

Direct determination of ultra-trace levels of metals in fresh water using desolvating micronebulization and HR-ICP-MS: application to Lake Superior waters

M. Paul Field* and Robert M. Sherrell

Institute of Marine and Coastal Sciences, 71 Dudley Road, Rutgers University, New Brunswick, NJ 08901-8521, USA. E-mail: field@imcs.rutgers.edu

Received 29th October 2002, Accepted 11th December 2002

First published as an Advance Article on the web 29th January 2003

We report a method for the rapid ultra-trace (<1 ppb to < 1 ppt) quantification of P, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Mo, Cd, Re, Tl and Pb in fresh water. High sensitivity ($>2 \times 10^6$ cps ppb⁻¹ In) combined with a careful blank control provide unprecedented detection limits (e.g., Fe = 0.81 ppt and Pb = 0.014 ppt) that are approximately 10 fold better than previously published methods. Such low detection limits are required for the investigation of biogeochemical cycling of elements in some natural systems. One example is Lake Superior, where dissolved trace element and phosphorus concentrations in offshore waters are all less than 1 ppb, with some metals (such as Co, Re, Tl and Pb) reaching levels lower than 1 ppt. Depth profiles from Lake Superior exhibit the lowest concentrations of certain metals (Fe, Mn, Co, Zn, Re, Tl and Pb) ever measured in natural fresh waters. The precision of the method is better than $\pm 20\%$ (2σ) for all analytes of interest except Co (30%; 2σ) and accuracy determined from the analysis of certified reference material SLRS-4 indicates excellent (within certified 2σ) agreement for all elements.

Introduction

Studies of the geochemical behavior of trace metals in large, low productivity lakes are one kind of investigation that can benefit from the application of a fast and sensitive multi-element analysis technique. Previous investigations of metal cycling in the world's large lakes have been relatively limited, in part because of this analytical constraint. For example, only one paper has been published using modern sampling and analytical techniques for understanding multi-element distributions in Lake Superior, USA.¹ Earlier studies of metal-phytoplankton interactions² pre-dated the development of modern metal-clean techniques, compromising results, or reported values below detection limit for several elements.³ More recent work has quantified the concentration and distribution of a number of metals in other large lakes, such as Lake Erie,^{1,4-7} and Lake Baikal.⁸

The challenge in studying large, relatively pristine lakes is that the metal concentrations are lower, typically, than in most other fresh water bodies, since water residence times are long and hydrologic catchment areas may be small relative to lake area.^{1,8} For this reason, all of the studies listed above required laborious preconcentration techniques, not because matrix simplification was necessary (as with sea-water) but simply because metal concentrations in the lake water were below the detection limits of the methods employed. This need for careful sample processing has limited the sample throughput necessary to investigate temporal/spatial relationships that are required to elucidate progressive seasonal processes in large lakes. Geochemical understanding is also limited by restricted multi-element capabilities. Inter-relationships among the distributions can be important to interpretations, but are only possible if all relevant elements are analyzed. The HR-ICP-MS multi-element method we present in this paper addresses all of these problems because it requires no sample processing (only a one-step reagent mixing at the time of analysis) and is therefore relatively rapid and contamination-free.

Owing to its multi-element capability and low limits of detection, ICP-MS technology has been exploited in most, if not all, fields of research that require determination of trace metals (biological, geological, marine and environmental⁹⁻¹⁶). The analysis of fresh water is perhaps the most straightforward environmental application of ICP-MS because the sample is already in solution, has low total dissolved solids (TDS) and therefore minimal matrix suppression/interferences. However, many elements of interest below mass 80 (such as first row transition metals) are often subject to spectral interferences.¹⁷ To compensate for interferences, analysts using low resolution ICP-MS have employed one or more of the following techniques: mathematical corrections, matrix removal, cold plasma, collision cells and dynamic reaction cells.¹⁸⁻²³ At our detection limits, medium resolution (4300 $M/\Delta M$ at 10% peak height; Element-1) is capable of resolving all the significant polyatomic interferences present in a fresh water matrix. Both low and high resolution ICP-MS instruments have been used successfully in the determination of trace metals in a variety of types of fresh water samples. The improved sensitivity of newer generation instruments and/or sample preconcentration result in ultra-trace detection limits (10s of ppt range) that are now being reported in the literature.²⁴⁻²⁸ The method reported here exploits the high sensitivity, low blank, and high resolution capabilities of the ELEMENT 1 (Finnigan MAT, Bremen, Germany) to obtain detection limits (<1 ppt) required for ultra-trace element determinations in fresh water samples. The method has unprecedented detection limits for a number of elements, and it includes 16 elements of interest, measured simultaneously. The analyte group includes P, of interest since productivity in many large lakes is limited by P availability, and dissolved P concentrations are often below detection limit using conventional spectrophotometric techniques. With modifications to the standard addition composition and range, this method is suitable for the direct analysis of almost any fresh water sample.

Experimental

Reagents and materials

Ultrapure 16 N nitric acid (HNO₃) was purchased (Fisher OPTIMA grade). Deionized, distilled water (ddH₂O) and doubly deionized water (2dH₂O) were prepared by glass distillation and Milli-Q deionization of house deionized water, respectively. Primary standards (10 mg L⁻¹) used to prepare working standard mixtures (in 3% HNO₃) were purchased from High-Purity Standards (Charleston, SC, USA). A 500 mL Teflon bottle was used to prepare gravimetrically an internal standard (indium; 10 ppb) in 30% HNO₃.

Polypropylene and polyethylene materials and apparatus used for sample handling and storage were leached in 1 N HCl (reagent grade in ddH₂O) at 60 °C for 12 h followed by thorough rinsing in ddH₂O and a pre-rinse with sample. PFA materials were leached in reagent grade 12 N HCl (boiling), 16 N HNO₃ (boiling) and freshly made *aqua-regia* (room temperature).

Sample collection and preparation

To ensure accurate determination of low level metals it is important to avoid contamination during all stages of sample collection and preparation. Sample collection was performed using an in line, polypropylene body, Teflon diaphragm pump (Graco, Model 307, Midland Pump, NJ) mounted on deck, and connected to a Teflon lined polyethylene tube (0.5 inch ID, 0.625 inch OD; Berghof-America, Coral Springs, FL) in a system adapted from Vink *et al.*²⁹ and Boyle *et al.*³⁰ The major difference is the larger diameter of the tube and its length, allowing either underway surface sampling or vertical profiling to 180 m. The pump outflow runs directly to an in-line 0.45 µm pore size all-polypropylene cartridge filter (Calyx capsule, Osmonics Corp., Westborough, MA, USA), located in a HEPA-filtered Class 100 laminar flow clean bench. All components of this system were acid leached prior to assembly, then again as a complete unit. The system has a dead volume of 4 L; therefore, 12 L (4 min pumping time) of lake water is flushed through the system prior to each sample collection. Samples are collected in acid-cleaned 250 mL HDPE bottles which are first rinsed with sample, filled, then frozen for transport back to the laboratory. Upon arrival in the laboratory, samples are thawed and acidified (250 µL of Optima HNO₃) 2 d to 1 month prior to analysis.

Sample preparation is very simple (designed to minimize blanks) and is performed gravimetrically in a HEPA-filtered Class 100 laminar flow clean bench at the time of analysis. To minimize contamination of the sample uptake tube, no auto-sampler is used, but rather the sample uptake tube is transferred manually between samples prepared in 20 mL PFA vials. Blank levels are determined initially in several vials and the cleanest ones are used repeatedly throughout the subsequent analytical run. To prepare samples a polypropylene syringe, fitted with a 20 cm length of 1/16" id PFA tubing (internal volume of 1.1 mL), is used to dispense approximately 1 g of the internal standard. Sample is then poured into the vial, bringing the final mass to about 10 g; exact masses are recorded and used to calculate the dilution accurately. Blanks are prepared in a similar manner, but Milli-Q water (2dH₂O) is used instead of sample.

Instrumentation

The magnetic sector inductively coupled plasma mass spectrometer used (the Element 1, Finnigan MAT, Bremen, Germany) has three nominal resolution ($R = M/\Delta M$ at 10% peak height) settings: low (LR: $R = 300$), medium (MR: $R = 4300$), and high (HR: $R = 9000$). For this method we configure the mass spectrometer to perform E-Scans in both LR and MR. First, Y,

Mo, Cd, In, Sb, Re, Tl and Pb are scanned in LR, then P and the first row transition metals V, Cr, Mn, Fe, Co, Ni, Cu, Zn and In are scanned in MR, which is sufficient to resolve all matrix and plasma based interferences associated with this sample type. A grounded metal shield (CD-1, Finnigan MAT, Bremen, Germany), inserted between the load coil and the torch increases sensitivity by approximately a factor of 10. This shielded torch configuration allows operation under "cold plasma" conditions (reduced forward RF power), but can also be operated under typical hot plasma conditions.

The sample is introduced to the plasma as a dried aerosol using a micro-concentric desolvation system (MCN-6000, Cetac Technologies, Omaha, NE, USA). The desolvating apparatus consists of a heated, vertically mounted spray chamber and ~2 m of heated porous Teflon membrane tubing. The original stock T-1 nebulizer and FEP spray chamber have been exchanged for a PFA spray chamber and a µFlow nebulizer (Elemental Scientific, Omaha, NE). Increased spray chamber temperatures (105 *versus* 75 °C) that are possible with PFA eliminate the droplet formation responsible for intermittent signal spikes. This, combined with aggressive cleaning protocols for PFA (spray chamber and nebulizer), results in very stable, low blanks that provide excellent detection limits. Al cones (Spectron, Ventura, Ca, USA) are used to minimize Ni blanks contributed by the more conventional Ni cones.

A peak at mass 100 has a width of 0.333 u in LR, but is only 0.023 u wide in MR. It is therefore crucial to have a stable mass calibration for accurate and efficient determination of MR spectra. Magnet hysteresis and temperature stability are arguably the two most important factors affecting the mass calibration stability of the high resolution mass spectra. It is convenient to have one mass calibration that is appropriate for all types of analysis, independent of the suite of analytes selected. The difference in magnet jumps between the mass calibration file and the analysis file, however, may result in a slight mass offset. Furthermore, small temperature changes (2 °C) result in mass dependent calibration drift. The mass calibration drift increases with decreasing mass and is therefore most problematic for medium and high resolution analysis in the low mass region of the spectrum. In the past, problems with mass calibration stability could be compensated by frequent recalibration of the mass spectra and by scanning areas larger (150–200%) than the peak width. The latest edition of the instrument software (version 2.1) has implemented two new features, a "Mass Offset" and a "Lock Mass". Relative to the mass calibration, all peaks in the analysis file can have a determined "Mass Offset". This compensates for the difference in the magnet jumps between mass calibration and analysis files, thereby ensuring exact mass centering. The "Lock Mass" function monitors a peak of choice (⁴⁰Ar/⁴⁰Ar in MR) during each analysis and compensates for mass calibration drift accordingly. In LR mass calibration drift is insignificant relative to peak width, therefore no lock mass peak is required. Combined, these features have greatly improved the duty cycle and mass calibration stability of the high resolution (4300 and 10 000) spectra.

Operating parameters

A 3% HNO₃ solution containing 1 ppb of indium is used to tune the MCN-6000 gas flows, low resolution lenses and torch position for maximum sensitivity and stability (2–4 × 10⁶ cps ppb⁻¹ In). Relative to a standard spray-chamber, dramatic changes in sensitivity with respect to torch position are observed using the MCN-6000. We attribute this to a more constrained, narrow central channel under dry plasma conditions. Once low resolution is tuned, the medium resolution lenses are then tuned for greatest resolution and peak symmetry, usually $R \sim 4300$. Finally, to optimize stability and sensitivity for the sample matrix, we prepare a sample with

1 ppb In and re-tune the MCN-6000 sweep and nitrogen flow rates. The μ Flow-100 nebulizer's sample uptake rate varies with sample gas flow rate, but generally reaches a plateau of $\sim 100 \mu\text{L min}^{-1}$ at a gas flow of 0.80 mL min^{-1} . We find the MCN-6000 works best when the sample flow rate is matched to its desolvating capabilities. At high sample flow rates ($150 \mu\text{L min}^{-1}$) droplets form, resulting in signal spiking, whereas at low flow rates ($25 \mu\text{L min}^{-1}$) electrostatic activity may increase signal noise. We interpret optimal flow rates as the point when droplets do not form in spray chamber and condensation in the sweep gas exhaust flow begins to form at about 5–10 cm from the exhaust port of the desolvator.

Operating, acquisition and evaluation parameters are outlined in Table 1. In medium resolution $^{40}\text{Ar}^{38}\text{Ar}^+$ is used as the lock mass peak. The lock mass and the mass offset features maintain stable mass calibration for a complete analytical run (5 d), without requiring any re-calibration. These features also make it possible to reduce the MR mass windows from 150 to 100%, thereby increasing the duty cycle from 61 to 86%.

Results and discussion

Blanks and detection limits

To ensure that the lowest possible blanks are obtained, all components of the sample introduction system go through a two stage cleaning process prior to analysis. First the system is disassembled and the components (cones, torch, injector, connector and tubing to MCN-6000, MCN-6000 and nebulizer) are cleaned separately in appropriate acids. This first stage involves manually filling and draining (after 30 min) the MCN-6000 with acids, then rinsing several (6–8) times with $2\text{dH}_2\text{O}$. Thorough rinsing is a crucial step that determines how long it will take the MCN-6000 to reach low blank levels. This is due to an approximate 10 mL retention volume that remains unavoidably in the MCN-6000 after each rinsing step. The cleanliness of the retentate will dictate the number of serial dilutions required to obtain $2\text{dH}_2\text{O}$ background levels. The MCN-6000 is then turned on and left to "bake out" the remaining water. Once the MCN-6000 is dry, the sample introduction system is reassembled for the second stage of cleaning. During this stage the plasma is turned on, the instrument is tuned and three blank prone elements (Fe, Zn and Pb) are monitored (in MR) through the tune window. Ultra-pure 3% HNO_3 solution (acid strength of samples) is first aspirated to determine the initial blank of the sample introduction system. These numbers are usually high and can be reduced significantly by initially aspirating acetone to

remove any organics, then alternating high purity 30% HCl, 30% HNO_3 and 30% HF. When no further improvement is observed in the 3% HNO_3 blank after alternation of strong acids, the system is left to aspirate 10% HNO_3 for an extended period of time. For low level analyses it is our routine to spend one day cleaning the MCN-6000 then leave it overnight to aspirate 60 mL of 10% HNO_3 . After approximately 10 h this volume is consumed: the MCN-6000 will then bake out for the next 6 h, and be ready for analysis first thing in the morning. When running we often leave the instrument on for 5 d straight, repeating this routine every night (requires minimal retuning of the sweep and gas flows each morning). Using this mode of operation we can determine routinely 60 samples per day with analytes in the ppq to ppt range.

At the beginning of each analytical day the blanks determined on 3% HNO_3 are only slightly greater than those determined on air (no solution aspirated) (Table 2). Procedural blanks are prepared and analyzed after every 10th unknown. No trend is observed in blank concentration throughout the run, therefore the average blank is subtracted from all of the samples. For most elements this is less than a 5% correction and does not introduce any significant uncertainty to the determined concentration of samples. Pb, one of the more contamination-prone metals, is an exception. Extremely low Pb concentrations, often between 0.5 and 1.0 ppt in Lake Superior, result in up to 20% blank subtraction (Table 2).

Detection limits, expressed as three times the standard deviation of the noise determined in 3% HNO_3 with 1 ppb In, are less than 1 ppt for all elements except the poor ionizers Zn and P (Table 2). At the sensitivities realized by the method, detection limits for most metals of interest are strongly influenced by blank control. Detection limits for some elements, however, could be improved with increased sensitivity. Cd, Re, V, Mn, Co, and Ni blanks are all less than 10 counts s^{-1} and have unmeasurable standard deviations of less than 1 count s^{-1} . For comparison, detection limits from other methods using micronebulization HR-ICP-MS (Element-1^{24,28}), ultrasonic nebulization HR-ICP-MS (Plasma Trace²⁵), flow injection preconcentration ultrasonic nebulization Q-ICP-MS²⁶ and online preconcentration ICP-TOFMS²⁷ are listed in Table 2. Not all methods use similar instruments, options (CD-1, desolvation), or clean room sample preparation, and are therefore not directly comparable. Furthermore, these methods have appropriate detection limits for the analytes of interest in their respective sample types. It is, however, important to note that all the analytes measured in this method have significantly better detection limits than in previously published methods. This is an important advance

Table 1 Operating parameters

Tune parameters			MCN-6000		
ELEMENT-1 with CD-1			MCN-6000		
Gas flow	L min^{-1}		Sweep gas flow	3.2 L min^{-1}	
Sample	0.9		Sweep gas temperature	175 °C	
Auxiliary	1.00		Spray chamber temperature	105 °C	
Cool	16.0		Nitrogen flow	8 mL min^{-1}	
Sample uptake	120 s		Nebulizer	μ -Flow	
Sample wash	30 s		Spray chamber	PFA	
Sample flow rate	100 $\mu\text{L min}^{-1}$				
Aquisition parameters			Evaluation parameters		
Resolution	Low	Medium	Resolution	Low	Medium
Mass window	10%	100%	Search window	100%	100%
Samples/Peak	200	30	Integration window	100%	45%
Sample time/ms	5	10	Integration type	Average	Average
Segment time/ms	100	300	Runs	3	3
			Passes	5	5

^aIn LR Cd and Ag had a sample time of 10 ms with segment time of 200ms.

Table 2 Blanks (3% HNO₃) and detection limits (ppt) for fresh water

Element	Isotope	Air/cps	Blank/cps	Blank (ppt)	DL (ppt)					Sample range (ppt)	
					This work	1 ^a	2 ^a	3 ^a	4 ^a		5 ^a
Y	89	43	46	0.04	0.016	N/D ^b	N/D	N/D	N/D	N/D	2.98–11.96
Mo	98	310	275	0.90	0.18	N/D	0.3	0.65	N/D	30	60.03–131
Cd	111	6	5	0.030	0.013	2	0.9	1.96	N/D	6	5.39–14.45
Sb	121	60	66	0.15	0.031	N/D	0.3	0.05	N/D	N/D	33–108
Re	187	2	3	0.0015	0.0015	N/D	N/D	N/D	N/D	N/D	0.27–0.91
Tl	205	11	26	0.014	0.057	N/D	N/D	N/D	N/D	N/D	0.85–3.42
Pb	208	31	117	0.090	0.014	6	0.6	0.39	0.44	26	0.34–7.59
P	31	244	306	109	20	N/D	N/D	N/D	N/D	N/D	547–2692
V	51	2	5	0.20	0.13	0.4	3	0.49	N/D	N/D	123–324
Cr	52	23	35	1.1	0.38	3	0.6	0.25	N/D	N/D	50–1285
Mn	55	5	10	0.28	0.16	4	1.8	0.26	0.26	N/D	16–420
Fe	56	4	89	3.8	0.81	80	33	4.2	N/D	N/D	63–7617
Co	59	1	1	0.05	0.080	N/D	0.3	0.23	N/D	4	0.31–63
Ni	60	0	3	0.41	0.31	N/D	N/D	1.4	0.86	22	69–2188
Cu	63	14	26	1.5	0.2	7	2.7	0.52	1.5	5	498–965
Zn	64	21	51	6.4	1.8	20	3	7.26	10	N/D	69–434

^a(1) Riondato *et al.*²⁴ (2) Barbante *et al.*²⁸ (3) Bensimon *et al.*²⁵ (4) Warnken *et al.*²⁶ (5) Benkhedda *et al.*²⁷. ^bN/D = Not determined.

for certain analytes and sample types. The improvement in detection limits is mainly attributed to blank control. This is evident from blank prone elements such as Pb and Fe that have detection limits 27–1800 and 5–100 times better than previous methods, respectively.

Standardization

A multi-element standard is prepared gravimetrically in 3% HNO₃ (v/v) from 10 ppm single element standards to obtain concentration ranges approximately 100 times that typical of filtered lake water samples. An internal standard of 10 ppb In is prepared in 30% HNO₃ (v/v) and approximately 1.0 mL added to all solutions (~10 mL), yielding a final concentration of 1 ppb In. Three point standard additions are prepared by adding 0.00, 0.25 and 0.50 mL of the multi-element standard to the sample matrix.

Intensities for the elements of interest in both LR and MR are corrected for variations in sensitivity by normalization to the initial sensitivity of In in each resolution. Signal drift is illustrated by the relative sensitivity of In plotted for 220 consecutive analyses performed over a three-day period (Fig. 1). The MCN-6000 was tuned on a sample solution at the beginning of day one, not tuned on day two and tuned again on day three. A number of important observations can be made from the data presented in Fig. 1: (1) there is a 20–40% enhancement in sample signal relative to blank; (2) there is minimal (10–15%) drift in MR over three days; (3) not tuning

on day two reduced the sensitivity of the LR signal but not the MR signal; and (4) MR and LR sensitivity co-varies if the MCN-6000 gas flows are optimized. The enhancement in sample sensitivity relative to simple 3% HNO₃ solutions is likely due to the precipitation of natural lake water salts that act as carrier particles during desolvation, enhancing sample transport. The features illustrated in Fig. 1 emphasize the need to tune on the sample matrix and to use an internal standard in both resolutions to ensure accurate quantification and blank correction.

After correction for sensitivity variations, the concentrations of P, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Sb, Re, Tl and Pb in unknown samples are then calculated by dividing the normalized intensities by the slope of a three point standard addition to one representative sample from an analytical batch. We refer to this as a method of pseudo-standard additions and have demonstrated its ability to determine accurate elemental concentrations in samples of similar matrix.^{13,31} Blanks are determined from normalized signals acquired from pure diluted acid (3% HNO₃ in 2dH₂O) and are subtracted as calculated concentrations.

Precision and accuracy

The mean concentrations and relative standard deviations for 10 replicate analyses of a Lake Superior sample are listed in Table 3. The data include analysis of the same sample performed

Table 3 Typical elemental concentration and 2σ precision obtained for a Lake Superior water sample measured on 3 separate analytical dates (n = 10)

Element	Concentration (ppt)	2σ	2σ (%)
Y	4.5	1.1	25
Mo	120	9.3	8
Cd	7.7	0.71	9
Sb ^a	53	8.7	16
Re	0.71	0.09	13
Tl	1.4	0.28	20
Pb	1.7	0.25	15
P	936	139	15
V	204	12	6
Cr	67	5.2	8
Mn	108	6.0	6
Fe	835	63	8
Co	1.2	0.35	30
Ni	112	6.6	6
Cu	744	47	6
Zn	133	14	10

^aMay be too high, see text.

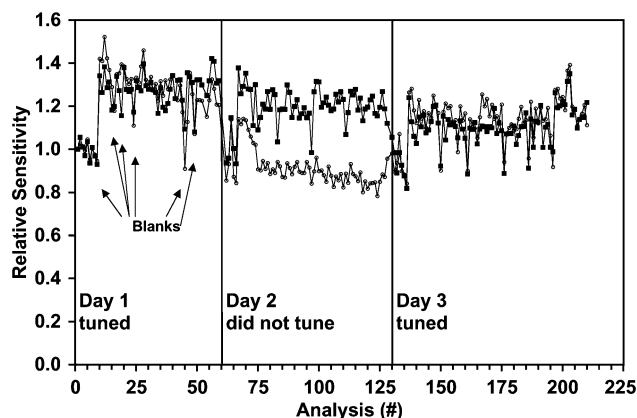


Fig. 1 LR (open circles) and MR (closed squares) relative sensitivity variation for ¹¹⁵In over three days and 220 analyses. Frequent single point dips in sensitivity, including the first few analyses of each day, occur during blank analyses.

on 3 separate analytical dates and therefore represent the inter-run reproducibility. The day to day precision (2σ) at natural concentrations typical of large lakes is $< \pm 20\%$ for all and $< \pm 10\%$ for most elements, except Co ($\pm 30\%$). Low natural concentration (approximately 1 ppt), combined with lower sensitivity in MR, results in insufficient counts for theoretical Poisson counting statistics for this element. The method is now modified to provide $< \pm 20\%$ precision for these extremely low levels of Co. The within run precision is estimated to be $< \pm 10\%$ (2σ) for all elements determined in SLRS-4 (Table 4).

To assess the accuracy of the method, analyses of SLRS-4, a St. Lawrence River reference material, are presented in Table 4. SLRS-4 contains substantially higher concentrations for a number of metals than does Lake Superior water (Pb = $80 \times$, P = $4 \times$, Mn = $40 \times$, Fe = $100 \times$, Co = $35 \times$, Ni = $8 \times$ and Zn = $10 \times$). These metals range beyond the concentration of our working standard and it is therefore necessary to determine SLRS-4 by preparing a more appropriate multi-element standard. Although using a different standard solution is not a true accuracy test, we believe there is minimal potential for error in our gravimetric preparation of multi-element standard concentrations. Our determined concentration values for SLRS-4 have 2σ confidence limits $< \pm 10\%$, and all elements (except Sb) fall within the 2σ confidence limits of the certified values (Table 4). For Sb, our determined value is significantly higher than the certified values (34%) and the difference exceeds the uncertainty envelopes of each determination. We attribute this to a fractional loss of Sb through the desolvation membrane that increases with concentration resulting in an artificially shallow slope of the Sb standard curve.

Application to Lake Superior

Data from samples collected at two stations in western Lake Superior (Fig. 2) are presented as vertical profiles for a subset of elements (Fig. 3). One station is located in a deep trench close to the northern shore near Two Harbors, MN, (CD-1) and the other is located in the middle of the western arm of the lake (WM, Fig. 3). The concentration range displayed is < 0.5 ppt (Pb in deep water at CD-1) to 255 ppt (Mn in surface water at CD-1). The profiles indicate the processes of near-surface metal input and subsequent removal by variably effective deep water particle scavenging. Mn and Co show intense maxima in the surface waters at CD-1, likely resulting from runoff or shallow sediment inputs at this near-shore station. By contrast, the profiles at the mid-lake station WM show either smaller surface maxima (Mn), likely the result of photochemical reduction of Mn oxides to Mn^{2+} , or slight photochemical depletion (Co). In the deep water, concentrations of Zn, Pb, Tl and Co are all lower at CD-1 than at WM, probably due to higher suspended particle concentrations in the trench at

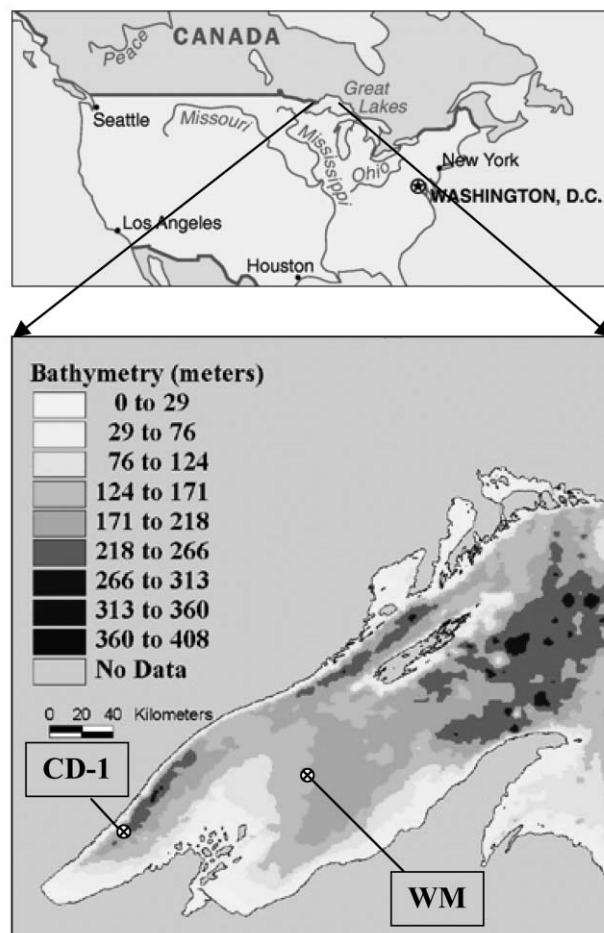


Fig. 2 Locations of stations sampled in Lake Superior.

CD-1, and therefore greater scavenging removal. The indistinguishable Mn concentrations in the deep waters at the two stations suggest a relatively long residence time for this element, and effective horizontal mixing in deep water. Pb shows near-surface increases at CD-1, as for Mn and Co, but Zn and Tl show no such effects, suggesting a significant lake-margin source for pollutant Pb, but not for the other elements.

A major advantage of the new method is that relatively subtle features can be discerned in distribution profiles or temporal trends, for a broad suite of elements, even at extremely low concentrations. In part this is because direct analysis, in addition to greatly increasing sample throughput, eliminates imprecision associated with chemical recovery in preconcentration techniques. The overall smoothness of the profiles is indicative of the precision of the data and of natural

Table 4 Determined and certified elemental concentrations (ppb) in SLRS-4 ($n = 5$)

Element	Isotope	Certified	2σ	Determined	2σ	2σ (%)	% diff. ^a
LR							
Mo	98	0.21	0.02	0.209	0.010	4.9	-0.6
Cd	111	0.012	0.002	0.0127	0.0009	6.2	5.9
Sb	121	0.23	0.04	0.308	0.0089	2.9	33.8
Pb	208	0.086	0.007	0.0834	0.0018	2.1	-3.0
MR							
V	51	0.32	0.03	0.340	0.0076	2.2	6.1
Cr	52	0.33	0.02	0.312	0.0087	2.7	-5.4
Mn	55	3.37	0.18	3.45	0.16	4.6	2.3
Co	59	0.033	0.006	0.0331	0.0026	7.7	0.4
Ni	60	0.67	0.08	0.708	0.039	5.5	5.7
Cu	63	1.81	0.08	1.86	0.062	3.4	2.7
Zn	64	0.93	0.1	1.02	0.025	2.4	9.5

^a% diff. = (determined - certified)/certified \times 100.

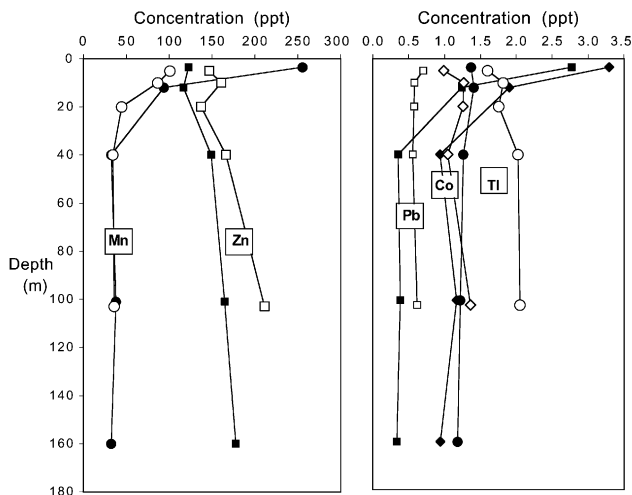


Fig. 3 Vertical concentration profiles of Mn, Zn, Pb, Tl, and Co at stations CD-1 (47°05.10'N, 91°24.36'W; closed symbols) and WM (47°20.16' N, 89°47.94' W, open symbols) in western Lake Superior.

mixing processes in the lake. In addition, the concentrations shown here are among the lowest ever measured for a natural freshwater body. The dissolved Pb concentrations, at <0.5 ppt, are 2–3 times lower than the lowest previously published Pb concentrations for natural waters, including those for the remote deep Pacific Ocean.^{32,33} The new analytical method is currently being used to assemble a large multi-element spatial/temporal description of metal distributions in Lake Superior, to answer questions about biological cycling of metals in large low productivity lakes and to define long-term pollutant trends.

Conclusions

We have developed a multi-element method for direct analysis of fresh water that is rapid, precise, and accurate. Most importantly, procedures developed for sample handling and cleaning the sample introduction system provide unprecedented multi-element detection limits. The demonstrated blank control, combined with the power of high resolution and high sensitivity, allows for the routine determination of metals in the sub-ppb to sub-ppt range. The element suite we have analyzed here includes P, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Re, Tl and Pb, but the method can easily be expanded to a broader range of analytes and can be applied to other natural fresh waters, drinking water or laboratory deionized water. Here, we have demonstrated its utility for quantifying geochemical distributions and biogeochemical cycling of ultra-trace elements in large lakes, with Lake Superior as an example. To the best of our knowledge, the concentrations of a number of the elements in Lake Superior (P, Fe, Mn, Co, Zn, Re, Tl and Pb) are the lowest ever measured in natural fresh waters.

Acknowledgements

We thank our collaborators, Erik Brown, Robert Sterner and Mike McKay, and their research teams. We are very grateful to the captain and crew of the R/V Blue Heron, and especially to Jason Agnich for his careful coordination of the field sampling efforts. Louise Bolge was very helpful during the laboratory analyses at Rutgers. Mark Wells made helpful suggestions in

the design of field sampling equipment. The final manuscript benefited from comments made by two anonymous reviewers. This work was carried out under support from NSF Chemical Oceanography and Coastal Oceans Program (OCE-9902660 to R.M.S).

References

- 1 J. O. Nriagu, *Environ. Sci. Technol.*, 1996, **30**, 178.
- 2 C. L. Schelske, L. E. Feldt, M. A. Santiago and E. F. Stoermer, in *Proceedings of the 15th Conference on Great Lakes Research, International Association for Great Lakes Research*, 1972, p. 149.
- 3 R. Rossman and J. Barres, *J. Great Lakes Res.*, 1988, **14**, 188.
- 4 K. H. Coale and A. R. Flegal, *Sci. Tot. Environ.*, 1989, **87**(88), 297.
- 5 T.-S. Lin and J. Nriagu, *Environ. Sci. Technol.*, 1999, **33**, 3394.
- 6 M. R. Twiss, J.-C. Auclair and M. N. Charlton, *Can. J. Fish. Aquat. Sci.*, 2000, **53**, 86.
- 7 M. R. Twiss, in *Lake Erie at the Millennium—Changes, Trends, and Trajectories*, eds. J. J. H. Ciborowski, M. N. Charlton, J. R. G. Kreis and J. M. Reutter, Canadian Scholars' Press, Toronto, Canada, 2001.
- 8 K. K. Falkner, T. M. Church, C. I. Measures, G. LeBaron, D. Thouron, C. Jeandel, M. C. Stordal, G. A. Gill, R. Mortlock, P. Forelich and L.-H. Chan, *Limnol. Oceanogr.*, 1997, **43**, 329.
- 9 A. T. Townsend, *J. Anal. At. Spectrom.*, 2000, **15**, 307.
- 10 I. Rodushkin, F. Odman, R. Olofsson and M. Axelsson, *J. Anal. At. Spectrom.*, 2000, **15**, 937.
- 11 T. Prohaska, G. Kollensperger, M. Krachler, K. D. Winne, G. Stingeder and L. Moens, *J. Anal. At. Spectrom.*, 2000, **15**, 335.
- 12 H. P. Longerich, G. A. Jenner, B. J. Fryer and S. E. Jackson, *Chem. Geol.*, 1990, **83**, 105.
- 13 M. P. Field, J. T. Cullen and R. M. Sherrell, *J. Anal. At. Spectrom.*, 1999, **14**, 1425.
- 14 M. P. Field and R. M. Sherrell, *Anal. Chem.*, 1998, **70**, 4480.
- 15 B. Klaue and J. D. Blum, *Anal. Chem.*, 1999, **71**, 1408.
- 16 S. J. Hill, T. A. Arowolo, O. T. Butler, S. R. N. Chenery, J. M. Cook, M. S. Cresser and D. L. Miles, *J. Anal. At. Spectrom.*, 2002, **17**, 284.
- 17 U. Gießmann and U. Greb, *Fresenius' J. Anal. Chem.*, 1994, **350**, 186.
- 18 J. L. M. de Boer, *J. Anal. At. Spectrom.*, 2002, **15**, 1157.
- 19 D. Beauchemin and S. S. Berman, *Anal. Chem.*, 1989, **61**, 1857.
- 20 K. Y. Patterson, C. Veillon, A. D. Hill, P. B. Moser Veillon and T. C. O'Haver, *J. Anal. At. Spectrom.*, 1999, **14**, 1673.
- 21 K. Sakata and K. Kawabata, *Spectrochim. Acta, Part B*, 1994, **49**, 1027.
- 22 Z. Du and R. S. Houk, *J. Anal. At. Spectrom.*, 2002, **15**, 383.
- 23 H. Louie, M. Wu, P. Di, P. Smith and G. Chapple, *J. Anal. At. Spectrom.*, 2002, **17**, 587.
- 24 J. Riondato, F. Vanhaecke, L. Moens and R. Dams, *J. Anal. At. Spectrom.*, 2000, **15**, 341.
- 25 M. Bensimon, J. Bourquin and A. Parriaux, *J. Anal. At. Spectrom.*, 2000, **15**, 731.
- 26 K. W. Warnken, G. A. Gill, L. Wen, L. L. Griffin and P. H. Santschi, *J. Anal. At. Spectrom.*, 1999, **14**, 247.
- 27 K. Benkhedda, H. Goenaga Infante, E. Ivanova and F. C. Adams, *J. Anal. At. Spectrom.*, 2000, **15**, 1349.
- 28 C. Barbante, G. Cozzi, G. Capodaglio, K. van de Velde, C. Ferrari, C. Boutron and P. Cescon, *J. Anal. At. Spectrom.*, 1999, **14**, 1433.
- 29 S. Vink, E. A. Boyle, C. I. Measures and J. Yuan, *Deep-Sea Res.*, 2000, **47**, 1141.
- 30 E. A. Boyle, S. S. Husted and B. Grant, *Deep-Sea Res.*, 1982, **29**, 1355.
- 31 J. T. Cullen, M. P. Field and R. M. Sherrell, *J. Anal. At. Spectrom.*, 2001, **16**, 1307.
- 32 B. K. Schaule and C. C. Patterson, *Earth Planet. Sci. Lett.*, 1981, **54**, 97.
- 33 A. R. Flegal and C. C. Patterson, *Earth Planet. Sci. Lett.*, 1983, **64**, 19.