

Catalytically enhanced spectrophotometric determination of manganese in seawater by flow-injection analysis with a commercially available resin for on-line preconcentration

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Abstract

The sensitive, laboratory- and ship-based, flow-injection (FI) method for the determination of dissolved manganese in seawater developed by Resing and Mottl (*Anal. Chem.* 1992;64:2682-2687) has been significantly modified and improved by incorporating five significant changes. The three major changes are the use of a commercially available iminodiacetate (IDA) resin (Toyopearl AF-chelate 650M) in place of 8-hydroxyquinoline for on-line preconcentration of manganese and matrix removal, the addition of nitrilotriacetic acid as an activator ligand which increases sensitivity by a factor of 7 and decreases the limit of detection, and the on-line buffering of acidified samples before column loading. Two minor improvements include use of the more soluble sodium periodate in place of potassium periodate and elimination of Brij-35 surfactant. To accommodate these changes, the pH of samples was adjusted to 8.5 (vs. 7.8), a higher acid concentration was required to elute the Mn from the IDA resin, and stronger reaction buffer was required to neutralize the acid. The accuracy of the method was evaluated with the use of NASS-4 standard seawater and by a comparison study of samples from the California coast that were analyzed by this method and an FI method coupled to inductively coupled plasma sector field mass spectrometry detection. The detection limit and precision of the method depend on the amount of sample preconcentrated onto the column. By preconcentrating 1.6 mL of sample, a detection limit of 0.03 nM (3 times the standard deviation of a blank) and precision of 3.2% (as percent relative standard deviation) were obtained. The method was used on board ship to determine dissolved manganese in coastal waters off Oregon and Washington.

Introduction

In addition to being an essential micronutrient, dissolved manganese can serve as a tracer of a wide variety of marine biogeochemical processes, such as coastal inputs (Landing and Bruland 1980; Jones and Murray 1985), river plume dispersion (Aguilar-Islas and Bruland in press), hydrothermal activity (Klinkhammer and Hudson 1986; Mottl et al. 1995), anoxic/suboxic conditions (Johnson et al. 1996, Rue et al. 1997), and eolian inputs (Shiller 1997). As a result of its biogeochemistry,

dissolved manganese is found in a large range of concentrations in the ocean, from less than 100 pM in the deep ocean (Landing and Bruland 1980; Statham et al. 1998) and the surface waters of the Ross Sea (Sedwick et al. 2000), to values of 10 μ M or greater in pore waters of shelf and slope sediments (Shaw et al. 1990; Luther et al. 1998; Berelson et al. 2003), to thousands of μ M in hydrothermal solutions (Von Damm et al. 1985; Butterfield et al. 2003). An ideal method for the determination of dissolved manganese in seawater would therefore have a flexible analytic window (pM to μ M) and the ability to carry out measurements in near real-time. Determination of dissolved manganese in seawater is made difficult not only by its low concentrations, but also by the presence of a matrix of major ions at concentrations generally 10^6 to 10^{10} times greater than that of dissolved manganese itself. Consequently, removal of the seawater matrix and an increase in the concentration of dissolved manganese are essential for successful determination of its levels in seawater. These tasks have been effectively accomplished through a preconcentration step using a chelating resin (e.g., Resing and Mottl 1992; Ndung'u et al. 2003; Lohan et al. 2005). To date, the most common

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chelating resin used for this key step contains 8-hydroxyquinoline (8-HQ) as the chelating group. The 8-HQ resin is appealing because of its affinity for binding several metals; however, it is not commercially available and its synthesis is somewhat involved (Landing et al. 1986), producing resins of varying quality. Dierssen et al. (2001) simplified the synthesis of the 8-HQ resin, but unfortunately the resin produced retains manganese poorly. Commercially available resins suitable for on-line preconcentration of metals are preferable, because the quality of the resin is reproducible, and because their use simplifies system setup.

In recent years, new methods for the determination of dissolved manganese in seawater using flow injection (FI) have been developed (e.g., Chapin et al. 1991; Resing and Mottl 1992; Mallini and Shiller 1993). The advantages of these methods include rapid analysis, ship-board use, low sample and reagent consumption, and reduction in the risk of contamination. In particular, FI is ideal for kinetic catalytic methods (e.g., Resing and Mottl 1992; Mallini and Shiller 1993) because the catalytic role of the analyte makes these methods time dependent, and FI provides reproducible reaction times and reagent addition. The sensitivity of a kinetic catalytic method is enhanced by increasing reaction times, which in FI is accomplished through longer reaction coils or slower flow rates. However, increasing the length of the reaction coil increases not only the time of analysis, but also dispersion, which lowers sensitivity, while slower flow rates result in a decrease in mixing efficiency (Selavka et al. 1987).

An alternative approach to improve sensitivity is the use of activator ligands. An activator is a chemical species that is not the catalyst, but its presence increases the reaction rate considerably and, "from an analytical point of view, yields a better sensitivity and lower limit of detection in a catalytic determination" (Mottola 1988). Nitrotriacetic acid (NTA) has been used as an activator in a batch method (Mottola and Harrison 1971) for the oxidation of malachite green by periodate, a reaction catalyzed by manganese. The enhanced catalytic effect exerted by the presence of NTA appears to be related to the formation of NTA-Mn complexes (Nikolelis and Hadjiioannou 1978; Mottola 1974), although the exact mechanism is not well understood. One hypothesis is that NTA participates in the regeneration of Mn(II) (Mottola 1988) by keeping Mn(III) in solution. A second hypothesis is that the NTA-Mn complex introduces favorable steric factors (Mottola 1988) that facilitate the catalytic role of Mn.

This article presents significant improvements to the method described by Resing and Mottl (1992). In addition to minor modifications, three major changes to the method were carried out. The first was to replace the 8-HQ resin with a commercially available iminodiacetate (IDA) chelating resin (Toyopearl AF-chelate 650M) with a high affinity for binding manganese ions at pH 8 to 9. The second was the addition of an activator (NTA) to the color-forming catalytic reaction. The third change involved the on-line adjustment of sample pH

using a borate buffer before the preconcentration step. These changes improved the method's ease of use and sensitivity and reduced the risk of contamination from sample handling. This is a versatile method that can be easily adjusted to optimally detect dissolved manganese over a wide range of concentrations.

Materials and procedures

Apparatus—A schematic diagram of the flow-injection manifold is illustrated in Figure 1. The manifold consists of one 8-channel peristaltic pump (Dynamax, Rannin), two electronically actuated 6-port valves (VICI, Valco Instruments), three 1-m mixing coils, one 3-m reaction coil, a preconcentration column (made of chlorotrifluoroethylene [KEL-F]) with a tapered inner chamber (85 μ L) and nonmetal frits (1-cm mini-column; Global-FIA), a variable wavelength spectrometer (USB-2000; Ocean Optics), a tungsten light supply (LS-1; Ocean Optics), two optical fibers with SMA-905 connectors (diameter 100 μ m, length 1 m; Ocean Optics), a cuvette holder with SMA adaptors (CUV-UV; Ocean Optics), and a 10-mm pathlength quartz flow cell (Starna Cells). The mixing and reaction coils (knotted as described by Selavka et al. [1987]) and all other manifold tubing are 0.5-mm i.d. PFA Teflon tubing (Upchurch Scientific). All pump tubing is 2-stop PVC tubing (Fisher Scientific). All connections are 1/4-28 low-pressure Tefzel flangeless fittings (Upchurch Scientific). The preconcentration column is filled with Toyopearl AF-Chelate-650M resin (Tosohass). The 3-m knotted reaction coil is kept at constant temperature (35 $^{\circ}$ C). We used a custom-made column heater and wrapped the reaction coil around it, although we have also successfully used a modified, commercially available dry bath (see Resing and Measures [1994]). The data acquisition and valve control software (FIALab Instruments) is operated using a laptop computer (IBM). To minimize contamination, solution bottles are placed within a class-100 flow bench.

Reagents—All solutions were prepared with deionized water (18 M Ω cm $^{-1}$) from a Milli-Q analytical reagent-grade water purification system (Milli-QW; Millipore). Subboiling quartz-distilled 6 M hydrochloric acid (Q-HCl) was prepared by a single distillation from trace metal grade 6 M HCl (Fisher Scientific) in a quartz-finger subboiling still. Trace metal grade glacial acetic acid (HAc) (Fisher Scientific) and trace metal grade ammonium hydroxide (NH $_4$ OH) (Fisher Scientific) were used as received. Ammonium acetate crystals were prepared by bubbling anhydrous ammonia gas into subboiling quartz distilled glacial acetic acid (Q-HAc) (prepared by single subboiling distillation from trace metal grade glacial acetic acid [Fisher Scientific]) and allowing the solution to cool slowly. Leucomalachite green (LMG) (Acros), sodium periodate (NaIO $_4$) (Acros), NTA (Fisher Scientific), and boric acid (Fisher Scientific) were used as received. Reagents were prepared and stored in acid-washed low-density polyethylene bottles. A solution of 0.4 mM LMG was prepared in a dark 1-L bottle by adding 2 mL of 6 M HCl to 100 mL of Milli-QW, followed by

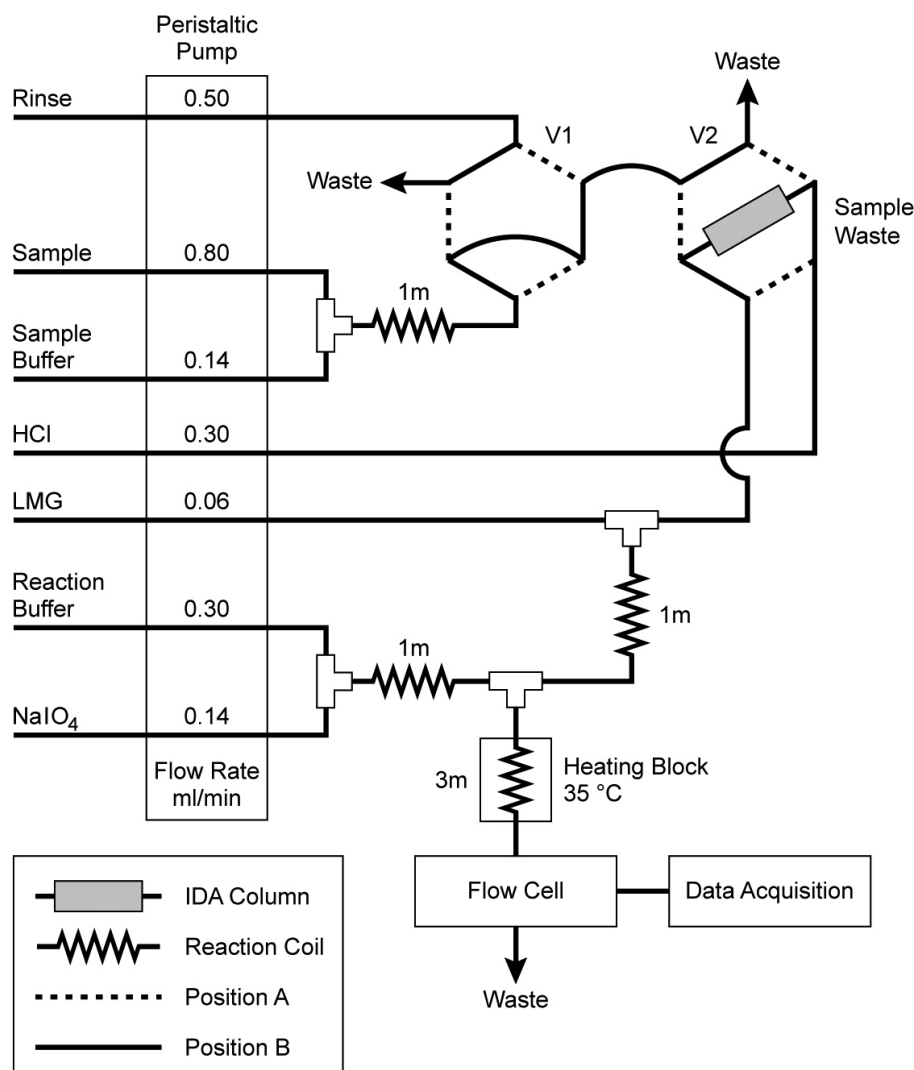


Fig. 1. Schematic diagram of FI system manifold.

the addition of 120 mg LMG. The solution was stirred slowly for 2 h and brought up to a final volume of 1 L with Milli-QW. The final solution was stirred overnight, filtered, and kept in a dark bottle. We have also filtered LMG in line using polyethylene or PEEK bottom of the bottle filters (Upchurch Scientific). This reagent is stable for at least 1 month (Resing and Mottl 1992). Sodium periodate (0.01 M) was prepared by adding 2.2 g NaIO₄ to 1 L Milli-QW. This reagent is stable for approximately 1 month. A stock ammonium acetate buffer (3 M) was prepared by diluting 156 mL of a saturated ammonium acetate solution (made from ammonium acetate crystals) to 1 L. This reagent is stable indefinitely. A working ammonium acetate buffer (3 M) was prepared by adding 2 g NTA per 500 mL stock buffer. The pH was adjusted to 5.3 using either 3 M NH₄OH or 3 M HAC. This reagent is stable for approximately 1 month. An ammonium borate sample buffer

(0.5 M) was prepared by dissolving 30.9 g boric acid in 1 L of 0.5 M ammonium hydroxide (pH 9.4). This reagent is stable indefinitely. An ammonium borate (0.05 M) rinse solution was made from the ammonium borate buffer.

Procedure—Samples, standards, and blanks were acidified to approximately pH 1.7 with 6 M Q-HCl at least 30 min before analysis. The manifold setup is shown in Figure 1. Valves 1 and 2 are placed in position A and the peristaltic pump is set at speed 4.5, resulting in the flow rates shown in Table 1. During the loading phase, the column is first conditioned with the rinse solution for 30 s; valve 1 is then switched to position B and the buffered sample is loaded onto the column for a fixed amount of time (10 to 180 s) depending on the expected manganese concentration. Valve 1 is switched back to position A and the major seawater cations are rinsed from the column for 30 s. Manganese is then eluted by switching valve 2

Table 1. Pump tubing, reagent flow-rates, and concentrations in flow stream.

	Tubing i.d. (inches)	Flow rate (mL min ⁻¹)	Concentration in flow stream (mM)
Sample/standard	0.06	0.80	—
Borate buffer	0.02	0.14	—
Rinse	0.045	0.50	—
Eluting acid	0.03	0.30	330
LMG	0.016	0.06	0.03
Periodate	0.02	0.14	3.77
Reaction buffer with NTA*	0.03	0.30	

*1 × 10³ ammonium acetate, 7.8 NTA.

to position B, causing the eluting acid to flow through the column in the opposite direction from that during the loading phase. The column is eluted for 180 s while a new sample is placed on-line, and the procedure is repeated. During the loading phase, the eluting acid mixes directly into the reagents downstream, producing a baseline for absorbance. The system is flushed daily with HCl (pH ~1) prior to shutdown.

Assessment

Method development and system optimization studies were initially carried out to assess the use of Toyopearl AF-Chelate-650M resin in the preconcentration step and to assess the feasibility of buffering samples on-line. The method was then used to analyze acidified (pH 1.7) samples from the California coast. The results were compared to those obtained for the same suite of samples analyzed by a FI system coupled to inductively coupled plasma sector field mass spectrometry (ICP-SFMS) detection (Beck et al. 2002). Recently, the method was further optimized to include NTA as an activator, and the periodate salt was changed from potassium periodate (KIO₄) to NaIO₄ owing to the higher solubility at neutral pH of the latter (see Resing and Mottl [1992] for the preparation of KIO₄). The method as presented here reflects these additional changes and has been used successfully on board ship to determine dissolved manganese off the Washington and Oregon coasts.

Preconcentration column—A commercially available tapered column was used. The main advantage these columns have over custom-made columns is in their tapered design, which produces sharp elution peaks. These columns are available in 2- and 1-cm lengths. The 1-cm column (85 μL) holds sufficient resin to allow loading the volumes of sample presented here without exceeding the column's capacity, while creating less backpressure in the system than the 2-cm columns. Therefore a 1-cm column was used for preconcentrating the sample.

Rinsing and conditioning of the preconcentration column—The optimal rinsing time to remove the seawater matrix from the column was evaluated by loading samples of varying salinities (100%, 50%, and 10% seawater) for 180 s onto the column followed by rinsing the column for 0, 30, or 60 s, and then elut-

ing the column with HCl. The eluted effluent was collected into acid-washed polyethylene vials and analyzed for Ca, Mg, Na, and K by inductive couple plasma optical emission spectrometry. With the 30-s rinse K⁺, Na⁺, and Mg²⁺ were efficiently removed from the column (100%, 99%, and 97%, respectively, for all samples), but Ca²⁺ was partially retained by the resin. After the 30- and 60-s rinses, a similar Ca²⁺ concentration (~ 3 mg/L) was eluted from the column for the three tested salinities (~ 43% of the Ca²⁺ retained by the column for the 100% seawater sample during the 0-s rinse). Thus the use of the IDA preconcentration column and subsequent rinsing of the column provides a constant and low Ca²⁺ concentration for salinities > 3 (≥ 10% seawater) and efficiently removes K⁺, Na⁺, and Mg²⁺ (see Resing and Mottl [1992] for Mg²⁺ effects on sensitivity). To investigate the potential effect of Ca²⁺ on sensitivity, a batch test (25-min reaction time) with varying Ca²⁺ concentrations (0, 3, and 500 mg/L) was conducted. It was found that for the first 7 min of the reaction (the reaction takes ~ 5 min in the 3-m coil of the FI system), the sensitivity in the 0 mg L⁻¹ and 3 mg L⁻¹ Ca²⁺ solutions was identical, whereas the 500 mg L⁻¹ Ca²⁺ solution showed a 9% decrease in sensitivity. Thus for the method's reaction time (~ 5 min) the constant and low Ca²⁺ concentration (3 mg/L) present in the reaction stream (for salinities > 3) does not appear to affect sensitivity.

The rinse solution was also passed through the column before sample loading to remove the remaining acid and condition the resin, ensuring the pH of the column was optimal when sample loading was initiated. This is important to convert the chelating resin from the acidic to the ammonium form and ensure quantitative recovery of Mn during the entire loading step.

Column loading pH—Toyopearl AF-Chelate-650M has been successfully used to quantitatively preconcentrate manganese from seawater at pH 8.8 and 9.0 (Warnken et al. 2000; Beck et al. 2002). To confirm and establish the optimal pH at which the IDA groups of the resin bind Mn(II), a series of acidified (pH < 1.7) seawater samples with dissolved manganese concentrations ([Mn²⁺]) of ~ 10 nM were used. The sample pH was adjusted (from 5.5 to 9) using ammonium chloride. An optimal response was found for pHs between 8 and 9. To bring acidified samples to this pH, an ammonium borate buffer (buffering range from pH 8.5 to 10.2 and pK_a of 9.24 in distilled water) was used. At ionic strength ~ 0.5 M, the pK_a of ammonium borate is 8.97, thus shifting its buffering range in seawater to slightly lower pHs. A detailed pH study was carried out using a series of ammonium borate buffer concentrations (0.2 to 1.0 M) (Table 2) and seawater samples with [Mn²⁺] ~ 20 nM. The peak area (i.e., amount of manganese present in the reaction) was not significantly different when loading samples from pH 8.3 to 8.7 (Table 2). This is in contrast to the optimal loading pH of 8.8 determined by Warnken et al. (2000). An advantage of having a wider loading pH range is the flexibility in making the buffer solution (especially at sea). A 0.5 M ammonium borate solution was chosen as the sample buffer

Table 2. pH of loading (ammonium borate) buffer and system response.

[Borate]	Buffer pH	Loading pH	Peak area
0.2 M	9.2	6.0	0.006*
0.3 M	9.3	8.3	0.210 ± 0.002†
0.4 M	9.3	8.4	0.213 ± 0.003†
0.5 M	9.3	8.5	0.215 ± 0.002†
1.0 M	9.4	8.7	0.212*

* $n = 1$; † $n = 3$.

(sample loading pH of 8.5). Tris(hydroxymethyl)aminomethane-HCl buffer (see Resing and Mottl [1992]) could also be used as sample buffer; however, its lower pK_a suggests that more buffer or a higher pH might be required.

Eluting acid concentration—The strength of acid required to efficiently elute Mn off the IDA resin was investigated using different concentrations of HCl ranging from 0.1 to 1.5 M HCl. First a seawater sample with a relatively high $[Mn^{2+}]$ (~ 40 nM) was loaded (for 60 s) and eluted (for 180 s) three consecutive times. After the third sample, a blank (pH 1.7 Milli-QW) was loaded for 1 s and eluted for 180 s. This blank contained residual manganese present in the column and, by comparing the magnitude of its peak to that of an actual blank, it was determined that the lowest concentration of HCl capable of completely removing manganese from the column in 180 s was 0.9 M. This is a considerable increase in acid concentration from that (0.04 M) used in the method of Resing and Mottl (1992), in which manganese was eluted from an 8-HQ resin.

Reaction pH—The optimal reaction pH was expected to be different from that in the method of Resing and Mottl (1992) owing to the addition of NTA and the exclusion of the surfactant Brij-35 (see below). The pH of maximum response for the preconcentration method of Resing and Mottl (1992) was ~ 4.15; whereas the optimum reaction pH for this method was found to be ~ 4.0. Because the concentration of the eluting acid was increased to 0.9 M, the flow rate and the concentration of the reaction buffer were increased to maintain the reaction at its optimal pH.

Resing and Mottl (1992) used the surfactant Brij-35 to decrease peak width and peak tailing; its presence also prevents bubbles from sticking to the walls of the manifold tubing. The use of Brij-35 was excluded from this method for two reasons. The additional sensitivity gained by the presence of NTA allowed the reaction temperature to be decreased from 50 °C to 35 °C, which subsequently lowered the likelihood of degassing and the formation of bubbles in the reaction stream. In addition, having a higher eluting acid concentration and a column with a tapered inner chamber resulted in absorbance peaks that were more narrow with less peak tailing.

System response to NTA concentration—Reaction buffers with varying concentrations of NTA were prepared (0, 2.1, 5.2, 10.5, and 21 mM, yielding final concentrations in the reaction

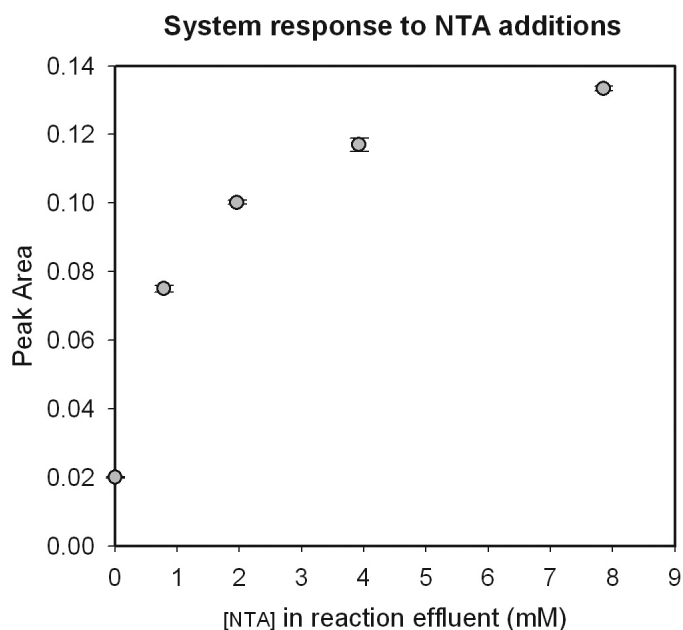


Fig. 2. System response to various NTA additions. Seawater samples contained ~20 nM Mn.

stream of 0, 0.79, 2.0, 3.9, and 7.9 mM, respectively). Because the addition of NTA lowers the pH of the buffer, 3 M ammonium hydroxide was added to the buffers to keep the pH of the solution constant. Figure 2 shows the response of the system to NTA additions. At the highest NTA concentration tested (7.9 mM in the reaction stream), the system response versus NTA concentration curve was still increasing. Higher concentrations of NTA were not tested, as at this concentration the sensitivity of the method had increased substantially (~ 7-fold), and the solubility of NTA in the buffer solution was approaching saturation. As a result 7.9 mM in the reaction stream (21 mM NTA in the buffer solution) was chosen for the method.

Depression in baseline signal due to changes in reaction pH—Typical elution profiles (Figure 3) show a depression in the signal prior to peak formation for samples with low dissolved manganese concentrations. This signal depression is produced by a pH change. A small volume of rinse solution (< 85 μ L) remains in the preconcentration column after the rinsing step and is transported downstream in front of the eluent, producing an area of higher pH in the sample stream. LMG reacts with periodate even in the absence of Mn, producing a baseline signal. The localized zone of higher pH is above the optimal pH for the reaction and produces a depression in the baseline signal prior to peak formation (Figure 3). However, when the elution stream produces large amounts of dye, this depression in the signal is not apparent (Figure 3) as it is obscured by the shoulder of the analyte absorbance peak. One way this pH discrepancy has been counteracted in other FI methods is by increasing the acidity of the rinse solution with a weak acid such as acetic acid (M.C. Lohan, A.M.A.-I., K.W.B., unpublished

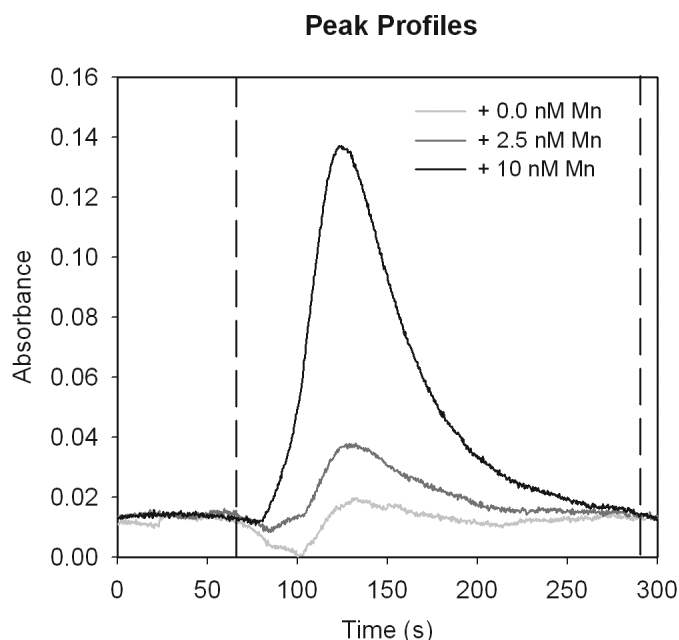


Fig. 3. Elution profiles showing signal depression prior to peak formation in standards with lower Mn concentrations, and the absence of signal depression in a standard with high Mn concentration. Dash lines indicate the integration window. Standards were prepared as standard additions to low-Mn UV-oxidized seawater.

observations). Unfortunately this is not a viable option for this method, as a more acidic rinse solution would strip manganese off the column. This signal depression might be minimized by reducing the strength of buffer in the rinse solution.

Aligning peak profiles shows that the signal depression happens inside the peak area of profiles with higher dissolved manganese concentrations (Figure 3). This poses a problem during peak integration. To overcome this problem, peaks can be base-aligned and shifted upward in such a way as to have the lowest depression (usually from a blank profile) at zero absorbance units (see Figure 3). The peaks are then integrated (including the depression) over the same time frame, starting at the time the largest peak (highest standard) begins to appear (see Figure 3). The data presented here were obtained using this integration approach, although we note that peak height could also be used for quantification.

Standardization—Primary standards were prepared by dilution of $1000 \mu\text{g L}^{-1}$ stock solutions (SPEX plasma standard) in acidified (pH 1.7) Milli-QW to concentrations of 500 and $100 \mu\text{g L}^{-1}$. Manganese seawater standards were prepared as standard additions of the primary standards to acidified UV-oxidized seawater (UVSW) (where trace metals and metal chelating organic ligands are removed from seawater) (Donat and Bruland 1988) and were used to generate standard curves which were applied to samples. Standard curves tended to be parabolic at higher concentrations (Figure 4) requiring a parabolic least-squares fit, but had a linear fit over a lower range of concentrations. Because the formation of color depends

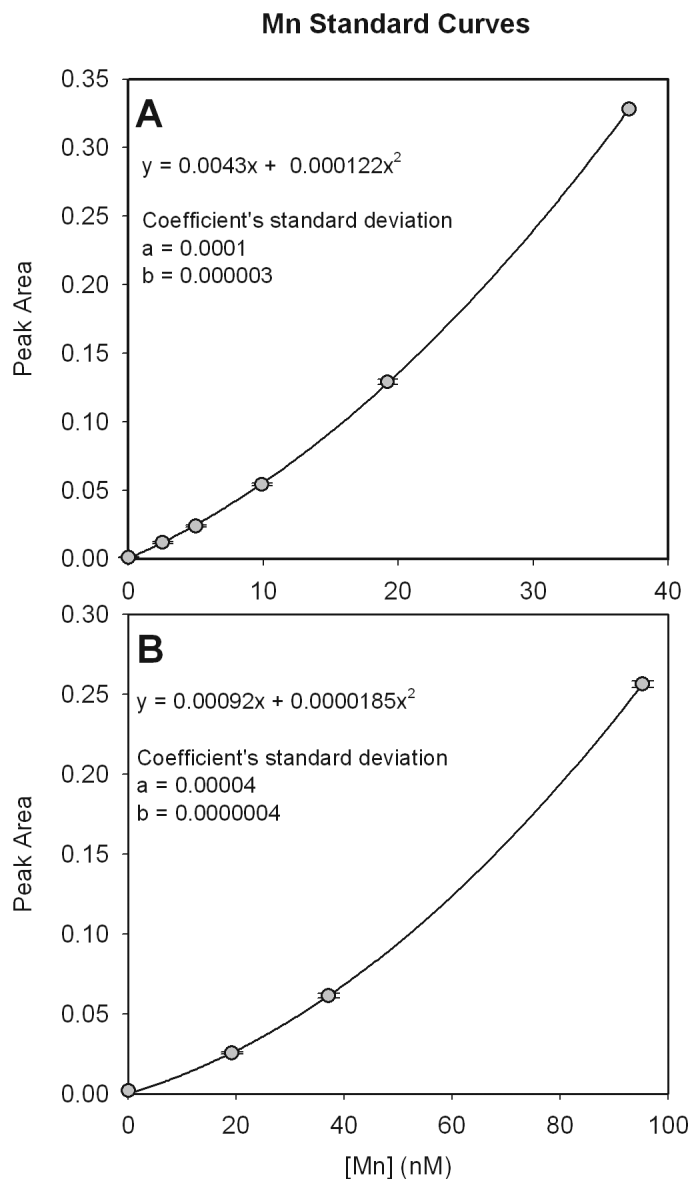


Fig. 4. Parabolic standard curves. (A) Standards loaded for 60 s (0.80 mL loaded). (B) Standards loaded for 10 s (0.17 mL loaded).

not only on the manganese concentration of the standard, but also on the preconcentrated amount, the manganese concentrations that produced the linear portion of a given standard curve varied.

Blanks and detection limits—Blanks were determined using acidified (pH 1.7) Milli-Q water, which was analyzed in the same manner as the standards and samples. This blank includes blanks associated with all reagents as well as with the manifold. The blanks associated with the sample buffer and the rinse solution are particularly important because of the concentration of these reagents onto the preconcentration column during the loading phase. The manganese concentration corresponding to the signal of three times the standard

Table 3. Figures of merit for 1-min (0.8 mL) and 2-min (1.6 mL) loading times.

	0.8 mL loaded [Mn] (nM)	1.6 mL loaded [Mn] (nM)
Blank	0.12 ± 0.06	0.07 ± 0.01
Detection limit	0.18	0.03
Precision (%RSD)	6.2*	3.2*
NASS-4	6.6 ± 0.2	6.7 ± 0.2
NASS-4 certified value (95% confidence limit)	6.9 (± 0.42)	

The precision is calculated as the percent relative standard deviation (%RSD). * $n = 4$.

deviation of the blank ($n = 4$) was used to define the detection limit (Table 3).

Precision and accuracy—The accuracy and precision of the method were tested using the certified reference material NASS-4 (National Research Council, Canada) (Table 3). When loaded for 2 min (1.6 mL), a value of 6.7 ± 0.2 nM manganese was determined for NASS-4 (see Table 3 for values when loading for 1 min [0.8 mL]). This value is within 3% of the certified value of 6.9 ± 0.4 nM. A precision of 3.2% was determined for NASS-4. For samples with lower manganese concentrations, a precision of 6.9% ($n = 17$) was determined at sea over 3 intense days of analyses when loading a 0.71-nM dissolved manganese sample for 3 min (2.4 mL) interspersed between tens of sample analyses.

Method intercomparison—The following method intercomparison was carried out without the addition of NTA, and with the use of KIO_4 as the periodate salt in the spectrophotometric method, as these modifications were only recently incorporated. Surface samples collected from California coastal waters (acidified to pH 1.7 and stored at room temperature > 2 years) were analyzed by this method as well as by a previously published ICP-SFMS method (Beck et al. 2002). A minor modification to the Beck et al. (2002) method was the use of a pH 8.8 rinse solution (1:10 dilution of the sample pH modifier) in place of the pH 5.6 rinse solution. This was done to ensure complete retention of Mn^{2+} by the column during the rinsing step. The seawater standards used in this intercomparison were made as standard additions to 3000-m deep North Pacific water (0.32 nM Mn). The same preconcentration column and set of standards were used during the analysis in both methods. During ICP-SFMS analysis, 1.0 mL sample was concentrated onto the column; 1.4 mL sample was loaded for the spectrophotometric analysis. A paired 2-tailed t test was conducted to assess the statistical significance of the differences between the concentrations measured by the two methods. Sample concentrations ranged from 2.0 nM to 24.5 nM (Table 4).

Assuming the precision (obtained from low Mn samples) of each method is constant over the above range of concentrations, and that errors, whether random or systematic, are inde-

Table 4. Dissolved manganese concentrations in acidified California coastal water samples as determined by two FI methods and their differences.

[Mn] (nM) ICP-SFMS RSD 4%	[Mn] (nM) Catalytic RSD 6%	Difference in [Mn] (nM)
2.4	2.0	0.4
3.7	3.2	0.5
4.3	4.3	0.0
5.2	4.6	0.6
6.3	6.2	0.1
7.2	7.1	0.1
8.4	8.0	0.4
9.9	9.5	0.4
11.1	11.5	-0.4
12.5	11.8	0.7
13.5	13.4	0.1
15.2	15.5	-0.3
19.5	20.0	-0.5
21.9	24.5	-2.6

pendent of concentration, the obtained t test statistic of 0.18 indicates the measured concentrations were not statistically different between the two methods at the 95% confidence level ($P = 0.05$) (the critical value of t is 2.16 for 13 degrees of freedom). The coefficient of determination (r^2) between the methods was 0.99, assigning the ICP-SFMS data to the x -axis.

Shipboard determination of Mn—This method was used successfully at sea. Samples were collected and analyzed aboard the RV *Wecoma* during August 2005. Vertical profiles of dissolved manganese (Figure 5) over the Oregon and Washington slopes show the expected surface enrichment. Oregon surface samples are particularly high due to the influence of the Columbia River plume.

Discussion

The method presented here is significantly easier to use and implement than those presented previously owing to the use of a commercially available IDA resin. The use of this resin provides reproducible results and eliminates the need to synthesize the resin and to establish its quality before analysis. In addition, the resin is packed into a commercially available column, thereby eliminating the need to construct columns in the laboratory that are both leakproof and reproducible. The method presented here is simpler and less prone to contamination through the on-line adjustment of sample pH. In addition, the catalytic reaction is significantly more sensitive due to the addition of NTA, resulting in shorter reaction times and lower reaction temperatures. Finally, the method as constructed here eliminates the use of surfactant in the reaction stream.

This method is ideal for the determination of manganese in the marine environment because it can easily be adapted to measure dissolved manganese at the wide range of concentra-

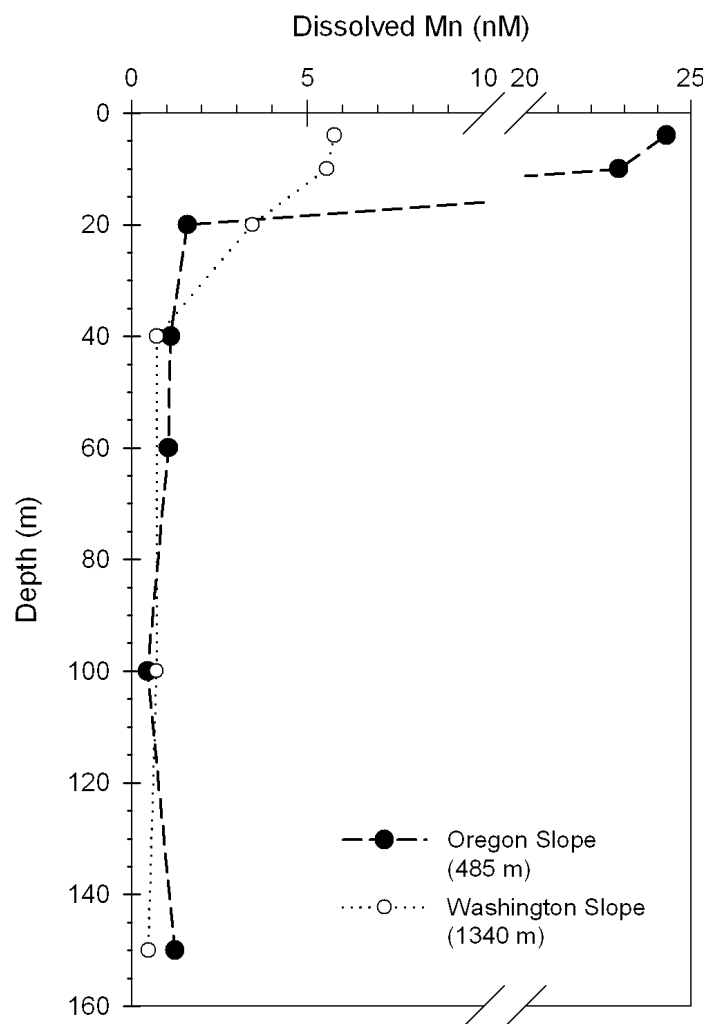


Fig. 5. Vertical profile of dissolved manganese over the Oregon and Washington slopes.

tions (pM to μ M) found in the ocean, and because variations in sample salinity (for salinities > 3) do not affect the method's sensitivity. The ability of this analytical technique to provide near real-time measurements is valuable when studying marine biogeochemical processes for which dissolved manganese serves as a tracer.

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