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Determination of manganese by cathodic stripping voltammetry on a microfabricated platinum thin-film electrode

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Abstract

In this work, we report on the determination of trace manganese (Mn) using cathodic stripping voltammetry (CSV) using a microfabricated sensor with a Pt thin-film working electrode. While an essential trace metal for human health, prolonged exposure to Mn tends to gradually impair our neurological system. The potential sources of Mn exposure make it necessary to monitor the concentration in various sample matrices. Previous work by us and others suggested CSV as an effective method for measuring trace Mn. The analytical performance metrics were characterized and optimized, leading to a calculated limit of detection (LOD) of 16.3 nM (0.9 ppb) in pH 5.5, 0.2 M acetate buffer. Further, we successfully validated Mn determination in surface water with ~90% accuracy and >97% precision as compared with ICP-MS “gold standard” measurement. Ultimately, with stable, accurate and precise electrochemical performance, this Pt sensor permits rapid monitoring of Mn in environmental samples, and could potentially be used for point-of-use measurements if coupled with portable instrumentation

Keywords

Electrochemical sensor; cathodic stripping voltammetry; manganese determination; Pt working electrode

Introduction

Manganese (Mn) plays a critical role in many enzyme-related physiological activities in metabolism, and a trace amount of Mn is necessary for human health. Yet studies in neurobiology and child neurodevelopment [1–6] show that chronic exposure to elevated

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levels of Mn, primarily Mn(II) and Mn(III) [7,8], can lead to neurological disorders, including manganism, pre-Parkinson's syndrome, and impaired mental development. Meanwhile, exposure to Mn occurs through a wide range of sources, including particulate matter in air, water, or food that contain abnormally high concentrations of Mn. These exposures are of particular concern for individuals and families residing and working in proximity to ferro-manganese processing facilities [3,5].

To monitor and limit human exposure, regulations for Mn levels have been established. The World Health Organization (WHO) recommends 0.4 mg/L (ppm) Mn limit in drinking water [9]. The ATSDR [10] provides guidelines for the normal range of Mn in blood (4–15 µg/L or ppb), urine (1–8 µg/L), and serum (0.4–0.85 µg/L). Monitoring manganese exposure in the environment is conventionally accomplished by spectroscopic methods, including inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS), which offer accurate and sensitive measurements with detection limits at the sub-ppb level [11–15]. However, the high cost of instrumentation, and the need for highly-skilled operators, and the use of relatively large sample volumes (mL) lead to inability to address the growing demand for simple and convenient monitoring approaches.

Electrochemical techniques, including anodic and cathodic stripping voltammetry [16–18], offer attractive alternatives that are not only sensitive and reproducible, but are rapid and are easy to miniaturize [19,20]. These approaches have been demonstrated for the determination of Mn(II) with bulk electrodes fabricated from a wide range of electrode materials, including mercury [21,22], bismuth [23,24], boron-doped diamond [24,25], carbon [26–30], and carbon nanotubes [31]. To address the need for a portable detection system, microscale electrodes are necessary—for instance a stencil-printed carbon ink electrode on transparent film reported by Bert. *et al.* [32], platinum (Pt) microdisk electrodes or microelectrode arrays reported by Herzog *et al.* [33,34], and disposable Pt or copper (Cu) microband electrodes from Xiong *et al.* [35]. Our group also introduced a disposable gold (Au)-based sensor and Cu-based sensors for determination of zinc (Zn(II)) [36], lead (Pb(II)) [37] and Mn(II) [38] using anodic stripping voltammetry (ASV) and Mn(II) using cathodic stripping voltammetry (CSV) [39]. A variation of the Cu-based sensor contained a thin layer of electrodeposited palladium (Pd) coated on top of the Cu working electrode, which yielded a calculated limit of detection (LOD) of 334 nM (18.3 ppb) for Mn(II). This Cu-Pd sensor provided successful and accurate determination of Mn(II) in different surface water samples, but it suffered from stability issues in complex samples that contain strong oxidants, such as HNO₃.

In this work, we use a microscale electrochemical sensor with Pt thin film electrodes for CSV analysis of Mn(II) and demonstrate significantly improved LOD, precision, and accuracy. Mn is conventionally determined by the ASV, which suffers from challenges related to an extremely negative reduction potential. Little has been reported on Mn CSV, and we found no literature on using thin film Pt electrodes; most of the literature for stripping voltammetry of Mn is using the more-popular ASV technique. As Pd and Pt are both from the platinum group, we expect them to behave similarly in electrochemical experiments. We found one comparison between Pt and Pd stating that Pt is more difficult to oxidize (requires > 0.94 V to be oxidized [40]) than Pd (starts to be oxidized at ~ 0.6 V [41]). Thus, Pt provides a larger positive potential window with smaller interference from

electrode oxides that are formed during predeposition than Pd.. This Pt sensor was optimized and calibrated for Mn determination in pH 5.5, 0.2 M acetate buffer and provided a calculated LOD of 16.3 nM (0.9 ppb), a 20× improvement over our previous results with Pd. Determinations of Mn in real-world water samples (from a pond in Burnet Woods, Cincinnati, OH) were performed, and the results show 92.5% agreement with ICP-MS measurements. Ultimately, we expect this Pt sensor to be a useful and convenient measuring component of a point-of-care system that can be widely applied in clinical or environmental sites.

Experimental methods

Reagents

Reagents were prepared from chemicals purchased from ThermoFisher Scientific, unless noted otherwise. Fluka brand acetate buffer (pH 4.65, 0.2 M) was purchased from Sigma-Aldrich, and the pH was adjusted to 5.5 by addition of NaOH(s). Acetic acid (>99.99% trace metal basis) and sodium acetate trihydrate (BioUtra, >99.5% (NT)) were purchased from Sigma-Aldrich to make 1 M acetate buffer. A 1 M borate buffer was purchased, then diluted with DI water to 0.1 M, while the pH was adjusted to 9 by addition of NaOH(s). Solutions containing Mn were prepared by diluting Mn stock solution (manganese standard solution for AAS, 1 mg/mL Mn²⁺ in 2% nitric acid, Acros Organics) with acetate buffer or borate buffer. AAS stock solutions of 1 mg/mL Zn, Cu, Au, Mg, Pb and FeSO₄(s) were also purchased to make solutions for the interference study. The silver plating solution (Silver Cylless® II 10.00 GM per 1.00 GL) was purchased from Technic Inc. A 1 M KCl solution was prepared from salt and used to chloridize the silver RE into silver/silver chloride. A 0.1 M KCL solution was diluted from the 1 M KCL solution for cleaning Pt electrodes. Nitric acid (TraceMetal™ Grade) was purchased for acidification of water samples.

Sensor

The sensors (ED-SE1-Pt) used in this study were purchased from Micrux Technologies (Oviedo, Spain). The sensors consisted of three electrodes - a circular working Pt electrode (WE) with 1 mm diameter, a Pt reference electrode (RE) that we transformed into a Ag/AgCl RE, and an auxiliary Pt electrode (AE) (Fig. 1), which is a similar design to our Cu-Pd sensor. Electrodes were confined by a SU-8 resin protective layer with a 2-mm circular opening to ensure the same electrode surface area in all experiments. The WE and AE were composed of a 150 nm thick Pt film on top of a 50 nm Ti seed layer. The Ag/AgCl RE was formed by electroplating Ag on the original Pt RE with a 3 mA/cm² cathodic current for 240 s followed by chloridizing in 1 M KCl with a 3 mA/cm² anodic current for 120 s. Before any modification of electrodes and experiments, the sensors were electrochemically cleaned by scanning 10 cycles of cyclic voltammetry (CV) in the ±1.5 V range at 100 mV/s in 0.1 M KCl solution.

Sample preparation

Water samples were collected from Burnet Woods pond (Cincinnati, OH, Oct. 21, 2015) in conical tubes (Falcon™ 50 mL Conical Centrifuge Tubes). After letting samples settle at room temperature for approximately 1 h, 29.7 mL of clear supernatant was acidified by

adding 300 μL of 1% trace metal grade HNO_3 . These samples were then stable for storage at room temperature. We spiked 50 ppb Mn into the acidified sample for further analysis. For stripping voltammetry at more neutral pHs, the samples were diluted by 2 $\times$ using pH 5.5, 1 M acetate buffer which brought the pH from ~ 1.1 to 5.02.

Experiments

The procedure of the experiments was similar to our previous work [36,39,42,43]. A miniature USB Potentiostat (WaveNow, Pine Instruments, Inc.) with AfterMath Data Organizer software was used for all electrochemical measurements. A sensor was inserted into the interface and connected to the potentiostat. The sample volume was 10 μL for all the experiments in buffer unless otherwise stated. We performed CV and CSV in acetate and borate buffer to compare the potential window of the Pt electrode and the position of the Mn reduction peak in the two buffers. After a series of optimizations of CSV parameters in pH 5.5, 0.22 M acetate buffer, we used the following parameters: 10 μL sample volume, preconcentration at 0.7 V for 900 s, stripping range from 0.7 V to -0.5 V, and waveform parameters for square wave voltammetry of 70 ms period, 4 mV increment and 25 mV amplitude. Mn from 5 ppb (91 nM) to 50 ppb (910 nM) in acetate buffer was used to construct the calibration curve and calculate LOD following $3\sigma/\text{slope}$. We used the same stripping parameters for the determination of Mn concentrations in surface water samples, while applying the standard addition method to calculate the concentration of Mn(II) in the original samples. Independent measurements of the pond water were performed using Agilent 7700x ICP-MS instrument.

Results and discussion

Optimization of CSV conditions

The experimental conditions were thoroughly investigated and optimized. First, we compared Mn(IV) reduction in two buffers – a pH 5.5, 0.2 M acetate buffer and a pH 9, 0.1 M borate buffer. The selection of pH 9 borate buffer was based on the optimal buffer condition of the Pd electrode which could enable direct comparison to our previous results [39]. Acetate buffer of pH 5.5 was selected based on work from collaborators [44] that showed buffers with a barely-acidic pH facilitate the stripping of Mn oxides and thus improve CSV peak signal [45], and also due to our endeavor to develop a sensor for the determination of multi-metals since this buffer was optimal for Pb as well [37]. We used cyclic voltammetry (CV) in these two buffers alone to obtain their potential windows, and in 20 ppm Mn^{2+} in both buffers to locate the reduction peaks of deposited MnO_2 . Background scans in Fig. 2a show a large anodic current at the positive 1.2 V starting potential, which we attribute to oxide formation on the Pt electrode, and a large cathodic current on the forward scan to negative potentials that is off scale beginning around 0 V. While both buffers provide a potential window of approximately 1 V, the window in acetate buffer is shifted ~ 250 mV more positively, which facilitates the formation of Mn oxides of Mn(III) and Mn(IV) (Fig. 2a). Addition of Mn^{2+} caused its oxidation to insoluble MnO_2 at the initial positive potential and gave a reduction of MnO_2 wave on the forward negative potential scan to reform soluble Mn^{2+} .

We observed double reduction peaks of Mn in both buffers. In acetate buffer the voltammogram with Mn peaks (solid line) overlaps well with the background voltammogram (dashed line) and it is very straightforward to evaluate the peak potential and amplitude; but in borate buffer the reduction wave descends far below the background, making it more difficult to measure the peak current. Figure 2b shows voltammograms for CSV over a more restricted potential range. We scanned the background and 100 ppb Mn^{2+} in both buffers, using 0.7 V and 1 V as preconcentration potentials in borate buffer and acetate buffer, respectively, based on CV. We observed that acetate buffer was able to provide much larger peak amplitude than borate buffer in CSV stripping voltammograms, while the background in acetate buffer agreed better with the voltammogram of 100 ppb Mn (Fig. 2b). Based on these comparisons, the pH 5.5, 0.2 M acetate buffer was selected for further analyses.

For stripping analysis, we examined experimental parameters including preconcentration time and potential, as well as the sample volume using a fixed 50 ppb Mn^{2+} solution. Since we focused on the main effect of all the parameters and considered their influences towards the resulting signal to be independent, we decided to ignore the secondary effects related to the sequence of which parameter was optimized first. Thus, we conducted the optimization of preconcentration time, sample volume and preconcentration potential, successively. In most cases, voltammograms presented as double peaks, which complicated analysis and selection of the optimal parameters. To quantify these voltammograms, we considered the amplitude of each peak, the mathematical sum of the two peak heights, and the entire peak area below both Mn peaks (Fig. 3a). For peak area measurements, we performed baseline subtraction to adjust tilted voltammograms horizontally to improve accuracy.

We selected a 900 s preconcentration time after a series of optimization experiments in which we performed CSV with preconcentration times of 120 s, 300 s, 600 s, 900 s and 1200 s to find a proper duration just before the saturation stage. Fig. 3b–c shows that the Mn reduction occurs at two separate potentials, and the amplitude of peaks grows linearly with increased preconcentration time. The increase in signal plateaued after 900 s, while at 1200 s the variation of measurements increased, indicating that the sensor might have gone through some degree of degradation. Thus, we selected 900 s due to the relatively high peak current and low coefficient of variation (C.V.) for each individual peak height, sum of peak heights, and sum of peak areas (0.2–7.4% range).

We also maximized the peak current by optimizing the volume of sample used with the sensor and selected the volume of 10 μL . Though the sample volume in our previous work [36,39,42] was 100–200 μL , this sensor only holds a droplet of up to 15 μL , due to its dimensions of 10 mm $\times$ 6 mm $\times$ 0.75 mm. Therefore, sample volumes of 5–15 μL were tested by directly pipetting onto the surface of the sensor, while volumes of 20 and 50 μL were tested with an additional PMMA batch-cell component to hold the excess, which resembled the PDMS well structure in our previous work [36,39]. The results in Fig. 3d–e show that the peak current does not follow the increasing of sample volume, but decreases drastically when we applied larger volumes in the external component. Based on the long preconcentration time of 900 s and the associated evaporation effect of reducing a large portion of droplet volume, we found the smaller droplets to be more advantageous in “on-

chip concentrating” compared to large volumes of sample in a well. Still, the volume of 5 μL is low and the limited amount of Mn ions could not generate a comparable signal even if they were completely deposited on the electrode. Therefore, 10 μL was chosen as the sample volume for the following experiments.

We investigated the preconcentration potential, which strongly affects the reduction process of Mn, and selected the optimal value of 700 mV. Fig. 3f–g show that with a deposition potential 700 mV, only one reduction peak occurs at ~ 340 mV with the largest peak currents and peak areas. For potentials in the 0.8–1.0 V range, double peaks occur, suggesting the reduction has gone through an intermediate state of Mn (III) [46–49]. Also it is common for double stripping peaks to occur on solid electrode [45,50], due to stripping of the bulk portion of the deposited analyte occurring at a different potential than stripping of the first monolayer on the electrode. Typically, double peaks are not preferred due to the increased analysis difficulties. Also the amplitude of peak height for each individual peak or the sum of the two peak heights/areas is smaller than those from the 700 mV voltammograms. Furthermore, 1.1 V is not preferred not only due to the low level of signal, but the background peak that occurs at ~ 900 mV indicating the electrode has been oxidized as well. Based on the comparison, the 0.7 V potential was selected for deposition of Mn even though this potential is at the edge of the potential window.

Calibration of Pt sensor

To further explore the electrochemical characteristics of the Pt sensor, we calibrated it in 0.22 M, pH 5.5 acetate buffer under the optimized conditions. We selected the range of Mn^{2+} from 5 ppb to 50 ppb to bracket the physiologically relevant range in our applications which is 4–15 ppb [10], and the safety limit of drinking water which is 50 ppb [9]. The calibration plots and voltammograms are shown in Fig. 4. Each data point was repeated $3\times$ ($n = 3$) to obtain standard deviation and C.V., while the lowest measured concentration of 5 ppb was repeated $6\times$ ($n = 6$) for the calculation of LOD. A new sensor was used for each concentration to eliminate interferences from the previous sample.

We present a series of representative voltammograms in Fig. 4a, after performing the Savitzky-Golay Smoothing technique to reduce any insignificant noise. We noticed the reduction peak of Mn(IV)O_2 gradually shifts from ~ 377 mV to ~ 325 mV with increasing Mn(II) concentrations. For all the concentrations, the reduction process (the peak) starts at approximately 500–600 mV. At higher concentrations, such as 35 or 50 ppb, it is possible that the larger amount of oxide deposited requires longer time to reduce. That leads to a longer stripping process (from ~ 600 mV to ~ 200 mV) and thus less positive Mn peaks. The Mn oxides from the lower-concentration samples are easier and faster to reduce, so they are mostly stripped before ~ 350 mV. Apart from the Mn peak, the background voltammogram of pH 5.5, 0.22 M acetate buffer is clean and does not show any minor reduction peak of Pt oxide at ~ 300 mV, as in the case of the Pd WE [39]. However, we consider it necessary and beneficial to subtract the baseline (background) from the measurement voltammograms since the baseline is not 100% horizontal below the peaks of the voltammograms, and thus the Mn reduction peaks are located at the foot of a slope.

The baseline subtraction approach ensures accurate measurements of Mn peak for plotting the calibration curve. As in our previous work, first a virtual average baseline (the gray curve in Fig. 4a) was acquired by averaging 8 baseline curves in pH 5.5, 0.22 M acetate buffer from 8 separate scans on different sensors. Then we subtracted this virtual baseline from every original voltammogram to flatten the starting and ending point of a Mn peak to the horizontal level (Fig. 4b). After subtracting the baseline, we measured the amplitude (current) and area (charge) of the Mn reduction peak and plotted the calibration curves for both (Fig. 4c) in two units (nM, ppb). This calibration demonstrates 99.6% of linear relationship between the stripping peak current and the concentration of Mn. The correlation equation of peak amplitude measurements is $I \text{ (nA)} = (1.39_4(\pm 0.03_8))([Mn \text{ (nM)}]) - 8.6(\pm 17.7)$ ($R^2 = 0.996$ for 7 data points), with a sensitivity of 1.39 nA/nM or 25.38 nA/ppb ($177.49 \text{ nA/nM/cm}^2$ or $3.23 \text{ } \mu\text{A/ppb/cm}^2$ when normalized to WE area). The LOD is calculated as 16.27 nM or 0.89 ppb based on $3\sigma/\text{slope}$ ($n = 6$). The correlation equation of peak area measurements is $Q \text{ (nC)} = (3.55(\pm 0.1_6))([Mn \text{ (nM)}]) + 162.4(\pm 74.2)$ ($R^2 = 0.990$ for 7 data points), with a sensitivity of 3.55 nC/nM or 64.6 nC/ppb (451.7 nC/nM/cm^2 or $8.2 \text{ } \mu\text{C/ppb/cm}^2$ when normalized to WE area). This LOD is calculated as 31.60 nM or 1.736 ppb based on $3\sigma/\text{slope}$ ($n = 6$), which is less favorable than the calculation based on peak amplitude; thus, we selected the peak height calibration curve with a LOD of 16.27 nM (0.89 ppb) as the better procedure. Compared with our previous work using a Cu-Pd sensor [39], the LOD has been improved 20× lower, and the sensitivity improved by almost 32×. The performance is also comparable to work by others using bulk electrodes and solutions reporting LOD in the nM range [24,31]. Furthermore, by calculating C.V. we achieved an average precision of 97%, and by calculating Mn concentrations from the equation, we achieved an average accuracy of 96%.

Sensor performance

In addition to calibration, we evaluated other factors that contribute to the electrochemical performance of the sensor. As we discussed previously, the sample droplet underwent an “on-chip concentrating” effect through evaporating a large portion of volume during the 900 s preconcentration step, which facilitates the predeposition of Mn. To quantitatively study the advantage of evaporation, we performed measurements of the same 50 ppb Mn solution with two types of operations with five different time combinations. “Pure evaporation” refers to the process when the sample was placed on the sensor without any bias on the WE, while “preconcentration” refers to the preconcentration step in CSV with the WE biased at 0.7 V. In all cases the samples were agitated by a vibration mixer. We tested the conditions where only the preconcentration step with biased WE is involved (Fig. 5: I, II), and also tested the condition with the pure evaporation step in advance of the CSV preconcentration step (Fig. 5: III, IV, V).

The comparisons of Mn peak height in Fig. 5 demonstrated that 900 s of long preconcentration time with biased WE is the most critical factor for achieving amplified signal. First we tested a sample with 900 s preconcentration time without any evaporation (I) as we put the sample in a tape-sealed well, then compared it with the results that had evaporation (II) during the 900 s preconcentration. This comparison confirmed that evaporation improved the signal by 6×. For the two experiments that both include 900 s

deposition time with evaporation (II, III), the 300 s extra evaporation step (III) only increased signal by 1%, which is negligible. With less than 900 s predeposition time (IV, V), the peak heights are only 60–70% of that with 900 s, even though the droplets have been exposed and evaporated for the same duration if counting the first non-biasing step.

We quantitatively evaluated the advantage of the sample evaporation effect by measuring the volume before and after each analysis. The measurements of the weight of sample droplets applied in 27 independent CSVs showed an average of $10 \pm 0.056 \mu\text{g}$ which proved that the sample volume was accurately $10 \mu\text{L}$ each time. The final weight/volume was also measured and it turned out to be $3.08 \pm 1.01 \mu\text{L}$, with a large C.V. of 32.9%. Since the final volumes which decide the final concentration had no impact on all the voltammograms, and our calibration provided ~97% of precision (C.V. $\approx$ 2.8%), we hypothesized the variation in final sample volume did not affect the reproducibility of measurements, and this sensor behaves in a “mass-sensitive” manner instead of “concentration-sensitive”.

To further test the reproducibility of the Pt sensor and determine the precision of the measurements, we performed CSV of 10 ppb Mn on 6 different sensors, repeating $3 \times (n = 3)$ for each sensor. The selection of 10 ppb Mn was made based on the physiological range of Mn in blood. The measurements of peak current and C. V. (Fig. 6) illustrate consistent current values from ~180 nA to 210 nA with an average of ~200 nA. Also, 5 out of 6 sensors generated C. V. values lower than 10%, with an average C. V. of 9%. Thus, we have confirmed that this commercial sensor is capable of performing reproducibly with precision above 90%.

Study of interferences

We performed a series of studies of metals that might potentially interfere with Mn CSV, to ensure accurate and reliable determination of Mn in real-world samples. Though CSV is less susceptible to interferences of intermetallic species than ASV [25], we are aware of some metals that either strip at potentials similar to Mn, or affect the deposition/stripping process of Mn. We selected several metal ions including Pb^{2+} , Fe^{2+} , Au^{3+} , Zn^{2+} , Cu^{2+} , and Mg^{2+} to investigate based on literature [21,24,25,51]. Pb^{2+} and Fe^{2+} are considered the most common interferences for Mn, Au electrodes generated a reduction peak at ~300 mV in our previous study, and the other metals are among the typical essential elements in surface waters or blood. The influences of different levels of these metals – 0, 10, 100, 1000 ppb were analyzed by spiking them into 10 ppb Mn solution, followed by comparisons of the peak amplitudes and voltammogram definition of CSV under the exact same conditions.

We confirmed that with a ratio of 100:1, Au, Zn, Cu and Mg have no significant influence on the Mn stripping signal, but Pb and Fe(II) are interfering with Mn CSV (Fig 7a), Fig 7bc demonstrates that Pb partially affects the stripping of Mn when the ratio of Pb: Mn is high (orange, and navy curves in Fig. 7b), and it has no noticeable influence on Mn as long as they are at a similar level. According to ATSDR, the Pb concentration in healthy human blood should be below $5 \mu\text{g/dL}$ (50 ppb). Thus, we are not concerned about the minute amount of Pb when we are measuring blood samples. In extreme cases where a subject shows high Pb blood level, immediate attention should be focused on Pb not Mn due to the higher toxicity. On the other hand, Fig. 7d–e indicate that Fe(II) is directly impeding Mn

CSV – the Mn peak diminished as Fe^{2+} was added, and was completely suppressed when the Fe^{2+} concentration reached the ppm range. Fortunately in natural water samples, the concentration of Fe metal would normally be at sub ppm levels [52] with an even lower level of Fe^{2+} , which ensures the determination of Mn would not be influenced. Nevertheless, literature showed Fe(II) can be easily oxidized chemically (for instance, acidification in sample preservation) or electrochemically to Fe(III) which does not affect Mn CSV [25].

Determination of Mn in surface water

We used the Pt sensor for the determination of Mn in pond water from Burnet Woods, Cincinnati, since surface waters are related to the long term exposure of humans. In this study, we tested two water samples using the standard addition approach: the original Burnet Woods pond water (BWPW) sample (1) with 1% acidification using nitric acid, and sample (3) with 50 ppb Mn addition into sample (1) to simulate a highly-polluted water sample. We analyzed both samples using ICP-MS for confirmation and to compare the accuracy of our measurements. Titration of additional NaOH(s) to adjust sample pH was not preferred as this method can randomly reduce the amount of free Mn^{2+} by creating a temporarily-highly-basic region in the bulk sample, which might cause the formation of Mn oxide precipitates. Thus, we performed a simple dilution of the samples by 2× using a pH 5.5, 1 M acetate buffer to raise the pH of the sample to ~5, which yields a dilution factor of 0.495.

For both samples, CSV was performed after dilution and addition of three different concentrations: 10, 20, 30 ppb Mn. The representative voltammograms of diluted BWPW#3 sample are shown in Fig. 8a. Compared to the background in acetate buffer (pH 5.5, 1 M), we observed the baseline part of the curves (red arrow in Fig. 8a) from water sample (pH 5.02) shifted positively by 80~96 mV due to a combination of a change in reference electrode half-cell potential and a change in the peak potential caused by the pH dependence of the redox processes. As a result, the Mn stripping peak also shifted from ~325 mV to ~400 mV in parallel, suggesting the minor amount of nitric acid did barely affect the RE. Since the shift is small, we do not view this as a problem. Also note that we were only targeting the peak current which was not directly related to peak potential, thus we neglect this minute shift of Mn peak potential introduced by the naked RE.

After baseline subtraction, we measured peak area instead of peak height since the Mn peaks broadened due to the complexity of the matrices and we did not consider measuring peak height sufficiently accurate. The resulting standard addition plot of peak area (Fig. 8b) provides a correlation equation of $Q \text{ (nC)} = (50.5(\pm 7.3))[\text{Mn (ppb)}] + 2541.2 (\pm 136.5)$ ($R^2 = 0.96$ for 4 data points), with a sensitivity of 2.88 nC/ppb, which is in the same order of magnitude as the sensitivity of calibration in buffer (64.6 nC/ppb). Using this equation and the dilution factor, we calculated the Mn concentration in BWPW#3 to be 101.7 ppb, leading to an accuracy of 92% in comparison to the ICP-MS result of 94.6 ppb. The precision of this experiment was 96.4%. The BWPW#1 was also analyzed following the same procedure and we determined 52.3 ppb Mn with a 95.3% precision and an 89.5% accuracy compared to ICP-MS result of 47.3 ppb.

Conclusions

We found the performance of the Pt sensor described here for CSV determination of Mn to be superior to that of the Cu-Pd sensor that we reported earlier [39]. Although Pt is considered an expensive material, this sensor can be simply batch-fabricated at a reasonable cost, and can be reused for multiple determinations if cleaned properly by scanning CV. Moreover, it only requires less than 20 μL of sample, which is a great advantage for POC applications over the conventional methods such as AAS or ICP-MS. This type of microfabricated Pt sensor that is commercially available from a number of vendors (such as Micrux) was found to be suitable for this application, which makes the method we have developed more readily available.

We investigated the potential window, optimized the experimental conditions and calibrated the Pt sensor and found Pt to have similar electrochemical properties to Pd, but improved robustness for this application. Most importantly, we obtained a calculated LOD of 16.3 nM (0.9 ppb) in pH 5.5, 0.2 M acetate buffer (97% precision and 96% accuracy for calibration), which is an improvement of 20 $\times$ over the calculated LOD of 334 nM (18.3 ppb) that we reported for the Pd electrode [39]. We also carefully studied the performance of the sensor, with respect to evaporation of the very small sample and reproducibility between different sensors. The study of potentially interfering metal ions demonstrated that samples of environmental origin that contain Fe and Pb would require more caution during analyses. We applied this Pt sensor for the determination of Mn in a surface water sample, and achieved average precision >97% and accuracy of ~90% by validation using independent ICP-MS measurements. With stable, accurate and precise electrochemical performance, this Pt sensor enables convenient on-site monitoring of Mn in environmental samples when coupled with portable instrumentation, and could potentially be used for biological samples with appropriate sample preparation.

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Fig. 1. Microfabricated sensor with thin film Pt electrodes. (a) A microscopic image of the three electrodes: Pt WE and AE, Ag/AgCl RE (WE = working electrode, RE = reference electrode, AE = auxiliary electrode). (b) Interface for the convenient connection between a sensor and potentiostat (sensor dimensions: 10 mm $\times$ 6 mm $\times$ 0.75 mm).

Fig. 2.

Comparisons of electrochemical performance of the Pt sensor in acetate and borate buffers. (a) CVs of the Pt sensor in pH 5.5, 0.2 M acetate buffer (5.5AB) and pH 9, 0.1 M borate buffer (9BB) alone, and with additional 20 ppm Mn to illustrate the location of Mn reduction peak(s). (b) SWCSV background scans in the two buffers and with 100 ppb Mn to show the Mn stripping peaks. With the comparison of CV and CSV voltammograms, pH 5.5, 0.2 M acetate buffer was selected for the following experiments.

Fig. 3.

Optimization of experimental parameters for Mn CSV by comparisons of the peak height (current) and peak area (charge) of the Mn stripping peak in 50 ppb Mn in pH 5.5, 0.2 M acetate buffer. (a) Demonstration of how the peak heights of the left and right peaks, sum of both peak heights, and peak area were quantified. Optimization of (b–c) preconcentration time, (d–e) sample volume and (f–g) preconcentration potential. Eventually we chose 900 s, 10 μL and 0.7 V for the preconcentration step.

Fig. 4. SWCSV determination of Mn in pH 5.5, 0.2 M acetate buffer for the 5–50 ppb (91 nM–910 nM) range. (a) Stripping voltammograms of Mn after baseline subtraction. (b) Calibration plot of peak current (blue) and peak area (red) measurements after baseline subtraction, each is shown in two units: the solid-colored (red and blue) font refers to Mn concentrations in nM, while the faint-colored font refers to ppb. CSV parameters: 0.7 V and 900 s preconcentration; 10 μL sample volume; 70 ms period, 4 mV increment and 25 mV amplitude for the square wave.

Fig. 5.

Comparison and validation of the evaporation effect of 10 μ L sample droplets during the 900 s preconcentration step. Two types of operations with five different time/duration combinations are compared. The times of pure evaporation without any bias on WE are shown in the red dashed boxes, while the times of standard preconcentration step in CSV with WE biased at preconcentration step are directly listed as well. Details of each profile: I. 900 s preconcentration with the sample well sealed by a tape to eliminate evaporation effect; II. 900 s standard preconcentration (WE biased to preconcentration potential) directly; III. 300 s pure evaporation (WE not biased) + 900 s preconcentration (WE biased); IV. 600 s evaporation + 300 preconcentration; V. 300 s evaporation + 600 s preconcentration.

Fig. 6. Study of reproducibility by measuring 10 ppb Mn on 6 different sensors, and comparing the peak amplitudes with coefficients of variation (C.V.).

Fig. 7.

Study of potentially interfering metals for Mn CSV by measuring 10 ppb Mn in the presence of 0, 10, 100, and 1000 ppb of an additional metal. (a) Peak height comparisons of 10 ppb Mn with 1000 ppb of six other metals. Detailed study of (b–c) Pb and (d–e) Fe affecting Mn measurements as the concentration increases. CSV parameters: 0.7 V and 900 s preconcentration; 10 μ L sample volume; 70 ms period, 4 mV increment and 25 mV amplitude for the square wave.

Fig. 8.

Determination of Mn in Burnet Woods pond water (BWPW#3) using SWCSV and method of standard additions. (a) Voltammograms of the diluted sample with and without Mn additions. (b) Standard addition plot of peak area after baseline subtraction. The original concentrations of Mn in the water sample can be calculated using the equations from (b) and dilution factors. CSV parameters: 0.7 V and 900 s preconcentration; 10 μL sample volume; 70 ms period, 4 mV increment and 25 mV amplitude for the square wave.