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Talanta 65 (2005) 423–429

Talanta

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Manganese detection in marine sediments: anodic vs. cathodic stripping voltammetry

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Received 15 March 2004; received in revised form 1 June 2004; accepted 16 June 2004
Available online 20 August 2004

Abstract

Three different electroanalytical techniques for the detection of manganese in marine sediments are evaluated. The anodic stripping voltammetry of manganese at an in situ bismuth-film-modified boron-doped diamond electrode and cathodic stripping voltammetry at a carbon paste electrode are shown to lack the required sensitivity and reproducibility whereas cathodic stripping voltammetry at a bare boron-doped diamond electrode is shown to be reliable and selective with a limit of detection, from applying a 60 s accumulation period of 7.4×10^{-7} M and a sensitivity of 0.24 A M^{-1}. The method was used to evaluate the manganese content of marine sediments taken from Šibenik, Croatia.

Keywords: Manganese; Anodic stripping voltammetry; Cathodic stripping voltammetry; Bismuth-film electrodes; Boron-doped diamond electrodes; Marine sediments

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1. Introduction

Manganese is an essential micronutrient for all organisms [1], but at high concentrations can be toxic [2], contributing for example to the early development of Parkinson's disease symptoms in susceptible people [3]. Manganese toxicity is also a serious constraint to crop cultivation since manganese is taken-up by plants and can easily be passed into the food chain again causing symptoms of Parkinson's disease [4].

Various techniques have been utilised for manganese detection including X-ray fluorescence [5] and atomic absorption spectrometry [6]. These techniques however usually need pre-concentration steps to achieve the appropriate selectivity and sensitivity, but often only meet one of these two criteria [7]. Electroanalytical methodologies hold potential for trace metal determination in complex samples due to the sensitive, selective, rapid and portable nature of the techniques [7]. Anodic stripping voltammetry of manganese using mercury electrodes has been reported [8–10]. However, this is fraught with difficulty due to the low solubility of manganese in mercury and the large reduction potential required to reduce Mn(II) to Mn(0).

An alternative to mercury is through the use of solid electrodes such as glassy carbon, carbon paste or boron-doped diamond, which are fast becoming the favoured choice as electrode materials in electroanalysis. In many cases, the sensitivity at such electrodes can be increased to allow use in real sample matrices through the adoption of sonoelectroanalysis in which the electrode are insonated to improve sensitivity and eliminate electrode passivation [11,12].

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0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.06.038

Recently, bismuth-modified electrodes have been reported as being an environmentally friendly substitute for mercury electrodes [13]. Wittstock et al. [14] were the first to describe the use of bismuth-modified platinum electrodes for the amperometric detection of glucose. Subsequently, bismuth-film-modified electrodes have been applied in the detection of lead [13,15–20] cadmium [15–17] zinc [18], copper [21] cobalt [22–24] and nickel [24,25]. However, all of these metals can be detected using bare electrodes. In the following, we attempt the analysis of manganese, via anodic stripping voltammetry at a bismuth electrode, constituting a much more severe test as to the generality of the replacement of mercury by bismuth for electroanalysis.

In this paper, we first report three possible electroanalytical techniques for manganese detection in marine sediments. First, the anodic stripping voltammetry of manganese at an in situ formed bismuth-film-modified boron-doped diamond electrode is explored. Second, carbon paste electrodes utilising cathodic stripping voltammetry are investigated. Third, cathodic stripping at a bare boron-doped diamond electrode is considered [29]. The relative merits are established and the last technique then applied to give indications of pollution near the site of a former ferromanganese factory in the town Šibenik, Croatia. It is known that manganese can be dissolved from the sediments by the reduction with organic compounds in seawater [26]. Due to the brackish water, the Krka river estuary is suitable for the cultivation of molluscs, but this production could be endangered if manganese ions appear in toxic concentrations. Careful monitoring in this area is essential to ensure that surrounding land and water do not get polluted; consequently monitoring in soil and marine sediments is imperative.

2. Experimental

2.1. Reagents

All reagents were used as received without any further purification. These were as follows: bismuth nitrate (98%, Aldrich), sodium acetate buffer solution (pH 5.2, Aldrich), manganese(II) perchlorate (Aldrich, 99%), nitric acid (70%, Aldrich, ACS reagent), ammonium nitrate (Aldrich, 99.9%), hydrochloric acid (35%, Aldrich), carbon powder (>20 μm, Aldrich). All solutions were prepared with deionised water of resistivity not less than 18.2 MΩ cm (Vivendi Water Systems, UK).

2.2. Instrumentation

A three-electrode arrangement was used in the electrochemical cell with a boron-doped diamond disc (3 mm diameter, Windsor Scientific Ltd., UK, available from [27]) or bismuth rod (6 mm diameter, Alfa-Aesar, UK) serving as the working electrodes, and a large area bright platinum wire used as the counter electrode. A saturated calomel reference (Radiometer, Copenhagen, Denmark) electrode completed the circuit. The working electrodes were polished in between experiments using diamond-lapping compounds. All solutions were degassed with nitrogen before commencing experiments. pH measurement was done before experiments using a pH meter (Jenway, UK).

Voltammetric measurements were carried out on a μ-Autolab (Eco-Chemie) potentiostat. Using the software provided with Autolab, the voltammetric curves from the analysis of marine sediments were base-line corrected using a third order polynomial. The voltammetric cell was thermostated at 22 °C throughout.

The carbon paste electrode was prepared by mixing 700 mg of carbon powder with 700 mg of mineral oil in a beaker for 5 min. This was then packed into a plastic syringe (tip diameter 2 mm) with a wire to make electrical contact. The electrode was allowed to dry for two hours at an ambient temperature [28].

2.3. Preparation of the sediment samples for electroanalysis

The samples were taken from the Krka river estuary, which is situated in the central part of the eastern Adriatic coast, in Croatia. The samples were collected from the bottom of the estuary at four locations; first at a depth of 6 m near the site of the former ferromanganese factory in the town Šibenik and second, 1 km upstream, then third, 500 m away from the first point, near the opposite bank of the estuary and finally 2 km downstream, close to the mouth of the river. The sampling was performed by a diver using a 20 cm long acrylic glass tube with a 6 cm internal diameter. The tube was inserted into the seabed to a depth of ca. 17 cm, and plugged with a polyethylene stopper. The cores were frozen, sliced, dried and placed into plastic bags [5].

Independent analysis of the samples via AAS was conducted at the University of Surrey.

3. Results and discussion

3.1. Anodic stripping voltammetry utilising an in situ formed bismuth-film-modified boron-doped diamond electrode

A 0.1 M (pH 4.6) acetate buffer solution containing 100 μM manganese(II) was prepared and studied using a boron-doped diamond electrode. The potential of the latter was cycled negative from + 0.2 V to −2.0 V and back to the starting potential. Fig. 1A shows the cyclic voltammetric response with no reduction waves observed. Next, 20 μM bismuth(III) was added to the solution and the potential sweep re-run. As can be seen in Fig. 1C, a reduction wave with a peak potential E_p = −1.75 V (versus SCE), is clearly observed. Comparison with previously published data suggests that this corresponds to the reduction of manganese(II) to

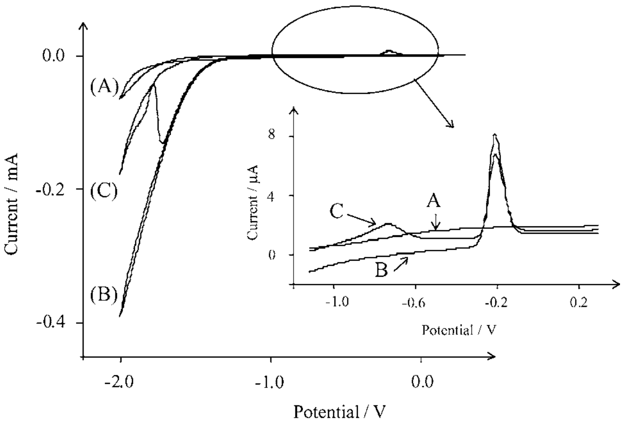

Fig. 1. Cyclic voltammograms of: (A) 100 μM manganese(II) and (C) with 20 μM bismuth(III) using a boron-doped diamond electrode in 0.1 M acetate buffer solution using a scan rate of 25 mV s^{-1}. For comparison, 20 μM bismuth in the absence of manganese(II) is shown (B).

manganese metal. [8] The oxidation wave corresponding to the oxidation of manganese metal to manganese(II) ions can also be seen at −0.8 V (versus SCE). For clarity, the response of bismuth without manganese is shown (Fig. 1B), where the oxidation peak corresponding to the oxidation of bismuth metal to bismuth ions is clearly seen at −0.2 V (versus SCE). We next turn to attempting to optimise the system for use as an analytical technique for manganese detection.

Using square-wave anodic stripping voltammetry (frequency 50 Hz, scan rate 15 mV s^{-1}, step potential 0.3 mV, amplitude 25 mV, 120 s at −1.9 V), the effect of pH on the position and signal of the manganese-stripping peak was explored. It was found that pH 1.0 produced the sharpest and largest signal, while being sufficiently resolved from the bismuth-stripping peak and the hydrogen evolution wave. Using this pH, the added bismuth concentration was investigated by monitoring the manganese-stripping peak via square-wave anodic stripping voltammetry using a using a fixed concentration of 80 μM manganese. As depicted in Fig. 2, the manganese-stripping peak current steadily rises to ca. 7.2 μM which then dramatically decreases. Consequently, a bismuth concentration of 7.2 μM was used in subsequent work. It was observed that increasing the bismuth concentration resulted in the background current increasing with the amount of deposited bismuth which is similar as that observed by Kefala et al. [18]. The thickness of the bismuth film was also observed not to affect the manganese-stripping peak potential, but the manganese peak width was observed to increase at higher film thickness.

Next, the deposition potential for the reduction of manganese(II) to manganese metal was explored. Using a 0.01 M nitric acid solution, the manganese-stripping peak was monitored as the deposition potential was increased. As depicted in Fig. 3, no signal is observed until the potential is held at −1.9 V (versus SCE), which remains at the same magnitude until a potential of −2.5 V is reached. At more negative potentials, the signal dramatically increases up to −3.0 V. However, hydrogen gas evolution was found to occur at potentials more negative than −2.3 V which explains why the manganese-stripping signal significantly increases beyond −2.3 V as a result of the hydrogen evolution creating significant convection and enhanced deposition.

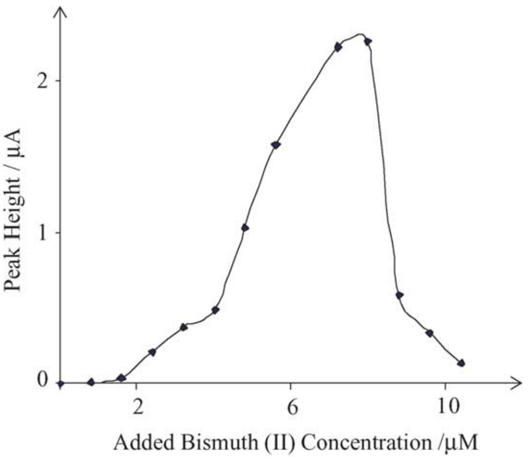

Fig. 2. Optimisation of bismuth-film concentration using a fixed concentration of 120 μM manganese, by applying square wave anodic stripping voltammetry at a boron-doped diamond electrode using a deposition potential of −1.9 V for 120 s. Parameters: frequency 50 Hz; step potential 0.3 mV; amplitude 25 mV.

The response of the in situ formed bismuth-film-modified boron-doped diamond electrode to increasing concentrations of manganese(II) to a 0.01 M nitric acid solution was sought using square-wave anodic stripping voltammetry. A deposition potential of −1.9 V was applied for 120 s, followed by a potential sweep from −1.4 V to 0.1 V. Fig. 4 shows the response, where surprisingly, additions of manganese were linear only between 48 μM and 78 μM after which further addition of manganese results in the signal decreasing. The limit of detection (based on 3σ) was found to be 4 × 10^{-5} M. In principle, by controlling how the marine sam-

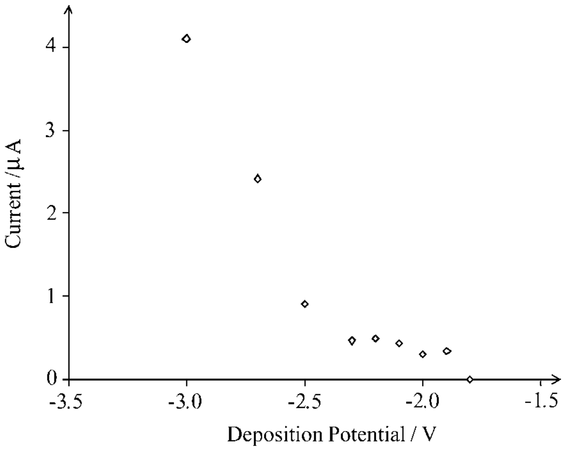

Fig. 3. Investigation of the effect of the deposition potential on the manganese-stripping signal using a fixed concentration of 80 μM manganese at a boron-doped diamond electrode with a bismuth concentration of 7.2 μM in 0.01 M nitric acid solution using SW-ASV using a deposition time of 120 s.

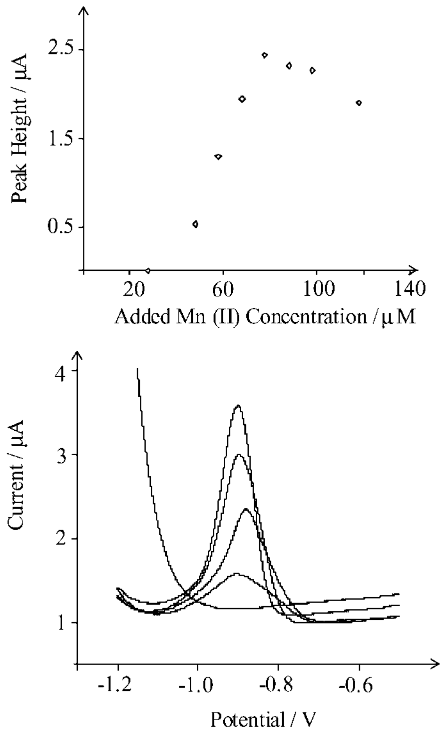

Fig. 4. Voltammetric response of increasing manganese concentrations to a 0.01 M nitric acid solution using a deposition potential of −1.9 V for 120 s with a bismuth concentration of 7.2 µM. Parameters: frequency 50 Hz; step potential 0.3 mV; amplitude 25 mV.

ple is diluted, ca. mM solutions of manganese can be prepared which can be diluted to coincide with the linear portion of the calibration graph shown in Fig. 4. However, this is clearly time consuming and an intrinsically unsatisfactory approach.

Nevertheless, an artificial sample was prepared by making a 0.01 M nitric acid solution and spiking with manganese(II) to a concentration of 1 mM. This was then diluted by a factor of ten in the electrochemical cell. As shown in Fig. 5, a standard addition plot was constructed to try and determine the spiked value of manganese: the response is unreliable with a large deviation in additions suggesting again that an in situ formed bismuth-film electrode is unsuitable for the electroanalytical detection of manganese.

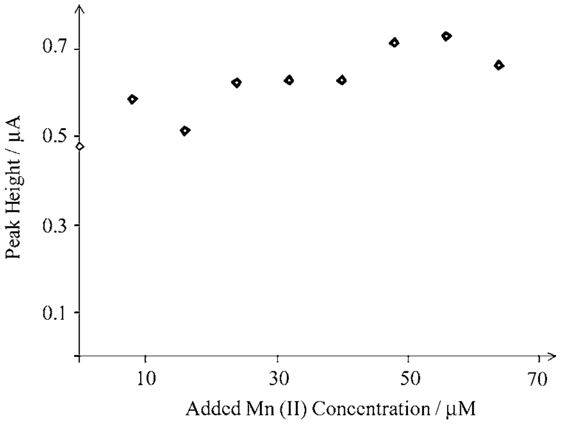

Fig. 5. Standard additions of manganese to an artificial sample using a boron-doped diamond electrode with 7.2 µM bismuth via SW-ASV. The sample is a 0.01 M nitric acid solution spiked with manganese.

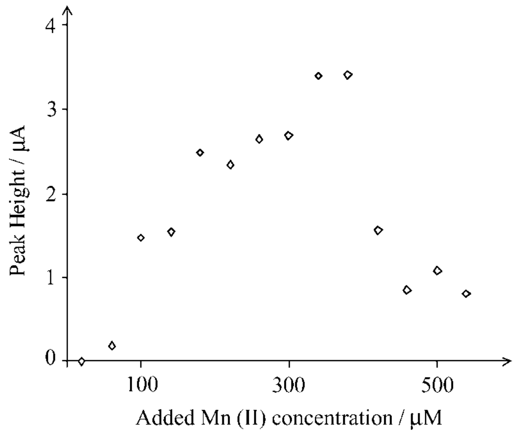

Fig. 6. Voltammetric response of increasing manganese concentrations to a 0.01 M nitric acid solution using a deposition potential of −1.9 V for 60 s at a solid bismuth electrode.

The question arises as to why manganese detection at a bismuth-modified electrode is so poor. To answer this, the response of additions of manganese using a solid bismuth electrode was explored. Increasing additions of manganese(II) were added to a 0.01 M nitric acid solution. A deposition potential of −1.9 V was applied for 60 s before using SW-ASV at a solid bismuth electrode. The response is shown in Fig. 6, where no signal is observed until concentrations of 60 µM are reached, after which the signal increases for concentrations up to 380 µM but then significantly decreases at higher values. Increasing the deposition time to 120 s did not improve the sensitivity or limit of detection. It was observed that hydrogen evolution appeared around −1.0 V. This is a less negative potential than seen on the in situ formed bismuth film. Comparison of additions of manganese to the nitric acid solution using the solid bismuth electrodes and the in situ formed bismuth film reveal that the detection of manganese is similar and electroanalytically useless in both cases. The formation of binary alloys between bismuth and the target metals in stripping analysis have been suggested [21] as a key feature for well-defined and undistorted stripping peaks giving high resolution and measurements down to the low µg L^{-1} level. Inspection of the phase diagram for Bi/Mn suggests the formation of a distinct alloy phase containing ca. 42% Mn. Given the poor electroanalytical response obtained, it may be that elemental Mn is preferentially formed on bismuth surfaces during deposition or that the kinetics of alloy formation in this case are insufficient.

Clearly, there is no benefit in using a bismuth-film-modified electrode for the electroanalytical detection of manganese; we therefore turn to investigating cathodic stripping voltammetry.

3.2. Cathodic stripping voltammetry using a carbon paste electrode

When carbon based electrode materials are used, cathodic stripping voltammetry is a sensitive and selective technique. [7] Manganese can be oxidized on an electrode surface forming insoluble manganese(IV) dioxide according to the equation [29]:

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

The above equilibrium is strongly dependent on pH. However, high pH values are not suitable for practical CSV because of the formation of $\mathrm{Mn(OH)_2}$ which is insoluble. At low pH, the equilibrium is shifted to the left due to the huge excess of hydrogen ions in solution. Thus, the optimal pH corresponding to the highest signal is in the reported range 7.0–7.6 [29] and 4.5–9.0 [7].

A carbon paste electrode was prepared as described in Section 2. A solution of 0.5 M ammonium nitrate (pH 7.0) with a fixed concentration of 5×10^{-7} M manganese(II) was studied to optimise the deposition potential. The magnitude of the manganese-stripping peak was monitored as the deposition potential was varied using square wave cathodic stripping voltammetry with a fixed deposition time of 120 s. As shown in Fig. 7, the optimum potential value for the deposition of Mn(IV) is at +0.85 V (versus SCE) which is in good agreement with that reported for a boron-doped diamond electrode [29] and carbon film electrodes [7]. Next, using this optimised deposition potential, the response of the system to increasing additions of manganese(II) was explored employing a deposition time of 120 s. Fig. 8 shows the voltammetric response of increasing additions of manganese(II). A linear dependence of stripping signal on added concentration of manganese was observed over the range 1×10^{-8} M to 6×10^{-8} M (I (A) = 236 [Mn(II)/M] + (2.02×10^{-7}) A; R^2 = 0.998) with a limit of detection based on 3σ criterion was found to be 3.5×10^{-9} M. However, reproducibility was found to be poor. The positive intercept reflects the experimentally seen background currents. The tiny linear range is disappointing and again signals a voltammetric approach useless for practical application, however pre-conditioning at highly positive potentials (>1 V) *may* improve the voltammetric signal [7].

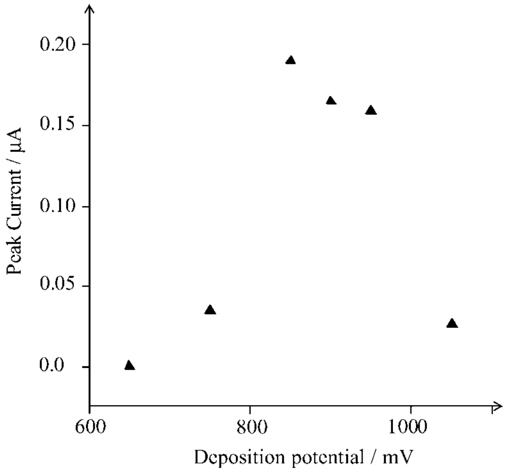

Fig. 7. Investigation of the deposition potential using SW-cathodic stripping voltammetry using a fixed deposition time of 120 s at a carbon paste electrode.

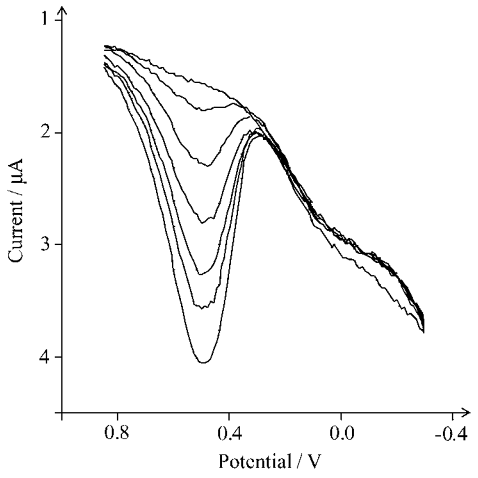

Fig. 8. Voltammetric response of increasing addition of manganese using cathodic stripping voltammetry at a carbon paste electrode using a deposition time of 120 s at +0.85 V.

3.3. Cathodic stripping voltammetry using a bare boron-doped diamond electrode

While cathodic stripping voltammetry at a boron-doped diamond has been explored under conditions of insonation and used in the determination of manganese in instant tea [29], it has not yet been used in environmental samples. A 0.5 M ammonium nitrate (pH 7) solution was first prepared. Using square-wave cathodic stripping voltammetry the response of increasing concentrations of manganese(II) to the solution was sought using a boron-doped diamond electrode from applying a deposition time of 60 s at + 0.85 V (versus SCE) followed by a potential sweep from + 0.85 V to −0.3 V. A linear response of peak height versus concentration over the range 1.25–25 μM was observed (I_{PH} (A) = 0.234 ([Mn^{2+}]/M) + (1.33×10^{-7}) A; R^2 = 0.998). Based on 3σ, the limit of detection was found to be 7.4×10^{-7} M. This large linear range and low detection limit for a 60 s deposition is useful for ‘in the field’ monitoring of manganese in real samples. If lower values of manganese need to be detected, the deposition protocol can be coupled with ultrasound [11,29], but in the context of marine sediment electroanalysis in quiescent conditions is un-suitable (see below). It should be noted that if ultrasound is indeed required, differential pulse voltammetry should be adopted [29]. We note that Filipe and Brett [7] have conducted similar experiments but using 2 Ω carbon resistors (sic) as the electrodes. They report a ‘dog-leg’ calibration curve attributing this to the possible formation of mono and multi-layers of $\mathrm{MnO_2}$ although the role of the curious choice of electrode material and surface may perhaps be important. The limit of detection judged from the more sensitive 'part of the dog-leg' corresponds roughly with the limit of detection seen on our experiments, given that we used a 60 s, rather than 180 s pre-concentration time.

Comparison of the carbon paste and the boron-doped diamond electrodes reveal that the latter has a larger linear response and *low* detection limit using a shorter deposition time. Furthermore, the boron-doped diamond requires no electrode preparation or renewal from sample to sample and as will be seen below, the BDD displays no memory effects providing a robust electrode for routine analysis in environmental samples. Consequently, the boron-doped diamond is next used for the determination of manganese in marine sediments.

3.4. Manganese quantification in marine sediments using cathodic stripping voltammetry at a bare boron-doped diamond electrode

A known mass of the marine sediment sample was weighted out and then mixed with 15 mL hydrochloric acid (12 M) and 5 mL nitric acid (16 M) to liberate the manganese from the soil sample. Care is needed when adding the acid due to the vigorous effervescence of chlorine gas. (This should be performed in a fume hood.) Next, 20 mL of 0.5 M ammonium nitrate was added to the mixture and stirred with a magnetic stirrer for 30 min. This was then diluted further to a final volume with ammonium nitrate. The solution pH was then adjusted to pH 7 using concentrated sodium hydroxide. The sample was subsequently filtered to remove precipitated iron hydroxide.

Using the cathodic stripping protocol as described above, standard additions were performed on the sample. Shown in Fig. 9 are typical voltammetric responses and standard addition plot for CSV analysis for manganese in marine sediments.

The manganese concentration of the marine sediment was found to be 1.52 (±0.04) $\times 10^{-3}$ M ($n = 3$), which agrees well with the value of 1.4 (±0.08) $\times 10^{-3}$ M, found independently via atomic absorption spectroscopy; this reflects the high levels of manganese pollution in Šibenik.

We note that Grotti et al. [30] has studied the interferences that affect many atomic absorption spectrometric techniques, namely sodium, potassium, calcium and magnesium. Since we are analysing marine samples, such interferences are likely to be present which may account for the ever so slight deviation seen between AAS and cathodic stripping voltammetry in the latter sampled. The interfering species Fe(II) was oxidised to Fe(III) during dissolution of the marine sediments (using a mixture of concentrated nitric and hydrochloric acids, 1:3) then precipitated as hydroxide when the pH was adjusted to pH 7. We further note, that the cathodic stripping technique is highly specific toward manganese detection [29] and is ideally suited to complex environmental samples such as those reported here.

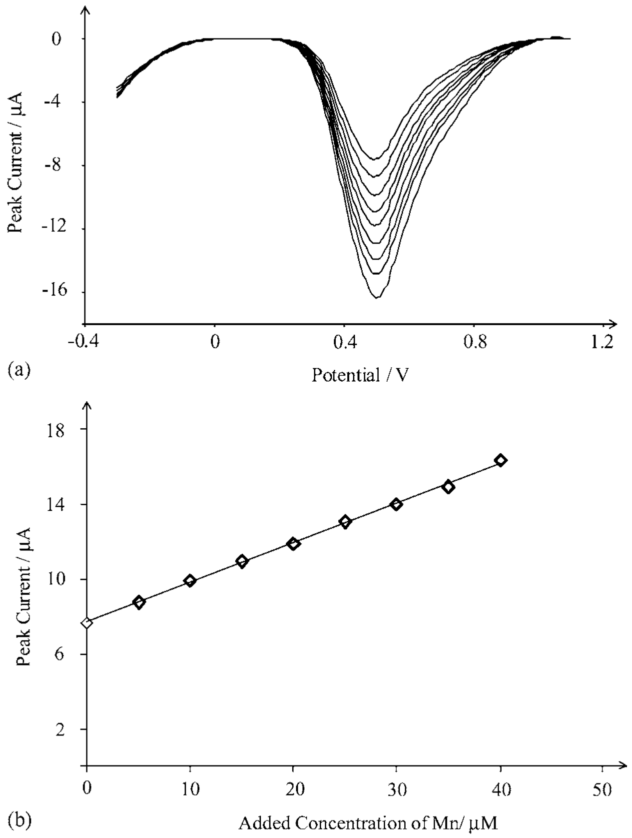

Fig. 9. Typical voltammetric responses (A) of standard additions to a marine sediment sample using the cathodic stripping protocol technique at a boron-doped diamond electrode using a 60 s deposition time at + 0.85 V (vs. SCE). B shows a typical plot of concentration vs. peak current from A.

4. Conclusions

We have evaluated three electroanalytical methods for the detection of manganese in marine sediments. First, anodic stripping voltammetry at an in situ formed bismuth film on a boron-doped diamond has been explored, but was found to lack the required sensitivity and reproducibility. Second cathodic stripping voltammetry at carbon paste and boron-doped diamond electrodes have been compared. The latter was found to be more suited to the environmental samples. In the case of cathodic stripping voltammetry at boron-doped diamond electrodes, good agreement with independently conducted AAS was found.

An extensive investigation of manganese pollution at a bigger number of locations near Šibenik is in preparation in order to decide whether permanent monitoring is necessary, or not. These investigations will use cathodic stripping voltammetry at boron-doped diamond electrode for manganese monitoring.

Acknowledgements

We thank the Royal Society for funding a Joint Project between the Oxford and Zagreb laboratories. C.E.B. and J.K.

thank the EPSRC for funding via a project studentship (Grant GR/R14392/01) and the Wellcome Trust (Grant 062759) respectively. D.P.T. thanks the EPSRC (GR/R72976/01) for financial support. We thank Mr. Neven Cukrov for collecting the marine sediments.

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