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Bare and Polymer-Coated Indium Tin Oxide as Working Electrodes for Manganese Cathodic Stripping Voltammetry

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Abstract

Though an essential metal in the body, manganese (Mn) has a number of health implications when found in excess that are magnified by chronic exposure. These health complications include neurotoxicity, memory loss, infertility in males, and development of a neurologic psychiatric disorder- manganism. Thus, trace detection in environmental samples is increasingly important. Few electrode materials are able to reach the negative reductive potential of Mn required for anodic stripping voltammetry (ASV), so cathodic stripping voltammetry (CSV) has been shown to be a viable alternative. We demonstrate Mn CSV using an indium tin oxide (ITO) working electrode both bare and coated with a sulfonated charge selective polymer film, polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene-sulfonate (SSEBS). ITO itself proved to be an excellent electrode material for Mn CSV, achieving a calculated detection limit of 5 nM (0.3 ppb) with a deposition time of 3 min. Coating the ITO with the SSEBS polymer was found to increase the sensitivity and lower the detection limit to 1 nM (0.06 ppb). This polymer modified electrode offers excellent selectivity for Mn as no interferences were observed from other metal ions tested (Zn^{2+} , Cd^{2+} , Pb^{2+} , In^{3+} , Sb^{3+} , Al^{3+} , Ba^{2+} , Co^{2+} , Cu^{2+} , Ni^{3+} , Bi^{3+} , and Sn^{2+}) except Fe^{2+} , which was found to interfere with the analytical signal for Mn^{2+} at a ratio 20:1 (Fe^{2+} : Mn^{2+}). The applicability of this procedure to the analysis of tap, river, and pond water samples was demonstrated. This simple, sensitive analytical method using ITO and SSEBS-ITO could be applied to a number of electroactive transition metals detectable by CSV.

Graphical abstract

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ASSOCIATED CONTENTS

Supporting Information

This information is available free of charge via the Internet at <http://pubs.acs.org/>

Includes deposition potential and time optimizations, table and graph of SSEBS film optimization, reproducibility, and a method comparison table with a calibration curve showing the dynamic ranges of bare and SSEBS-ITO.

Keywords

Manganese; Indium Tin Oxide; Stripping Voltammetry

INTRODUCTION

Manganese (Mn) has been found to cause a number of health issues when exposure reaches a chronic level.¹⁻³ While Mn is a required trace metal within the body, chronic exposure can cause symptoms such as memory loss, severe neurotoxicity, learning disabilities in children, impairment of male fertility, and development of manganism.²⁻⁶ Manganism is a neurologic psychiatric disorder with symptoms similar to those of Parkinson's disease.⁶ Mn is regularly found in most aqueous environments and especially in areas surrounding a Mn smelter.⁷ The Environmental Protection Agency's (EPA) maximum contaminant level (MCL) for Mn in drinking water has been set at the very low level of 910 nM (50 ppb) because of these health effects.⁸ Therefore, trace determination of Mn in drinking and environmental water is of importance.

A variety of detection methods are used for the determination of not just Mn, but many other trace metals as well. Within this realm, electroanalytical methods have been commonly used and can be found throughout literature. Electroanalytical methods offer a number of benefits compared to other analytical methods such as spectroscopy in that they are inexpensive, portable, and easily miniaturized.^{9,10} Stripping voltammetry is an attractive electroanalytical technique because of its exceptionally low limit of detection, a necessity when working with trace metal analytes. This excellent limit of detection is largely due to the incorporation of a pre-concentration or deposition step during which analyte(s) is accumulated onto the working electrode surface either by electrodeposition at a certain potential or adsorption. Once sufficient pre-concentration or deposition is reached, the working electrode potential is then swept in the positive (anodic stripping voltammetry) or negative (cathodic stripping voltammetry) direction to effectively "strip" the analyte off of the electrode surface.^{11,12} This stripping step results in a measureable faradaic current that is proportional to the concentration of the analyte(s) in solution.^{11,12}

Anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV), adsorptive stripping voltammetry (AdSV), and potentiometric stripping are commonly used forms of stripping analysis, with ASV being the most frequently found in literature.^{11,12} In ASV, the deposition potential is used to reduce analyte(s) onto the surface of the electrode before

sweeping the potential in the positive direction. This deposition potential is typically negative and is commonly used to determine a number of trace metals such as lead, cadmium, zinc, mercury, and copper. For Mn determination, the deposition potential needed is too negative for most electrode materials to reach before hydrogen evolution becomes an interference as the $\text{Mn}^{2+}/\text{Mn}^0$ redox couple has a standard reduction potential of -1.18 V .¹³

Stripping potentiometry is similar to stripping voltammetry in that both techniques require a pre-concentration/deposition step. However, rather than scanning a potential range to strip the metal off of the electrode surface, potentiometric stripping analysis uses an oxidizing or reducing agent for stripping.¹⁴⁻¹⁷ During stripping, the potential of the working electrode is measured as a function of time. The parameter dt/dE is then plotted vs E and changes in dt/dE are proportional to changes in concentration of the analyte. Scollary, et al. used a mercury film working electrode and oxygen (oxidizing agent) for the determination of Mn^{2+} in wastewaters and seawater, obtaining a detection limit of 0.5 nM (0.025 ppb).¹⁶ While this work only required a pre-concentration time of 80 s , the requirement of a mercury film makes it less attractive because of toxicity and disposal issues. Zhang, et al. used reductive potentiometric stripping analysis on glassy carbon with potassium hexacyanoferrate (reducing agent), achieving a detection limit of 5.0 nM (0.3 ppb).¹⁷

AdSV differs in that adsorption of analyte(s) onto the electrode surface replaces the electrochemical deposition step. Some AdSV techniques use mercury electrodes while others have used carbon paste. El-Desoky and Ghoneim used a carbon paste electrode modified with montmorillonite clay for the determination of Mn as a complex with 8-hydroxyquinoline, achieving a detection limit well into the pico-molar range.¹⁸

CSV is the most commonly used stripping technique used for the determination of Mn. In CSV, the deposition potential is usually positive to oxidize analyte(s) onto the electrode surface and during stripping the working electrode potential is swept in the negative direction.^{11,12} In the case of Mn, Mn^{2+} from the sample is deposited onto the working electrode surface as MnO_2 by the reaction below:

This deposition occurs at a potential that is well within the working range of many common electrode materials and that also offers excellent insensitivity to interfering metal ions and oxygen. Many electrodes have been used for such analyses: platinum, palladium, glassy carbon, boron doped diamond, and carbon nanotubes.^{10,19-23}

Indium tin oxide (ITO) is a working electrode material that is commonly used in spectroelectrochemistry.²⁴⁻³⁶ Its combination of good conductivity and optical transparency has made it especially useful as a spectroelectrochemical sensor that can incorporate multiple modes of selectivity.²⁴⁻³⁶ ITO also has an excellent positive potential window capable of measurements beyond $+1.5 \text{ V}$ in water samples, making it a suitable working electrode for voltammetric methods such as CSV.³⁶ Another feature of ITO is the incorporation of a charge selective polymer film on the electrode surface that allows for selective partitioning, creating a high local concentration of analyte(s) at the electrode

surface for measurement by internal reflection spectroscopy.^{25–36} This is an essential aspect of the spectroelectrochemical sensor for achieving low detection limit. Charged polymer films also provides some selectivity by rejecting interferences of the same charge. Polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene-sulfonate (SSEBS) is a negatively charged polymer shown to be useful for spectroelectrochemical purposes.^{32,35} It has been reported in literature that SSEBS is capable of uptaking positively charged analytes while repelling negatively charged interferences.^{32,35} ITO has been used for spectroelectrochemical stripping voltammetry where an optical change associated with the stripping of preconcentrated metal is used as the analytical signal.^{37–39} However, neither bare ITO nor SSEBS coated ITO have ever been used as an electrode material for CSV of Mn^{2+} .

In this paper, we use both bare and SSEBS-ITO working electrodes for Mn^{2+} CSV with the main goals of a low limit of detection, good selectivity, and accurate real sample analysis. Though ITO is not an electrode traditionally chosen for stripping analysis, it was investigated due to its excellent positive potential window, which is particularly important in CSV where preconcentration and stripping are often done in the positive potential range. ITO can also be used in acidic buffers, which proved to be important for this work. Because of the experience in our laboratory with polymer films that pre-concentrate charged analytes by ion exchange and provide selectivity, we also investigated the effect of charged polymer films on the CSV of Mn^{2+} .^{30,35} We compared SSEBS and Nafion, polymers that we have used previously to preconcentrate cationic analytes such as $\text{Ru}(\text{bipy})_3^{2+}$, $\text{Cu}(\text{bipy})_2^{2+}$, and $\text{Fe}(\text{bipy})_3^{2+}$ on ITO for spectroelectrochemical sensing.^{30,35} While the uncoated ITO proved to be an excellent electrode material itself for Mn^{2+} CSV, incorporating the SSEBS film increases sensitivity while lowering the detection limit. Overall, ITO proved to be an extremely good electrode material for CSV of Mn^{2+} as ppt/single-digit nM detection limits were obtained on both bare and polymer-coated electrodes.

EXPERIMENTAL SECTION

Chemicals and Materials

A 1000 mg/L Mn^{2+} atomic absorption standard was purchased from Acros Organics and diluted to desired concentrations. House distilled water that was further purified with a D2798 Barnstead water purification system was used for all standard solutions. Polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene-sulfonate 5% solution and Nafion perfluorinated resin solution (5 % in lower aliphatic alcohols) were purchased from Sigma Aldrich and diluted with isopropanol where appropriate. Glacial acetic acid (85 %, Pharmco Brookfield, CT) and sodium acetate (Fisher Scientific) were mixed in different proportions to yield different pHs of acetate buffer used for analyses. Trace metal grade HNO_3 was purchased from Fisher Scientific.

Instrumentation

CSV measurements were executed in a 20 mL conventional three electrode cell consisting of ITO coated glass slides (Corning 1737F, 11–50 Ω /sq, 135 nm thick film on 1.1 mm glass, Thin Film Devices, Anaheim, CA) with 10 x 40 mm dimensions as the working electrode, a

Ag/AgCl reference electrode (3.0 M KCl solution), and a platinum (Pt) wire auxiliary electrode. SSEBS films on ITO were prepared using a Model 1-PM101DT-R485 spin coater from Headway Research, Inc. The potentiostat was a BASi 100B Electrochemical Analyzer. The basic parameters for Osteryoung square wave voltammetry (OSWV) that was used for the stripping step were: square wave amplitude = 25 mV, step potential = 5 mV and frequency = 25 Hz. The extrapolated baseline current method described by Kissinger and Heineman was used to measure peak currents (i_p).^{11,12} GF-AAS measurements were performed using a Varian 2240FS Atomic Absorption Spectrometer equipped with a 256.8 nm Mn hollow cathode lamp and a Varian PSD 120 autosampler. Lamp current was 4 mA and a 13.50:2.00 L/min flow rate ratio of air:acetylene was used. Varian (coated)-graphite thermal analysis partition tubes were also used (Part No. 63-100012-00) for GF-AAS measurements. After the sample had been injected into the graphite tube, the temperature was slowly increased to 90 °C for 40 s, then increased to 120 °C for 10 s, and finally increased to 700 °C for 5 s. The sample was then ashed at 2400 °C while the absorbance was read. Gas flow was stopped during absorbance measurements.

Water Sample Collection

All water samples were collected in 50 mL plastic centrifuge tubes (Falcon). The tubes were thoroughly rinsed with DI water and dried before water sample collection. Tap water samples were collected from a well-used faucet in Crosley Tower at the University of Cincinnati on July 13, 2015. No specific flow of water was allowed prior to collection from the faucet. The tap water samples were immediately analyzed after collection with no further treatment. Environmental surface-water samples were collected on shore from the Ohio River (Covington, KY) and Burnet Woods Pond (Cincinnati, Ohio) on December 20, 2015. It had rained for three days prior to the water collection and the river was elevated. Both samples were collected and stored in 0.5 M trace metal grade HNO₃. The river water was filtered with a 10 µm pore size filter (Millipore, Darmstadt, Germany) and then analyzed one day after collection.

Nafion and SSEBS Film Preparation

Nafion and SSEBS films were prepared using the same procedure published previously.^{32,35} The ITO slides were thoroughly rinsed with water and ethanol and then allowed to dry before use. Film thicknesses were measured by spectroscopic ellipsometry using a variable angle spectroscopic ellipsometer (VASE) and accompanying software (J.A Woolam Co., Inc). One measurement per ITO electrode was made. The mathematical fitting with the J.A Woolam Co., Inc ellipsometer software yielded a film thickness within ± 10 nm.

RESULTS AND DISCUSSION

Comparison of Bare-ITO and SSEBS-ITO

Cyclic voltammetry (CV) was used to initially investigate the electrochemistry of Mn²⁺ at bare ITO and SSEBS-ITO. Figure 1A shows cyclic voltammograms of 455 nM (25 ppb) Mn²⁺ at both bare-ITO and SSEBS-ITO working electrodes. The potential was held at + 1200 mV for 60 s to oxidize Mn²⁺ to MnO₂ as shown by the equation above before

initiating the CV scans on each electrode. This short preconcentration step was necessary to give a detectable voltammogram at this very low concentration of Mn^{2+} .

As seen in Figure 1A, the starting potential of +1300 mV is sufficient to oxidize Mn^{2+} to Mn^{4+} (as MnO_2) where the reduction peak back to Mn^{2+} can be observed circa +750 mV. The CV shows a very well defined reduction wave that is well separated from the positive potential limit of ITO. The sharp peak shape of the voltammogram is characteristic of the reduction of material confined to the electrode surface, as would be expected for the reduction of MnO_2 precipitated on the electrode, rather than diffusing to the electrode. An identical experiment performed at a SSEBS-ITO electrode in which the potential was applied immediately after immersion of the electrode in the sample gave an equally well defined reduction wave with the same peak potential but with an increased peak current relative to the bare-ITO electrode. Rather than inhibiting the mass transport of Mn^{2+} to the underlying electrode for electrochemical deposition as MnO_2 , an increase in current is caused by the electrostatic attraction between the negatively charged SSEBS polymer and the positively charged Mn^{2+} . The reduction peak potential at both electrodes is ideally positioned in the working electrode range of ITO for CSV. The background current is larger for the SSEBS-ITO electrode due to the increase in capacitance that is usually associated with coating electrodes with charged films.⁴⁰

Similar results were obtained for CSV of 10 ppb Mn^{2+} as shown in Figure 1B. Well-defined cathodic stripping voltammograms for Mn^{2+} using OSWV for the stripping step were obtained at both bare ITO and SSEBS-ITO. Both background currents were very smooth with the SSEBS-ITO being larger due to the increase in electrode capacitance from the SSEBS film. The peak current for Mn^{2+} was also larger at SSEBS-ITO, as it was in CV. It can also be seen in Figure 1B that at a lower concentration of Mn^{2+} (5ppb), formation of double peaks is observed on bare-ITO whereas a single, larger peak is obtained on SSEBS-ITO. These results confirm that both ITO and SSEBS-ITO are exceptionally good electrodes for CSV of Mn^{2+} with a very smooth background current.

We found it to be better than glassy carbon in comparable experiments. Under optimized conditions, double peaks for Mn were observed in both the background scan and voltammogram. With this, SSEBS-ITO was found to significantly increase the peak current and peak sharpness even using shorter deposition times than required on glassy carbon to achieve quantifiable voltammograms. Other electrode materials such as Pt, carbon film, carbon paste and Pd can exhibit sloping and/or noisy backgrounds using CSV as well^{10,41,42} With this, Pt and Pd can also exhibit interfering oxide peaks in voltammograms.¹⁰ The improvement in sensitivity provided by the SSEBS-ITO electrode at these low concentrations and the importance of achieving the lowest possible limit of detection for Mn^{2+} caused us to focus primarily on this electrode in the subsequent studies.

Cathodic Stripping Voltammetry Optimizations

OSWV was used as the stripping step for CSV due to its ability to achieve low limits of detection by minimizing non-faradaic current.^{43,44} Deposition potential, deposition time, and solution pH were the parameters examined.

Deposition potential is a critical parameter in stripping voltammetry. In CSV, the deposition potential is typically a potential positive of the standard reduction potential to oxidize ions on the electrode surface as shown in the equation above for Mn^{2+} . Figure S-1A shows the deposition potential optimization on SSEBS-ITO; a range of +900 mV to +1600 mV was examined. Current response increased and reached a maximum between +1150–1300 mV. At more positive deposition potentials beyond +1300 mV, the current began to significantly decrease. This dramatic decrease is attributed to the oxidation of H_2O which was observed as small bubbles appearing on the electrode surface that interfered with MnO_2 deposition. A deposition potential of +1200 mV was chosen as the optimal potential and was used throughout the study.

Deposition time can affect current response significantly. As the deposition time increases, more analyte deposits at the electrode surface. This time can be increased to a point where analyte is effectively depleted from the solution onto the electrode surface. Often, these longer times are not needed to achieve sufficient detection limits for samples to be analyzed, but using a sufficiently long deposition time can be an important aspect of stripping voltammetry when the lowest possible detection limit is required. Figure S-1B shows the deposition time optimization on SSEBS-ITO. A range of 1–25 min was investigated. Current response increased up to 10 min where it began to level off up to 25 min. A deposition time of 3 min was chosen because it gave the best combination of linear response over a wide range and limit of detection when doing calibration experiments (*vide infra*). Longer deposition times of 5 and 10 min gave lower detection limits but have more limited linear ranges in the calibration plots compared to the 3 min deposition. Shorter deposition times such as 1 min were also studied and could be used for quantitative determination of Mn^{2+} in the water samples we collected (*vide infra*), albeit with a slight sacrifice in the detection limit.

Solution pH can significantly affect voltammetric measurements and, thus, is an important parameter to study. In the case of Mn CSV, many publications state that a basic pH supporting electrolyte is needed to aid in the formation of MnO_2 on the electrode surface,^{20,23} and pH 8.5–9.0 borate buffer or ammonium chloride buffer are commonly used supporting electrolytes. However, we found that acidic pH acetate buffer solution can be used for Mn CSV on ITO with increased sensitivity as seen in Figure 2. A range of pH 3.0–8.5 was investigated with both electrodes. Figure 2 shows stripping voltammograms in both acidic (2A) and basic (2B) pH buffer on bare ITO. The voltammograms shown in Figure 2B in pH 8.5 borate buffer were obtained at bare-ITO because the SSEBS film dissolves off the ITO surface in high pH. Comparison of the voltammograms at the two pH levels shows an obvious improvement in peak shape and peak height at the lower pH. In the pH 5.0 acetate buffer samples, sharp, quantifiable voltammograms are obtained. With the pH 8.5 borate buffer however, a background peak at +1100 mV and significant loss in peak current is observed. The sharpness in the peak is also diminished, as the peak has broadened with a shoulder circa +200 mV. As a result, all Mn CSV experiments were conducted in pH 5.0 acetate buffer.

Electrode Optimizations

As shown in Figures 1A and 1B, incorporation of a polymer film increased sensitivity for Mn^{2+} . There are a variety of charge selective polymer films available; the most commonly used polymer for pre-concentrating cations is Nafion, and we have also developed SSEBS for use in spectroelectrochemical sensors.^{31–35} Both polymers are negatively charged, sulfonated polymers that have a number of applications not just for electrochemical use. The main difference between the two polymers is that while Nafion has a sulfonated hydrophobic fluorocarbon backbone, SSEBS has the sulfonate groups as constituents on benzene rings stemming from a hydrocarbon chain. For these reasons, Nafion and SSEBS were investigated and compared for their applicability for Mn^{2+} CSV. The process for coating the ITO with Nafion is the same as was used for that of SSEBS described previously. For these experiments stock, undiluted SSEBS and Nafion solutions were pipetted onto the ITO surface and spun at a rate of 3000 rpm for 30 s yielding a 416 nm Nafion film and 367 nm SSEBS film. Figure 3 shows that both Nafion-ITO and SSEBS-ITO electrodes give well-defined cathodic stripping voltammograms, but SSEBS gives a better response to Mn^{2+} than does Nafion. Nafion only gives slightly higher peak currents than those at a bare ITO electrode. This is because diffusion coefficients are slower in Nafion compared to SSEBS.³² Consequently, SSEBS was chosen as the polymer film used for Mn^{2+} CSV.

Spin-coating at different spin rates and polymer concentrations allows films of different thicknesses to be deposited on ITO as shown in Table S-1. Reproducibility of film thickness is about 10 nm. Thicker films have more negatively charged sites to preconcentrate positively charged analytes compared to thinner films. However, thicker films can hinder diffusion of the analyte through the film to the electrode surface to undergo electrolysis. Figure S-2 shows the effect of SSEBS film thickness over the range of 43 – 367 nm on current response for CSV of Mn^{2+} . Current response levels off above the 122 nm samples, signifying that thicker films have no impact on Mn^{2+} CSV. For simplicity of the overall method with maximum sensitivity, films prepared with 5% SSEBS (367 ± 10 nm thickness) were used since no dilution of the stock SSEBS solution was needed. Because this thickness is in the plateau region of Figure S-2, the 10 nm uncertainty in film thickness has little effect on the stripping voltammetry results.

Reproducibility

To further characterize the SSEBS-ITO for Mn^{2+} CSV, a reproducibility study was completed using 7 different 367-nm thick SSEBS-ITO electrodes. The results are shown in Figure S-3. Current response varied by 6% using a concentration of 25 ppb and a deposition time of 60 s. Throughout all the work shown in the following section, a new, fresh SSEBS-ITO electrode was used each time. Replications of calibration curves and other experiments reported in this work were completed over several weeks and only minor deviations were observed from electrode to electrode.

Calibration Data

To evaluate SSEBS-ITO as a working electrode to quantitatively pre-concentrate and determine Mn^{2+} concentration in water samples, a series of Mn^{2+} standards was studied under the optimized conditions described above. Deposition times of 1, 3, 5, and 10 min

were investigated. Voltammograms for the 3 min deposition are shown in Figures 4A and Figure 4B, where voltammograms of the lower Mn^{2+} concentrations have an expanded current axis. For 1 min deposition time, the widest linear response was obtained from 270 to 2700 nM [$I = (0.008 \pm 0.001)c \text{ (}\mu\text{A/nM)} - (1.7 \pm 0.5) \text{ (}\mu\text{A)}$ $R^2 = 0.993$] with a calculated ($3\sigma/m$) detection limit of 1.8 nM (0.1 ppb).

For 3 min deposition time (Figure 4A & B), a linear response was obtained from 18 to 1800 nM [$I \text{ (}\mu\text{A)} = (0.06 \pm 0.01)c \text{ (}\mu\text{A/nM)} - (1.5 \pm 0.3) \text{ (}\mu\text{A)}$ $R^2 = 0.995$] with a calculated ($3\sigma/m$) detection limit of 1.1 nM (0.06 ppb). For 5 min deposition time, multiple linear ranges were obtained from 9 to 900 nM. First from 9 to 45 nM: [$I \text{ (}\mu\text{A)} = (0.05 \pm 0.01)c \text{ (}\mu\text{A/nM)} - (0.01 \pm 0.04) \text{ (}\mu\text{A)}$ $R^2 = 0.989$] with a calculated ($3\sigma/m$) detection limit of 0.8 nM (0.04 ppb). A second linear response was obtained from 45 nM to 450 nM: [$I \text{ (}\mu\text{A)} = (0.15 \pm 0.02)c \text{ (}\mu\text{A/nM)} - (2.4 \pm 0.4) \text{ (}\mu\text{A)}$ $R^2 = 0.999$] with a calculated ($3\sigma/m$) detection limit of 0.6 nM (0.03 ppb). As seen in Figure 4A and B and the calibration equations shown above, the 3 min deposition time samples are linear over a wider range than the 5 min deposition samples without sacrificing a significant loss in limit of detection.

Increasing the deposition time further reduces detection limit but current response begins to level off quickly with increasing concentrations of Mn^{2+} . In addition, at sub-ppb levels it becomes difficult to distinguish current response of the sample from the background. In order to obtain the cleanest background possible by electrochemically removing any trace Mn^{2+} contaminants prior to completing the calibration curve, a SSEBS-ITO electrode was submerged into a blank acetate buffer solution and the potential was held at +1200 mV for 20 min with stirring. The SSEBS-ITO electrode was then removed and replaced with a fresh, unused electrode and a clean background was obtained. With 10 min deposition, multiple linear responses were also obtained, similar to the 5 min deposition trials. First, from 4.5 to 135 nM (0.25 – 7.5 ppb), [$I \text{ (}\mu\text{A)} = (0.15 \pm 0.01)c \text{ (}\mu\text{A/nM)} - (0.5 \pm 0.3) \text{ (}\mu\text{A)}$ $R^2 = 0.996$] with a calculated LOD ($3\sigma/m$) of 0.4 nM (0.024 ppb). A second linear response was obtained from 18 nM to 270 nM [$I \text{ (}\mu\text{A)} = (0.25 \pm 0.01)c \text{ (}\mu\text{A/nM)} - (4.9 \pm 1.6) \text{ (}\mu\text{A)}$ $R^2 = 0.989$] with a calculated LOD ($3\sigma/m$) of 0.3 nM (0.018 ppb). Thus, deposition times of 5 and 10 min might be warranted for situations where Mn^{2+} concentrations are at levels below 18 nM (1 ppb). Whereas for routine water measurement, shorter deposition times of 1 and 3 min could be suitable.

Calibration data for a bare ITO electrode was also obtained and a comparison is shown in Table S-2. The widest linear range for both electrodes was found on SSEBS-ITO using a deposition time of 1 min (15–150 ppb). Both electrodes were linear over the same concentration range for 3 min deposition (1–100 ppb). The slopes are comparable where the SSEBS-ITO is slightly more sensitive. In addition the LOD is improved 5x on SSEBS-ITO compared to bare-ITO. The LOD improved further on SSEBS-ITO to 15x using 5 min deposition before regressing to 10x with 10 min deposition. In general, the SSEBS-ITO has a better LOD, slightly better sensitivity, and wider linear ranges for various deposition times at or below 100 ppb Mn^{2+} . However, the bare ITO has a larger dynamic range than SSEBS-ITO, as shown in Figure S-4. Using a deposition time of 1 min, the calibration curves intersect circa 125 ppb Mn^{2+} where the bare-ITO continues to increase linearly up to 350 ppb. It then levels off at 500 ppb Mn^{2+} whereas the SSEBS-ITO electrode response begins to

level off after 150 ppb. This phenomenon was observed at longer deposition times, but the calibration curves intersected at lower $[\text{Mn}^{2+}]$. This indicates that for highly polluted Mn waters (concentrations 125 ppb and above), bare-ITO should yield acceptable results whereas samples would require dilution before using the SSEBS-ITO electrode. Furthermore, this re-affirms that a SSEBS-ITO electrode is better suited for very trace detection of Mn^{2+} .

Interference Study and Selectivity for Mn^{2+}

Though the SSEBS film has the ability to selectively repel negatively charged ions by electrostatic repulsion, interference from other positively charged heavy metal ions was investigated. Some metal ions do not form an insoluble oxide at higher oxidation states and CSV itself provides selectivity against them. However, these metal ions can still interfere with the target metal ion by neutralizing some of the negatively charged sites on the SSEBS film, inhibiting the ability of the target metal ion to partition into the film. This was shown using two different methods. First, Zn^{2+} , Cd^{2+} , Pb^{2+} , In^{3+} , Sb^{3+} , Al^{3+} , Ba^{2+} , Co^{2+} , Cu^{2+} , Ni^{3+} , Bi^{3+} , and Sn^{2+} at concentrations up to 500 ppb were added to a solution containing 50 ppb Mn^{2+} and no decrease in peak current or interfering voltammetric peak was observed, as seen in Figure 5 where the voltammograms before and after addition of interferents essentially overlap.

However, Fe^{2+} was shown to interfere with the Mn^{2+} signal. Up to a Fe^{2+} concentration of 250 ppb (with all other interferences listed above at 500 ppb included), there was no observable change in the peak current, but as seen in Figure 5, the peak begins to slightly broaden. Further increase of $[\text{Fe}^{2+}]$ to 500 ppb caused a 25% decrease in signal, while an increase to 1000 ppb caused a 75% decrease. This could be due to the fact that Fe^{2+} chemically strips the MnO_2 back to Mn^{2+} faster than the potential range is able to be scanned. As described above, Fe^{2+} complexes have been reported in literature for reductive potentiometric stripping analysis of Mn^{2+} where hexacyanoferrate was used to chemically reduce MnO_2 back to Mn^{2+} .¹⁷ However, since the EPA's MCL for Fe is 300 ppb in drinking water, interference from Fe^{2+} is not a problem for routine monitoring of Mn^{2+} unless the water contains larger than acceptable levels of iron. This could become an issue with the analysis of environmental or well water samples, where Fe^{2+} concentrations can be above the 300 ppb MCL in drinking water described above. The World Health Organization (WHO) reports that the average concentration of iron in river water is about 0.7 ppm.⁴⁵ However, they also state that in anaerobic groundwater the Fe concentration can range from 0.5–10 ppm and even in some extreme cases as high as 50 ppm.⁴⁵ Khoo et al., reports that the addition of sodium citrate can mask Fe interferences for Mn CSV using carbon paste modified electrodes.⁴⁶

Natural and Finished Water Sample Analysis

Mn CSV at SSEBS-ITO has many advantages over bare-ITO and other electrode materials such as lower limit of detection, better sensitivity, and repulsion of negative interferences. To show that this electrode has the capability for the determination Mn^{2+} in real samples with complex matrices, environmental and tap water samples were analyzed. CSV results for the natural water samples were compared to results obtained using graphite furnace atomic

absorption spectroscopy (GF-AAS) and are shown in Table 1. For CSV analysis, the samples were diluted 10x, adjusted to pH 5.0 using acetate buffer, and a deposition time of 3 min was used. The standard addition method was used to determine Mn^{2+} concentration in each sample. Four 10 ppb increments of Mn^{2+} standard were added and current response was measured.

General agreement in $[\text{Mn}^{2+}]$ (85% confidence level) in each of the samples is observed between CSV and GF-AAS for the Burnet Woods and Ohio River samples as seen in Table 1. The tap water samples yield different results for the two methods. However, the AAS absorbance readings for the tap water samples was indistinguishable from the background absorbance, indicating that the detection limit for the method had been reached. Voltammograms for the Ohio River water samples are shown in Figure 6. The CSV measurements are slightly lower than that of GF-AAS. GF-AAS does have an advantage here over CSV in that there is no potential interference from increased concentration of Fe^{2+} . For the tap water sample, the signals for both samples were close to the limits of detection of the two techniques, degrading the precision. The similarities of the uncertainties and measured concentrations between CSV and GF-AAS for the environmental samples demonstrate that CSV with a SSEBS-ITO working electrode compares favorably with GF-AAS for the determination of trace Mn^{2+} in water samples.

CONCLUSIONS

An ultra-sensitive CSV method for the determination of Mn^{2+} in water samples using a SSEBS coated ITO working electrode was shown to yield reliable, accurate results. Bare-ITO also proved to be an excellent working electrode for Mn^{2+} (LOD: 6 nM, 0.3 ppb) and in cases where there is limited access to a spin-coater, bare-ITO could also be used for environmental/drinking water sample analysis. In situations where there is significant Mn^{2+} contamination (Mn^{2+} concentrations above 125–150 ppb), bare-ITO would possibly be a better option. However, for trace detection, SSEBS-ITO performed better. ITO or charge selective polymer films coated on ITO have never been used for Mn^{2+} stripping voltammetry, possessing potential applicability for CSV of other metal ions. By optimizing the CSV method and electrode configuration, a detection limit of 1 nM (0.06 ppb) was obtained using a deposition time of 3 min on SSEBS-ITO. Longer deposition times of 5 and 10 min improve the sensitivity and detection limit which could be used for Mn levels below 18 nM (1 ppb). SSEBS-ITO also exhibited excellent selectivity for Mn^{2+} as no interferences were observed from other heavy metal ions except Fe^{2+} at concentrations up to 500 ppb. 50 % of the analytical signal is still obtained at a 20:1 ratio of $\text{Fe}^{2+}:\text{Mn}^{2+}$. The SSEBS film, ITO working electrode, and CSV technique in general allow for analysis to be completed in a potential range where few other metal ions electrolyze. With this, few metals form insoluble metal oxides at the electrode surface as in Mn^{2+} CSV. The capability of this technique to be miniaturized coupled with its ease of execution lend this method to potential point-of-care analysis using microfabricated, disposable electrochemical cells.^{9,10}

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(A) Cyclic voltammograms of 25 ppb Mn^{2+} on SSEBS-ITO and bare-ITO in 0.2 M pH 5.0 acetate buffer. Potential held at +1300 mV for 60 s prior to scanning. Scan rate = 100 mV/s. (B) Cathodic stripping voltammograms with OSWV of 0, 5, and 10 ppb Mn^{2+} on SSEBS-ITO and bare-ITO in 0.2 M pH 5.0 acetate buffer. Deposition potential: +1200 mV. Deposition time: 60 s.

Figure 2. Cathodic stripping voltammograms of Mn^{2+} with increasing concentrations of Mn^{2+} on (A) SSEBS-ITO in pH 5.0 acetate buffer and (B) bare-ITO in pH 8.5 borate buffer. Deposition potential: +1200 mV. Deposition time: 3 min.

Figure 3.

Cathodic stripping voltammograms of Mn^{2+} on SSEBS-ITO and Nafion-ITO. Deposition potential: +1200 mV. Deposition time: 3 min. $[Mn^{2+}] = 455$ nM (25 ppb). SSEBS thickness = 367 nm thickness (5 % w/v SSEBS), Nafion thickness = 416 nm (5% w/v Nafion) .

Figure 4.

Cathodic stripping voltammograms of Mn^{2+} on SSEBS-ITO in pH 5.0 acetate buffer with increasing concentrations of Mn^{2+} . (A) Voltammograms from 1–100 ppb Mn^{2+} . (B) Voltammograms for lower Mn^{2+} concentrations (1–25 ppb) with expanded current scale. [SSEBS] = 5 % (w/v), 367 nm thickness. Deposition potential: +1200 mV, deposition time: 3 min.

Figure 5.

Cathodic stripping voltammograms of Mn^{2+} on SSEBS-ITO in pH 5.0 acetate buffer with added metal interferences and increasing $[\text{Fe}^{2+}]$. SSEBS thickness = 367 nm. Deposition time: 60 s. Deposition potential: +1200 mV. $[\text{Mn}^{2+}] = 910 \text{ nM}$ (50 ppb).

Figure 6. Cathodic stripping voltammograms of Ohio River water with successive additions of Mn^{2+} on SSEBS-ITO in pH 5.0 acetate buffer. SSEBS thickness = 367 nm. Deposition time: 3 min. Deposition potential: +1200 mV.

Table 1

Mn²⁺ determination in environmental water samples using a SSEBS-ITO electrode and GF-AAS

sample type	[Mn ²⁺] (ppb)	
	CSV	GF-AAS
Burnet Woods	62 ± 4	71 ± 4
Ohio River	92 ± 8	110 ± 14
Tap Water	1.8 ± 0.6	0.5 ± 0.1