The Analyst

Sono-cathodic stripping voltammetry of manganese at a polished boron-doped diamond electrode: application to the determination of manganese in instant tea

Andrew J. Saterlay, John S. Foord and Richard G. Compton*

*Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road,
Oxford, UK OX1 3QZ*

Received 23rd August 1999, Accepted 14th October 1999

Ultrasonically assisted cathodic stripping voltammetry at a boron-doped diamond electrode was developed for the detection of manganese. Differential-pulse voltammetry was used to give the analytical signal from a cathodic strip of electrodeposited MnO_2; linearity was observed from 10^{-11} M to at least 3×10^{-7} M, with 10^{-11} M being the detection limit for a 2 min deposition. The procedure involves both ultrasonic–anodic deposition of MnO_2 and ultrasonic–cathodic stripping. This novel analytical tool is robust, reproducible, mercury free, oxygen insensitive and highly specific towards manganese. The differential-pulse sono-cathodic stripping voltammetric technique was used to determine successfully the manganese content of two instant tea samples, giving excellent agreement with independent AAS analyses.

Introduction

Stripping voltammetry comprises several electrochemical techniques that are used routinely in many analytical applications, due largely to their greatly increased sensitivity compared with classical polarographic methods. Traditionally, electrochemical stripping analysis, consisting predominantly of anodic stripping voltammetry (ASV), adsorptive stripping voltammetry (AdSV) and cathodic stripping voltammetry (CSV), has allowed the determination of a wide range of inorganic and organic species down to concentrations of the order of 10^{-10} M in favourable conditions, whilst utilising relatively simple and inexpensive instrumentation. The techniques consist of two distinct steps. Initially, in a preconcentration step, the analyte of interest is accumulated from solution on to a suitable working electrode substrate. Depending upon the nature of the analyte, this can be achieved either by electrochemical deposition or by physical adsorption. The potential of the working electrode is then adjusted in such a way as to liberate the analyte as an ion from the electrode, with the resulting faradaic current allowing a direct quantification of the amount of analyte present.

ASV is probably the most commonly used form of electrochemical stripping analysis. When analysing metals, the ions are concentrated on a cathode electrolytically, either as a pure metal or often as an amalgam. The potential is then swept anodically and the metal ions are released from the electrode surface at their corresponding oxidation potentials. Numerous examples of anodic stripping voltammetry of metal ions, including manganese, have been reported.[1,2] Most recently developed ASV techniques for manganese detection, however, involve the use of a hanging mercury drop electrode[3–8] or, for example in the work of Buffle *et al.*,[9,10] a gel-protected mercury-covered iridium electrode. Although the majority of these techniques are successful, with detection limits approaching 10^{-9} M, they still all rely on the use of mercury. Current legislature already bans the use of mercury in Japan[11] and Sweden,[12,13] and Europe may not be far behind, with the EU Commission having already imposed a total ban on the use of mercury in batteries by the year 2000.[14]

Although less frequently used than ASV, AdSV is also commonly employed in electrochemical stripping analysis. As with ASV, most of the recently developed AdSV methods for manganese determination incorporate preconcentration at a mercury-based electrode,[15] often after complexation of the manganese ion.[16,17] However, a method has recently been developed for successful AdSV determination of a manganese–ammonium–acetate complex at a glassy carbon electrode.[18]

Cathodic stripping voltammetry of metal ions is the least commonly used of the three main electrochemical stripping techniques, which is surprising considering the potential benefits of CSV, including high specificity, mercury free and oxygen insensitive analyses. CSV is effectively the electrochemical inverse of ASV, where the analyte of interest is accumulated as an oxidised species on the electrode at a positive potential, and then quantified during the stripping step as the electrode potential is swept cathodically. Often, CSV techniques also involve complexation of the metal ions of interest, and the use of a hanging mercury drop electrode (HMDE).[19,20] Various CSV methods for directly analysing aqueous manganese have also been developed previously. These methods all employ the technique of first accumulating manganese from solution by electrodepositing MnO_2 anodically on the working electrode, and then stripping off reduced Mn^{2+} ions by sweeping the potential cathodically. Viltchinskaia *et al.*[21] and Labuda *et al.*[22] reported the use of graphite electrodes for CSV determination of manganese, with detection limits of the order of 10^{-8} M, and Khoo *et al.* obtained similar results using a 1-(2-pyridylazo)-2-naphthol-modified carbon paste electrode.[23] Work in this area has also been carried out using platinum electrodes to determine the manganese content of steel,[24,25] and detection limits approaching nanomolar (10^{-9} M) have been achieved using glassy carbon electrodes.[26,27]

Although not exhaustive, the above list contains the best of the recently developed CSV techniques for manganese determination, and this is also evident in various reviews.[28,29] With such a limited range of applications for CSV existing at present, an investigation of new electrode materials and electrochemical techniques in this area is easily justified, in order to extend the range of CSV-based electroanalytical techniques and further develop what is an under-utilised methodology.

Boron-doped diamond (BDD) is one such material which is only just beginning to be exploited for use in electroanalytical applications.[30,31] Owing mainly to the robustness of diamond, both structurally and chemically,[32] the material has been under extensive investigation for uses in electrochemical processes since the middle of the 1980s.[33] At high boron-doping levels, typically 10^{20}–10^{21} cm^{-3}, the material becomes semimetallic. As an electrode, the material suffers from very low levels of background interference, allowing it to be useful over a very wide potential window (*ca.* 3.5 V) in aqueous media. A combination of these electrical and mechanical properties has resulted in its use recently in a vast array of electrochemical applications.[34–37] Limited use, however, has been made to date in the area of electroanalysis, with the techniques described by Popa *et al.*,[30] Saterlay *et al.*[31] and Xu *et al.*[32] being amongst the first electroanalytical uses of diamond electrodes to be reported.

The merits of using ultrasound in electrochemical processes have become widely appreciated in recent times,[38] with much enhanced mass transport and continuous electrode activation being the main reasons for the effectiveness of the technique. It is the combination of these properties which makes ultrasound the preferred choice for greatly improved mass transport. This is in contrast with other hydrodynamic electrodes such as the rotating disc, which, although giving increased transport characteristics, offer no scope for electrode cleaning or surface activation. The properties of ultrasound have been found to increase significantly the efficiency of ASV applications for the quantification of trace metallic species in solution.[39–47] The effects of ultrasound on the deposition of metal ions from solution on to a glassy carbon electrode[48] and a BDD electrode[31] have been investigated recently, with ultrasound having been found to activate the electrodeposition process significantly. Compton *et al.* recently combined the use of power ultrasound and electrolysis at a boron-doped diamond electrode to produce hydrogen peroxide.[49] Ultrasound has also been shown to assist in the removal of ionic species from solid matrices,[50] another highly beneficial property which can be taken advantage of during its utilisation in electroanalysis.

Tea is a very popular beverage, in its various forms, on a global scale, and is a rich source of dietary manganese.[51] It has been reported previously that adults who drink tea daily will consume between 21 and 45% more manganese than those who abstain.[52] However, even though the levels of manganese in tea leaves have been known to be high for years, this has only ever been reported as beneficial, owing to the essential requirements of the human body for trace manganese in the role of cellular metabolism.[53] Apart from reports of the neurotoxic effects from chronic exposure to manganese,[54,55] there is no apparent issue of a toxicological problem from dietary manganese, as it is one of the least toxic of all metals,[56] and concentrations in excess of 1 mg g^{-1} in the diet are required before signs of toxicity are observed.[57] The study of manganese consumption via tea drinking is therefore an essential one. Work has already been carried out in this area, specifically in terms of the speciation of manganese in tea leaves,[58] which concludes that approximately 30% of the known manganese content of tea is in the form of Mn^{2+}, and is removed during aqueous extraction; 2.5% is present as organically bound manganese, the remainder being in the form of insoluble inorganic Mn oxides. Instant tea is essentially the freeze-dried aqueous extract of tea leaves, and therefore can only contain unbound manganese, in a readily soluble form. Data published by the Ministry of Agriculture Fisheries and Food (MAFF) in the UK support this, with high levels of manganese reported for instant tea granules, giving comparable levels of manganese in tea after dilution to those reported above.[59]

The aim of the work described in this paper was to investigate further possible electroanalytical advances arising from using a combination of boron-doped diamond, ultrasound and CSV. Cathodic stripping offers the potential benefits of a mercury-free electroanalytical system with increased specificity over existing ASV methodologies; CSV also eliminates intermetallic interferences, which sometimes plague ASV methods. The use of ultrasound in electrochemistry offers great increases in efficiency over classical silent techniques, whilst boron-doped diamond has opened up a whole new field of electrochemical research, but has yet to be fully exploited in terms of its use in trace-metal electroanalytical applications. This work was therefore aimed at combining these technologies in order to develop a novel electroanalytical technique for the determination of manganese, and applying it to a working system for the measurement of the manganese content of instant tea.

Experimental

Reagents and samples

Manganese standards were prepared in-house from hydrated manganese perchlorate (99%) supplied by Aldrich (Milwaukee, WI, USA). Ammonium nitrate (> 99.5%) used for the background electrolyte was supplied by Fisher Scientific UK, Loughborough, UK. All other reagents and the metal salts used for the interference experiments were of analytical-reagent grade of the highest commercially available purity. Solutions were prepared using UHQ grade water of resistivity not less than 18 MΩ cm (Elgastat, High Wycombe, UK).

The samples of instant tea analysed for manganese content were Tetley Pure Tea Granules (Tetley GB, Greenford, UK) and PG Tips Pure Tea Granules (Brooke Bond Foods, Croydon, UK) purchased from a local Oxford supermarket.

Instrumentation

The electrochemical cell used for this work, the characteristics of which have been thoroughly investigated previously,[60] is shown in Fig. 1. The dimensions of the cell are such that it allows a working solution volume of *ca.* 250 mL; it is thermostated at 25 ± 1 °C by means of a glass cooling coil attached to a thermostated water-bath. The working electrode consisted of a polished, boron-doped diamond film electrode (5 × 5 mm), supplied by DeBeers Industrial Diamond Division (Ascot, UK). The electrode was housed in a Teflon mounting using Araldite (Ciba Polymers, CY 219, Ciba Specialty Chemicals, Duxford, Cambridge, UK), with an electrical connection to the rear (graphite) side via a brass rod, attached using silver epoxy resin (RS). The rear of the electrode assembly was enclosed using a sealant wax, and the unit was placed near the bottom of the cell, directly opposite a 13 mm diameter titanium tip of a VXC400 ultrasonic horn (Sonics and Materials Inc., Danbury, CT, USA), capable of emitting 20 kHz ultrasound at intensities up to 63 W cm^{-2} (determined calorimetrically[61,62]). Ultrasound intensity of 14 W cm^{-2} was applied to the BDD electrode for all sono-electrochemical work described here. All electrochemical experiments were performed using a PGSTAT20 Autolab potentiostat (Eco-Chemie, Utrecht, The Netherlands), with the need for bipotentiostatic[63] control of the titanium horn itself being eliminated by insulating the transducer from the probe with a Teflon disk, and connecting the two with a screw-thread machined from Delrin. The transducer probe to working electrode distance was 7 mm for all experiments. A coiled platinum wire and a saturated calomel electrode (SCE) (Radiometer, Copenhagen, Denmark), were used as the counter and reference electrodes, respectively.

Results and discussion

Sono-cathodic stripping voltammetry of manganese: method development

Initially, simple qualitative experiments were carried out to determine the most suitable background electrolyte and general electrochemical parameters required to obtain the largest analytical signal for cathodic stripping of electrodeposited MnO_2. A range of supporting electrolyte materials were investigated, including dilute nitric acid, acetate buffers and ammonium nitrate. Broad signals and poor sensitivity were observed using dilute nitric acid. Acetate-based systems, although giving large stripping currents, were found to be very temperature sensitive, probably owing to the temperature dependence of the dissociation of acetate–metal ion complexes. Ammonium nitrate, when adjusted to pH 7 with 10.0 M NaOH, gave sharp and reproducible analytical signals for the cathodic stripping of MnO_2, and was therefore chosen as the supporting electrolyte for this investigation.

Various electrochemical stripping methods, including linear sweep voltammetry (LSV), square-wave voltammetry (SWV), normal-pulse (NP) and differential-pulse (DP) voltammetry, were also evaluated in terms of their suitability towards quantifying the resultant faradaic current from the stripping of MnO_2; the DP method was the only technique which gave a distinct and reproducible signal for the reduction of electrodeposited MnO_2. Finally, further optimisation of the electrodeposition and differential-pulse stripping parameters was performed until the most suitable analytical signal was achieved.

Sono-cathodic stripping voltammetry of manganese: linear range and detection limits

To determine the detection limits of the sono-CSV technique, the electrochemical cell was filled with 250 cm^3 of the ammonium nitrate supporting electrolyte as described above and micro-aliquots of Mn^{2+} standards, of increasing concentration, were added until an analytical stripping signal for MnO_2 reduction was observed. Addition of aqueous manganese standards of increasing concentration was then continued until a range beyond 'ultra-trace' had been achieved (10^{-11}–3×10^{-7} M). All of the solutions used were routinely not de-gassed, as it was found experimentally that the presence of oxygen did not affect the electrochemistry taking place. The analytical stripping response of Mn^{2+} in solution was measured using differential-pulse scan sono-CSV in two steps. First, enrichment of the analyte was performed *via* 120 s of insonated MnO_2 deposition at +0.85 V (*vs.* SCE). The accumulated MnO_2 was then quantified using an insonated-stripping scan from +0.85 to −0.3 V, with the following electrochemical parameters: step potential = 10 mV, interval time = 0.1 s, modulation amplitude = 150 mV, modulation time = 0.02 s and standby potential = 0.0 V. The electrode surface was cleaned ultrasonically for 30 s at 0.0 V between each scan to eliminate carry-over, ensuring high reproducibility. A single activation of the BDD electrode at a high anodic potential (+5.0 V) prior to all of the work described in this paper was found experimentally to be sufficient for the removal of any previous history of surface functionalisation of the electrode from previous electrochemical experiments.

The use of ultrasound in both stages of the cathodic stripping analysis of manganese is essential to the efficiency of the technique. During the electrodeposition of MnO_2 stage, greatly enhanced mass transport of aqueous Mn^{2+} ions from bulk solution to the electrode is observed in the presence of ultrasound. This occurs as a result of acoustic streaming of solution from the tip of the ultrasonic horn towards the working electrode, a beneficial effect of the kinetic shock caused by the ultrasonic vibrations of the static horn tip in a mobile fluid. The corresponding silent electrodeposition of MnO_2 over the same time period results in near total loss of analytical signal for the subsequent stripping step of the analysis, highlighting the dramatic effect that ultrasound has upon mass transport. The use of ultrasound during the stripping step is also advantageous over the silent procedure, owing to both mass transport and surface activation effects. Rapid removal of reduced aqueous Mn^{2+} ions from the surface of the electrode *via* ultrasonically enhanced mass transport ensures that a sharp analytical stripping peak is obtained. Continuous activation of the electrode surface *via* microjetting as a result of cavitational collapse near to the solid–liquid interface, during both the electrochemical stripping and cleaning steps, regulates the history of the BDD electrode surface and eliminates potential carry-over of MnO_2, which can occur under silent conditions.

A typical voltammogram for the differential-pulse scan CSV stripping response of this technique is shown in Fig. 2. The peak seen at *ca.* 0.49 V (*vs.* SCE) corresponds to the potential at which the surface bound manganese oxide species is reduced to

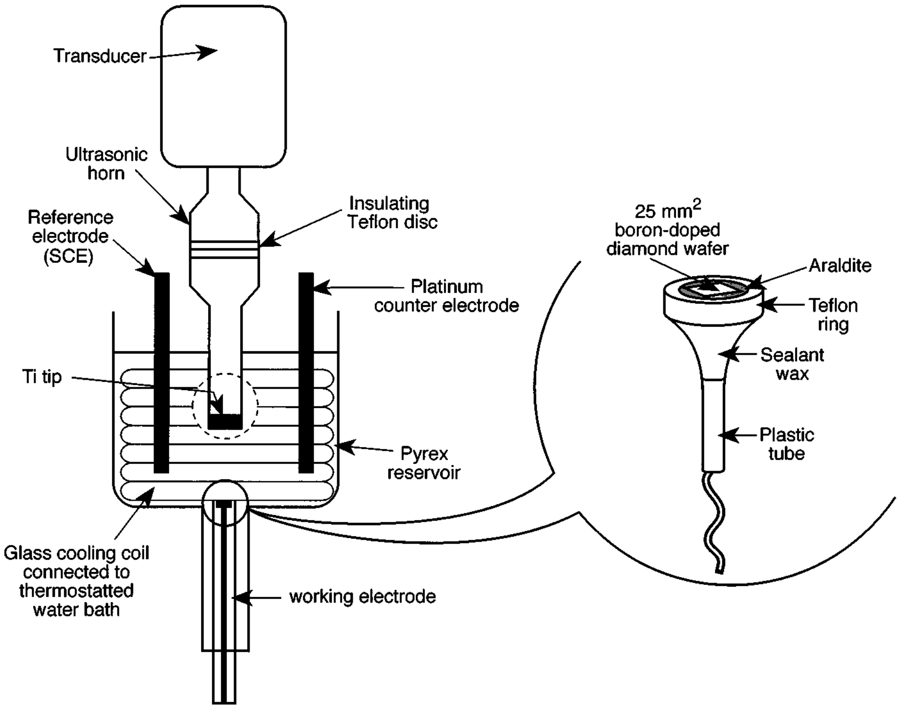

Fig. 1 Schematic diagram of the electrochemical cell used in all sono-CSV experiments. Inset: construction of BDD electrode housing.

aqueous Mn^{2+} ions. Using differential-pulse scanning, the sono-CSV technique was found to give a linear response for the detection of aqueous Mn^{2+}, as a plot of cathodic stripping current *vs.* aqueous Mn^{2+} concentration, from 10^{-11} to 3×10^{-7} M (Fig. 3), with 10^{-11} M being the limit of detection (based on a signal-to-noise ratio of 3) for a 120 s deposition step. The analytical stripping signal was found to scale linearly with deposition time, offering the potential for even more sensitive manganese determinations than those reported above, especially when combined with higher intensity ultrasound; limits of detection approaching low picomolar levels (10^{-12} M) are realistically within the scope of this technique. However, in order to extend the mechanical life of the electrode housing and keep the analysis times of the technique short, a detection limit of 10^{-11} M was deemed sufficient for most ultra-trace level manganese determinations.

Dependence of MnO_2 stripping potential on pH

The dependence of the reduction potential of the cathodic stripping of Mn^{2+} from electroplated MnO_2 was investigated using differential-pulse scan sono-CSV described above. Using a selection of appropriate buffers, measurements were performed as described above on solutions containing 10^{-8} M Mn^{2+} over the pH range 1.1–8.1. A plot of pH *versus* reduction potential (*E*) for the cathodic stripping peak (Fig. 4) shows a linear relationship, with a slope of 118.28 ± 3.78 mV. Eqn. (1) describes the chemical reaction taking place during the electrochemical stripping of MnO_2:

$$MnO_2 + 2e^- + nH^+ \rightarrow Mn^{2+} \qquad (1)$$

The corresponding version of the Nernst equation which can be used to describe this chemical reaction is hence

$$E = E^\circ - \frac{RT}{2F}\ln\frac{[Mn^{2+}]}{[H^+]^n} \qquad (2)$$

This can be rearranged to give

$$E = E^\circ + \frac{RTn}{2F}\ln[H^+] - \frac{RT}{2F}\ln[Mn^{2+}] \qquad (3)$$

Also,

$$pH = -\log[H^+] = -2.3026\ln[H^+] \qquad (4)$$

Therefore, a plot of reduction potential (*E*) *versus* pH has a gradient of

$$\text{slope} = -\frac{2.3026nRT}{2F} \qquad (5)$$

The slope obtained for this experiment (118.28 ± 3.78 mV) is extremely close to the value of 118.25 mV predicted for a four-proton ($n = 4$) reduction taking place in eqn. (1). It seems clear, therefore, that the stoichiometry of electrodeposition/stripping has been confirmed as

$$MnO_2 + 2e^- + 4H^+ \rightarrow Mn^{2+} + 2H_2O \qquad (6)$$

Since its first use as an electrical battery material well over 100 years ago, manganese dioxide has been one of the best studied materials in the field of electrochemistry.[64] The mechanism of electrodeposition of MnO_2 and evidence of water within the crystal structure have long been known, with the degree of hydration affecting only the overpotential of MnO_2 stripping and not the stoichiometry of the reaction.[65] A more detailed study of the electrodeposition of MnO_2 has been carried out recently by Rodrigues *et al.*,[66] who proposed the following multi-step mechanism:

step 1: $Mn^{2+}{}_{(bulk)} \rightarrow Mn^{2+}{}_{(surface)}$
step 2: $Mn^{2+}{}_{(surface)} \rightarrow Mn^{3+}{}_{(ads)} + e^-$
step 3: $H_2O \rightarrow OH_{(ads)} + H^+ + e^-$
step 4: $2\,Mn^{3+}{}_{(ads)} \rightarrow Mn^{2+}{}_{(ads)} + Mn^{4+}{}_{(ads)}$
step 5: $Mn^{2+}{}_{(ads)} + 2\,OH_{(ads)} \rightarrow MnO_2 + 2\,H^+$
step 6: $Mn^{4+}{}_{(ads)} + 2\,H_2O \rightarrow MnO_2 + 4\,H^+$

The fact that the value of 118.28 ± 3.78 mV obtained experimentally for the reduction potential shift per decade is so close to the value predicted by the Nernst equation [eqn. (3)] of 118.25 mV confirms that MnO_2 must be the species being electrodeposited and stripped to form Mn^{2+} during this analysis technique.

Interferences

The effect of possible interferences from other ionic metallic species was investigated by systematically adding a range of

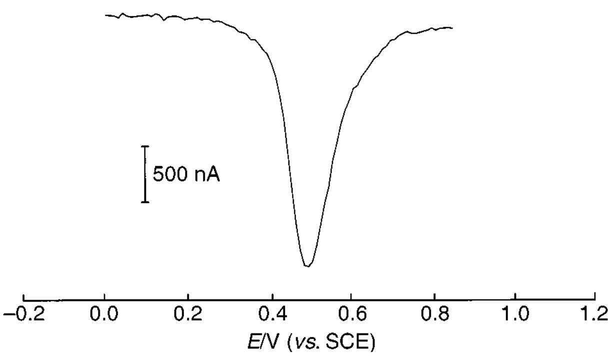

Fig. 2 Typical differential-pulse sono-cathodic stripping voltammogram of Mn^{2+} (10^{-8} M) in 0.5 M NH_4NO_3 (adjusted to pH 7.0 with 10.0 M NaOH). Experimental parameters: 120 s of insonated MnO_2 deposition at +0.85 V (*vs.* SCE); insonated-stripping scan (differential pulse) from +0.85 to −0.3 V step potential = l0 mV, interval time = 0.1 s, modulation amplitude = 150 mV; modulation time = 0.02 s, standby potential = 0.0 V.

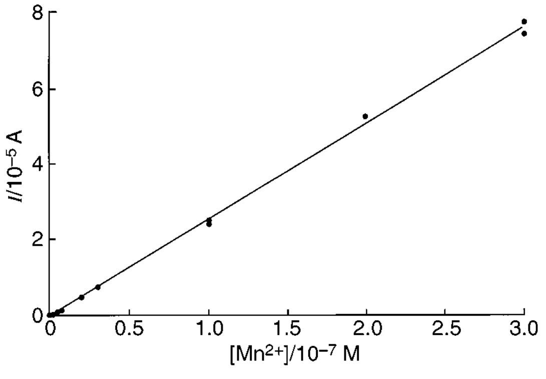

Fig. 3 Plot of reduction current (*I*) *vs.* Mn^{2+} concentration for differential-pulse sono-cathodic stripping voltammetry. Experimental parameters as in Fig. 2.

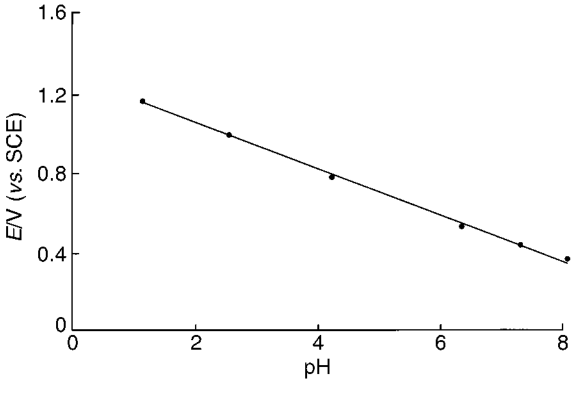

Fig. 4 Dependence of MnO_2 reduction potential on pH of background electrolyte. Experimental parameters as in Fig. 2.

other common heavy metals to an electrochemical cell containing 10^{-8} M Mn^{2+} in the above-described ammonium nitrate supporting electrolyte. Each possible contaminant was initially added at a similar concentration to that of the manganese analyte, and then at increasing concentrations until effects (if any) upon the analytical stripping signal from manganese were observed. Lead, copper, iron, zinc, mercury and aluminium, all of which are likely interferents in voltammetry, were tested. Zn^{2+}, Cu^{2+}, Pb^{2+} and Fe^{3+} were found to have no measurable effect upon the technique's response to manganese, even when present at concentrations exceeding 100-fold that of manganese. The presence of Hg^{2+} in solution at levels at least 50-fold those of manganese also had no effect. The technique was tolerant to nearly a fivefold excess over manganese of $A1^{3+}$. Aluminium is also present in tea at relatively high levels, although approximately half those usually observed for manganese.[59] The presence of Fe^{2+} in solution in amounts equal to that of manganese was sufficient to disrupt the analysis. However, this problem was easily overcome experimentally by oxidising the Fe^{2+} to Fe^{3+} electrolytically, by driving the potential of the working electrode anodically prior to analysis. The problem of Fe^{2+} interference can also be removed by complexation of Fe^{2+} ions with fluoride.[22]

The cathodic stripping technique described here is also free from interference by intermetallic species, a side-effect which often plagues anodic stripping voltammetry techniques.[67–70] Although not always a major problem, the formation of intermetallic species is most undesirable when attempting to determine trace amounts of heavy metal contaminants accurately.

Analytical integrity

The reproducibility of the sono-DPCSV technique was tested both intra- and inter-experimentally. The peak heights from four consecutive electroanalytical measurements of a 10^{-7} M Mn^{2+} solution had a relative standard deviation (RSD) of 1.46% (Table 1), and the calibration characteristics of the system over 5 d were found to be highly reproducible, with an RSD of 0.99% being observed for consecutive calibration slopes (Table 2). These statistics show the technique to be both robust and reproducible, with the stability of the electrode's calibration characteristics offering the scope not only for analysis using standard addition techniques, but also as an independent analytical probe.

Table 1 Relative standard deviation of peak height from four consecutive analytical scans of a solution of 10^{-7} M Mn^{2+}

Scan No.	Peak height/10^{-5} A
1	2.45
2	2.49
3	2.41
4	2.46
RSD	1.461%

Table 2 Relative standard deviation of calibration slope from five separate determinations of aqueous Mn^{2+}

Experiment No.	Calibration slope/A mol^{-1}	r^2 fit of slope
1	253.58	0.9980
2	257.40	0.9994
3	251.93	0.9986
4	253.56	0.9987
5	257.56	0.9984
RSD	0.994%	

Determination of manganese in instant tea using differential-pulse sono-cathodic stripping voltammetry

The manganese contents of two samples of instant tea (Tetley Pure Tea Granules and PG Tips Pure Tea Granules) were determined in two stages. Initially, a sample (100 mg) of each was pre-dissolved in 50 mL of water for 5 min in an ultrasonic bath. Aliquots (125 µL) of the tea solution were then diluted with supporting electrolyte (0.5 M NH_4NO_3 adjusted to pH 7.0 with 10.0 M NaOH) to a total volume of 250 mL, and this was placed in the sono-electrochemical cell described earlier. Differential-pulse sono-CSV was employed to obtain a response for the Mn^{2+} in solution. Additions of an aqueous manganese standard were then performed; an example of the corresponding electrochemical responses for the sample and the standard additions is shown in Fig. 5. Extrapolation of the stripping currents resulting from the standard manganese additions facilitated the quantification of manganese in the tea solutions, and hence the manganese content of the tea samples could be calculated (Table 3). The samples were also analysed independently using atomic absorption spectrometry (AAS), with a good correlation being observed between the sono-DPCSV technique, AAS and the reported MAFF data.[59]

Conclusions

The combination of sono-CSV and a boron-doped diamond electrode has been shown to produce an effective, highly sensitive electroanalytical technique for the determination of manganese, both in model aqueous solutions and in complex media such as instant tea. The application of power ultrasound both increases the efficiency of the electrochemistry taking place and, through continuous electrode activation from cavitational erosion, reduces the chances of electrode fouling from possible adsorption of organic species. The technique has proven to be highly specific towards manganese and free from

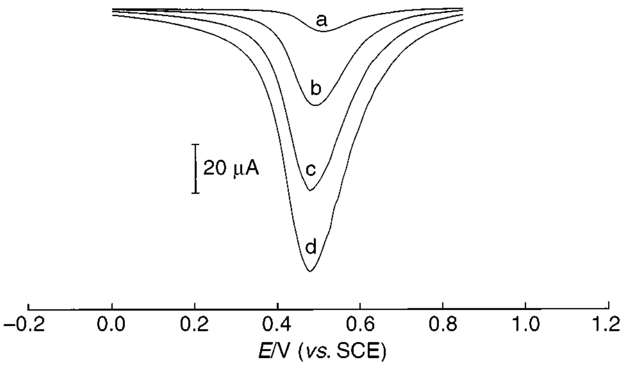

Fig. 5 (a) Differential-pulse sono-cathodic stripping voltammogram showing the response obtained for manganese from a solution of PG Tips Pure Tea Granules (100 mg of tea dissolved in 50 mL of water; 125 µL aliquot diluted to 250 mL with 0.5 M NH_4NO_3 [adjusted to pH 7.0 with 10.0 M NaOH]) and (b) after the addition of Mn^{2+} standard to 10^{-7} M, (c) after the addition of Mn^{2+} standard to 2×10^{-7} M and (d) after the addition of Mn^{2+} standard to 3×10^{-7} M. Experimental parameters as in Fig. 2.

Table 3 Comparison of manganese contents of instant tea samples

	Mn content/µg g^{-1}	
Method	Tetley Pure Tea Granules	PG Tips Pure Tea Granules
Sono-DPCSV	1859	914
AAS[a]	1800	1000
MAFF data[59]	2460	1200

[a] AAS analysis carried out independently by Rooney Laboratories Ltd.

interferences from a number of common metal ions. Employment of the much under-utilised method of CSV has removed the problem of intermetallic species interference, which often occurs when using ASV methodologies, allowed the use of a mercury-free working electrode, offering obvious environmental benefits, and also eliminated the need for a time-consuming and expensive de-gassing step in the analysis.

The sono-electroanalytical technique described here was used successfully to determine the manganese content of two samples of instant tea. The levels of manganese detected in the instant tea granules using this novel procedure and by AAS analysis by an independent laboratory and UK Government (MAFF) data are all in good agreement.

Acknowledgements

We thank Alcan and the EPSRC for a CASE studentship for A.J.S. and the EPSRC for financial support (Grant Number GR/L/36413) under the Analytical Sciences programme. We also thank G. Scarsbrook, R. S. Sussmann and A. J. Whitehead of DeBeers Industrial Diamond Division (UK), for the kind loan of the diamond electrode used in this work.

References

1 J. Wang, *Stripping Analysis: Principles, Instrumentation and Applications*, VCH, Deerfield Beach, FL, 1985.
2 Kh. Brainina and E. Neynam, *Electroanalytical Stripping Methods*, John Wiley and Sons, New York, 1993.
3 C. Locatelli, *Talanta*, 1996, **43**, 45.
4 W. Jin, V. D. Nguyen, P. Valenta and H. W. Nürnberg, *Anal. Lett.*, 1997, **30**, 1235.
5 C. Locatelli and G. Torsi, *Talanta*, 1998, **46**, 623.
6 M. Kopanica and V. Stara, *Electroanalysis*, 1993, **5**, 595.
7 Z. Komy, *Mikrochim. Acta*, 1993, **111**, 239.
8 J. Wang and J. S. Mahmoud, *Anal. Chim. Acta*, 1986, **182**, 147.
9 M.-L. Tercier-Waeber, C. Belmont-Herbert and J. Buffle, *Environ. Sci. Technol.*, 1998, **32**, 1515.
10 M.-L. Tercier-Waeber and J. Buffle, *Sea Technol.*, 1999, **40**, 74.
11 C. Agra-Gutiérrez, J. L. Hardcastle, J. C. Ball and R. G. Compton, *Analyst*, 1999, **124**, 1053.
12 http://vest.gu.se/homepages/old_bosse/Mercury/Nature/Swedish-flow/default.html.
13 E. Gustafsson, *Water Air Soil Pollut.*, 1995, **80**, 99.
14 http://www.planetark.org/dailynewsstory.cfm?newsid-=2382&newSdate=06-Nov-1998.
15 L. Wang, C. Ma, X. Zhang and J. Wang, *Anal. Lett.*, 1993, **26**, 1711.
16 A. Romanus, H. Müller and D. Kirsch, *Fresenius' J. Anal. Chem.*, 1991, **340**, 363.
17 J. Wang and J. Lu, *Talanta*, 1995, **42**, 331.
18 N. A. El-Maali and D. A. El-Hady, *Anal. Chim. Acta*, 1998, **370**, 239.
19 H. Zhang, R. Wollast, J.-C. Vire and G. J. Wollast, *Analyst*, 1989, **114**, 1597.
20 J.-Z. Zhang and F. J. Millero, *Anal. Chim. Acta*, 1994, **284**, 497.
21 E. A. Viltchinskaia, D. M. Zeigman, D. M. Garcia and P. F. Santos, *Anal. Lett.*, 1995, **28**, 1845.
22 J. Labuda, M. Vaníčková and E. Beinrohr, *Mikrochim. Acta*, 1989, **I**, 113.
23 S. B. Khoo, M. K. Soh, Q. Cai, M. R. Khan and S. X. Guo, *Electroanalysis*, 1997, **9**, 45.
24 T. Ishiyama and T. Tanaka, *Tetsu To Hagane (J. Iron Steel Inst. Jpn.)*, 1996, **82**, 923.
25 T. Ishiyama, *Bunseki Kagaku*, 1997, **46**, 847.
26 T. Tanaka, T. Muramatsu, N. Takada and A. Mizuike, *Bunseki Kagaku*, 1993, **42**, 587.
27 K. W. Bruland and J. S. Roitz, *Anal. Chim. Acta*, 1997, **344**, 175.
28 R. N. Goyal and A. Mittal, *J. Sci. Ind. Res.*, 1993, **52**, 607.
29 M. Esteban and C. Ariño, *Anal. Chim. Acta*, 1994, **285**, 377.
30 E. Popa, H. Notsu, T. Miwa, D. A. Tryk and A. Fujishima, *Electrochem. Solid-State Lett.*, 1999, **2**, 49.
31 A. J. Saterlay, C. Agra-Gutiérrez, M. P. Taylor, F. Marken and R. G. Compton, *Electroanalysis* in the press.
32 J. Xu, M. C. Granger, Q. Chen, J. W. Strojek, T. E. Lister and G. M. Swain, *Anal. Chem.*, 1997, **69**, 591A.
33 G. M. Swain, A. B. Anderson and J. C. Angus, *MRS Bull.*, 1998, **23**, 56.
34 F. Bouamrane, A. Tadjeddine, R. Tenne, J. E. Butler, R. Kalish and C. LevyClement, *J. Phys. Chem. B*, 1998, **102**, 134.
35 T. Yano, D. A. Tryk, K. Hashimoto and A. Fujishima, *J. Electrochem. Soc.*, 1998, **145**, 1870.
36 J. S. Xu, Q. Y. Chen and G. M. Swain, *Anal. Chem.*, 1998, **70**, 3146.
37 C. H. Goeting, F. Jones, J. S. Foord, J. C. Eklund, F. Marken, R. G. Compton, P. R. Chalker and C. Johnston, *J. Electroanal. Chem.*, 1998, **442**, 207.
38 R. G. Compton, J. C. Eklund and F. Marken, *Electroanalysis*, 1997, **9**, 509.
39 N. A. Madigan, T. J. Murphy, J. M. Fortune, C. R. S. Hagan and L. A. Coury Jr., *Anal. Chem.*, 1995, **67**, 2781.
40 A. M. Oliveira Brett, C. M. A. Brett, F.-M. Matysik and S. Matysik, *Ultrasonics Sonochem.*, 1997, **4**, 123.
41 F. Marken, T. O. Rebbitt, J. Booth and R. G. Compton, *Electroanalysis*, 1997, **9**, 19.
42 F.-M. Matysik, S. Matysik, A. M. Oliveira Brett and C. M. A. Brett, *Anal. Chem.*, 1997, **69**, 1651.
43 C. Agra-Gutiérrez, J. C. Ball and R. G. Compton, *J. Phys. Chem. B*, 1998, **102**, 7028.
44 R. P. Akkermans, J. C. Ball, T. O. Rebbitt, F. Marken and R. G. Compton, *Electrochim. Acta*, 1998, **43**, 3443.
45 R. P. Akkermans, J. C. Ball, F. Marken and R. G. Compton, *Electroanalysis*, 1998, **10**, 26.
46 C. Agra-Gutiérrez and R. G. Compton, *Electroanalysis*, 1998, **10**, 204.
47 C. Agra-Gutiérrez and R. G. Compton, *Electroanalysis*, 1998, **10**, 603.
48 J. González-García, J. Iniesta, A. Aldaz and V. Montiel, *New J. Chem.*, 1998, **22**, 343.
49 R. G. Compton, F. Marken, C. H. Goeting, R. A. J. McKeown, J. S. Foord, G. Scarsbrook, R. S. Sussmann and A. J. Whitehead, *J. Chem. Soc., Chem. Commun.*, 1998, 1961.
50 A. J. Saterlay, Q. Hong and R. G. Compton, *Ultrasonics Sonochem.*, 1999, in print.
51 J. J. Powell, T. J. Burden and R. P. H. Thompson, *Analyst*, 1998, **123**, 1721.
52 J. J. Fardy, G. D. McOrist and Y. J. Farrar, *J. Radioanal. Nucl. Chem.*, 1992, **163**, 195.
53 A. R. McEuen, *Inorganic Biochemistry*, Royal Society of Chemistry, London, 1981.
54 A. Iregren, *Neurotoxicology*, 1994, **15**, 671.
55 H. Frumkin and G. Solomon, *Am. J. Ind. Med.*, 1997, **31**, 107.
56 *Metal Contamination of Food*, ed. C. Reilly, Applied Science, London, 1980.
57 *Trace Elements in Human and Animal Nutrition* ed. E. J. Underwood, Academic Press, New York, 1997.
58 Y. Özdemir and Ş. Güçer, *Anal. Lett.*, 1998, **31**, 697.
59 http://www.maff.gov.uk/maffhome.htm.
60 R. G. Compton, J. C. Eklund and S. D. Page, *J. Phys. Chem.*, 1995, **99**, 4211.
61 M. A. Margulis and A. N. Mal'tsev, *Russ. J. Phys. Chem.*, 1969, **43**, 592.
62 T. J. Mason, J. P. Lorimer and D. M. Bates, *Ultrasonics*, 1992, **30**, 40.
63 F. Marken and R. G. Compton, *Ultrasonics Sonochem.*, 1996, **2**, S131.
64 A. J. Bard, *Encyclopedia of Electrochemistry of the Elements*, Marcel Dekker, New York, 1970, vol, 1, p. 349.
65 A. Tvarusko, *J. Electrochem. Soc.*, 1964, **111**, 125.
66 S. Rodrigues, N. Munichandraiah and A. K. Shukla, *J. Appl. Electrochem.*, 1998, **28**, 1235.
67 E .Y. A. Neiman, L. G. Petrova, V. I. Ignaton and G. M. Dolgopolova, *Anal. Chim. Acta*, 1980, **113**, 277.
68 O. L. Kabanova and S. M. Beniaminova, *J. Anal. Chem. USSR*, 1970, **26**, 94.
69 S. Dong and Y. Wang, *Talanta*, 1998, **35**, 819.
70 H. Gunasinghan and R. Dalangin, *Anal. Chim. Acta*, 1991, **246**, 309.

Paper 9/06851A