compton

Istražena je mogućnost određivanja koncentracije manganovih iona u prirodnim vodama korištenjem grafitne elektrode s radnom površinom okomitom na slojeve grafita u kombinaciji s voltametrijskom metodom koja se zasniva na redukciji manganova dioksida akumuliranog na površini radne elektrode. Ako se MnO_2 akumulira iz mirne otopine, osjetljivost grafitne elektrode je tri puta veća od osjetljivosti dijamantne elektrode dopirane borom. Kada se akumulacija provodi tokom 120 sekundi uz miješanje otopine, osjetljivost metode je 14,2 mol dm^{-3} A^{-1}, granica detekcije mangana je 14,2 nmol dm^{-3}, a odziv je linearna funkcija koncentracije mangana u rasponu od 25 do 250 nmol dm^{-3}. Grafitna elektroda osjetljivija je i pouzdanija i od elektrode sačinjene od žitke smjese čađi i mineralnog ulja. Točnost metode potvrđena je mjerenjem koncentracije manganovih iona u referentnom uzorku morske vode (NASS-5, Nacionalni istraživački savjet Kanade).