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Direct determination of 10 trace metals in 50 μL samples of coastal seawater using desolvating micronebulization sector field ICP-MS†

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Understanding the trace metal marine geochemistry of temporally variable coastal systems requires intensive sampling programs with attendant analytical burdens. Most established techniques for multi-element trace metal determinations are slow, require a skilled chemist, and are not easily automated. Advances in sample introduction systems and ICP-MS instrumentation now provide marine chemists with the sensitivity and mass resolution necessary to determine many trace metals at natural concentrations in coastal seawater. A new method has been developed for the rapid (10 samples h^{-1}) determination of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in diluted seawater, requiring just 50 μL of seawater and no reagents other than pure nitric acid. A sensitivity of 800 000–1 200 000 cps ppb^{-1} ^{86}Sr in a 10% sea water matrix is obtained when microconcentric desolvating nebulization is combined with a shielded torch and hot plasma high resolution ICP-MS. Analyses are standardized by a matrix-matched external calibration curve with variations in sensitivity corrected by normalizing to the natural internal standard Sr, a conservative ion in seawater. The method thus depends on mass bias stability for each analyte relative to Sr, which was examined as a function of forward power and matrix and found to be optimized at 1100–1350 W. Precision and accuracy are limited by appropriate correction for blanks, which derive mainly from the ICP-MS introduction system, and are equivalent to about 10% of typical coastal seawater concentrations for these metals. Preliminary evaluation of a new low-flow nebulizer (μFlow, Elemental Scientific, Omaha, NE, USA) suggested lower blanks and compatibility with solutions high in total dissolved solids compared with standard microconcentric designs. Determination of dissolved concentrations in reference seawater (CASS-3) demonstrate very good agreement with certified values (within 95% confidence limit) and a precision of 3–12% (1σ) for all elements except Cr (15%). The utility of the method is demonstrated by the determination of spatial trends for these metals in a transect of seawater samples from shelf waters off southern New Jersey, USA. The new technique is sufficiently sensitive to determine some of these metals in open ocean seawater and, with minor modifications, should be applicable to a larger suite of analytes in a wide variety of natural waters.

Processes which control the distributions and variability of trace metals in coastal zones remain poorly understood. Existing knowledge of most continental shelf waters is sufficient only to establish that nearshore trace metal concentrations are usually elevated relative to open ocean waters at similar depths, reflecting both natural and anthropogenic inputs at the ocean margins.[1–6] The limited understanding of the chemical variability in coastal waters is due in part to data limitations imposed by laborious and slow analytical techniques for determining metals in seawater.

An evaluation of the relative importance of potential controls on metal concentrations in coastal waters will require sampling approaches commensurate with the scale of spatial and temporal variability. Such dynamic systems require intensive sampling programs linked to appropriately efficient analytical capability. Indeed, any sample-intensive investigation can benefit from simple, rapid analytical techniques. The direct determination of trace metals in seawater would greatly reduce the time, effort and contamination danger associated with traditional preconcentration techniques, but this goal has remained elusive because of the challenge of low analyte concentrations and interferences from the complex seawater matrix. The use of ICP-MS for direct seawater analysis holds promise, but is currently limited to the more abundant or very high mass trace elements (*e.g.* Ba, U[7,8]) or has been constrained by performance limitations when applied to a broader suite of elements.[8]

The established methods for seawater analysis have generally required preconcentration and matrix removal by a number of techniques including coprecipitation,[9] ion exchange resins in columns[10–14] and in batch mode,[15] and liquid[11] or solid phase[16,17] extraction of soluble chelates. Column extractions using ion exchange resins such as Chelex-100 (iminodiacetate) and immobilized 8-hydroxyquinoline can preconcentrate a wide range of transition metals (*e.g.* Cd, Cu, Fe, Mn, Ni, Co, Pb, Zn,[14,16,18,19] with generally greater recovery efficiency than is achieved with coprecipitation techniques.[9,15] Solvent extraction of soluble metal chelates can be used to achieve very large preconcentration factors, but is time consuming, laborious, and vulnerable to contamination during multiple handling steps.[10] More recently, automated off-line and on-line preconcentration and matrix removal systems have been used with flame atomic absorption spectrometry,[20] inductively coupled plasma atomic emission spectrometry (ICP-AES),[21] electrothermal atomic absorption spectrometry (ETAAS),[22,23] and inductively coupled plasma mass spectrometry (ICP-MS).[23–28] On-line methods combined with the low detection limits of ICP-MS allow moderately rapid processing (15 min per sample) of small (5–10 mL) samples, but require data collection using time-resolved software and do not escape limitations imposed by reagent blanks. Simpler methods for very precise metal determination in small samples using $Mg(OH)_2$ coprecipitation and isotope dilution ICP-MS have been described recently for Fe, Cu, Cd, and Pb,[29,30] but

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have not been developed as a true multi-element method and are inappropriate for the determination of monoisotopic elements (*e.g.* Mn, Co).

Since 1993, the Element (Finnigan MAT, Bremen, Germany) high resolution ICP-MS (HR-ICP-MS) system has been commercially available.[31,32] By operating at relatively high mass resolutions ($R = M/\Delta M$ at 10% peak height = 3000), most spectral interferences resulting from molecular ion formation in high-salt seawater matrices can be eliminated. Such resolving power has been exploited in recent versions of established preconcentration techniques[17] but has also opened up the potential for trace element determination directly in seawater samples with no sample pre-treatment other than acidification, dilution, and addition of internal standards.[8] Rodushkin and Ruth[8] demonstrated that a suite of 15 trace metals could be determined by combining internal standardization with non-matrix-matched external calibration curves for three certified reference materials including two seawater standards, diluted 2–5-fold in purified 0.14 M HNO_3. Although the measured values for most elements agreed with certified values, those for Cd and Zn were less satisfactory, and sensitivity limitations dictated that the signal intensity was extremely low for some analytes (*e.g.* tens of counts per second for Cd), and blanks for a number of elements were comparable to analyte concentrations in the diluted seawater. While demonstrating the potential for direct analysis, these drawbacks suggested that this method was not optimized for the routine analysis of natural seawater.

We have built on the work of Rodushkin and Ruth[8] to develop a new method of direct seawater analysis for 10 trace metals using HR-ICP-MS. The new technique provides better detection limits, lower blanks, reduced interferences, and a simpler standardization scheme. In comparison with established preconcentration techniques, our technique is much faster, requires just 50 µL of seawater, minimizes handling steps, requires no reagents other than purified nitric acid, suffers no uncertainties from recovery corrections, and allows the determination of monoisotopic elements. Here we demonstrate this method for the analysis of a coastal seawater standard reference material and for a transect of natural seawater samples from the Mid-Atlantic Bight (east coast, USA), and discuss prospects for modifications to allow the determination of a larger suite of elements in a wide variety of natural waters.

Experimental

Reagents and materials

Clean 6 M HCl was prepared by double sub-boiling distillation of reagent grade HCl. Ultra-pure 16 M HNO_3 and 29 M HF were purchased (Fisher, Pittsburgh, PA, USA, OPTIMA grade and Tama-Pure, Moses Lake Ind., Moses Lake, WA, USA). De-ionized, distilled water (ddH_2O) was prepared from laboratory de-ionized water using finishing de-ionizing columns and glass distillation. Primary standards (1000 ppb) used for working standard mixtures (in 10% HNO_3) were purchased from High-Purity Standards (Charleston, SC, USA). Sargasso surface seawater (SSSW) was collected using a shipboard underway trace metal clean sampler in July 1998 and was diluted to 1.0% using 10% HNO_3 for use as a blank. This seawater sample was verified to be uncontaminated for Fe (0.016 ppb), one of the most easily contaminated trace metals (J.-F. Wu, Massachusetts Institute of Technology, personal communication). We assume that concentrations of other trace metals in this sample are comparable to those determined previously for these surface waters.[2]

Polypropylene and polyethylene materials and the apparatus used for sample handling were leached in 1 M HCl (reagent grade in ddH_2O) at 60 °C for 12 h followed by thorough rinsing in ddH_2O and a pre-rinse with sample.

Sample preparation

To avoid sample contamination, all handling and preparation steps were carried out in HEPA-filtered Class 100 laminar flow clean benches. Coastal seawater samples (500 mL) were collected using Teflon-lined lever-action Niskin bottles (General Oceanics, Miami, FL, USA) lowered on a Kevlar hydrowire from a small coastal research vessel. Samples were held in the dark at 4 °C for up to 12 h prior to filtration through pre-cleaned 47 mm diameter 0.45 µm pore size polysulfone membrane filters (Supor, Gelman, Ann Arbor, MI, USA), then acidified to pH <2 by addition of 4 mL L^{-1} doubly distilled 6 M HCl. For analysis, 100 µL of seawater were simply diluted to 1.0 mL with 10% V/V ultra-pure HNO_3.

Instrumentation

The magnetic sector inductively coupled plasma mass spectrometer used (Element) has three nominal resolution ($R = M/\Delta M$ at 10% peak height) settings: low resolution (LR, $R = 300$), medium resolution (MR, $R = 3000$), and high resolution (HR, $R = 7500$). The true resolution capability depends on slight variations in slit manufacture; measured resolutions on our instrument are 300, 4300, and 9300. The mass spectrometer has three modes of operation: B-Scan (magnetic), E-Scan (electric), and Syncro-Scan (combined), well described elsewhere.[31,32] For this method we configured the mass spectrometer to perform E-Scans in both LR and MR (Table 1). First, Cd and Pb are scanned in LR, then the first row transition metals are scanned in MR, which is sufficient to resolve all matrix and plasma based interferences associated with seawater nebulization into an argon plasma.[8] All operating conditions are listed in Table 1.

To reduce further water-derived interferences and increase sensitivity, a microconcentric desolvation system (MCN-6000, Cetac Technologies, Omaha, NE, USA) with a free aspirating T-1 microconcentric nebulizer (Cetac Technologies) was used for sample introduction. In addition, comparisons were made with the recently developed µFlow nebulizer (Elemental Scientific, Omaha, NE, USA), which can be adapted to fit into the MCN-6000. The desolvating apparatus consists of a heated vertically mounted Teflon spray chamber and ~2 m of Teflon desolvating membrane tubing passing through a heated chamber which is flushed with dry Ar. This configuration introduces the sample into the plasma as a dried aerosol, resulting in an approximately 10-fold increase in sensitivity and 100-fold reduction in oxide formation.[33]

To optimize the performance for seawater analysis, we tested desolvated sample introduction in combination with the recently introduced 'guard electrode' (CD-1, Finnigan MAT), consisting of a pneumatically driven cylindrical platinum shield which, when actuated, is inserted between the load coil and the torch. This shielded torch configuration allows operation under 'cold plasma' conditions (reduced forward rf power), but can also be operated under typical hot plasma conditions. Under each operating condition, the plasma, the MCN-6000 and the low resolution lenses are tuned for maximum sensitivity and stability at $^{86}Sr^+$. These parameters are then used in medium resolution and the high resolution lenses are tuned for maximum separation of the $^{56}Fe^+$ and $^{40}Ar^{16}O^+$ peaks.

Results and discussion

Optimization of operating parameters

Crucial to the direct determination of trace metals in diluted seawater are detection limits and blanks for the analytes of interest. Detection limits, defined as three times the standard

Table 1 Operating parameters

Tuning parameters—					
Element (Finnigan MAT) with CD-1:					
MCN-6000 (Cetac):					
			Sweep gas flow rate	4.3 L min^{-1}	
Sample gas flow rate	0.95 L min^{-1}		Sweep gas temperature	175 °C	
Auxiliary gas flow rate	1.00 L min^{-1}		Spray chamber temperature	75 °C	
Cooling gas flow rate	14.0 L min^{-1}		Nitrogen flow rate	14 mL min^{-1}	
Sample uptake	1 min^{-1}				
Sample wash	1 min^{-1}				
Sample flow rate:					
T-1	50 µL min^{-1}				
µFlow	100 µL min^{-1}				
Acquisition parameters—					
Evolution parameters—					
Resolution	Low	Medium	Resolution	Low	Medium
Mass window (%)	10	125	Search window (%)	100	100
Samples per peak	100	30	Integration window (%)	100	50
Sample time/ms	10	5	Integration type	Average	Average
Segment time/ms	100	190	Runs	3	3
			Passes	12	8

deviation ($n=10$) of the noise, are dependent on sensitivity and stability of the blank. Absolute blank levels are also of concern because large blank corrections ($>50\%$) may adversely affect accuracy. Here we investigated parameters which influence detection limits and blanks to determine the optimum operating parameters for the analysis of diluted seawater.

Sample introduction. The sample introduction system may significantly affect the overall sensitivity in a number of ways. For direct aspiration of diluted seawater the most significant factors are the nebulizer, the condition of the cones, the desolvating system, and the CD-1.

Most experiments for the development of this method were performed using the T-1 microconcentric nebulizer, the standard nebulizer supplied with the MCN-6000. The newly developed µFlow nebulizer allowed some comparisons to be made with the T-1. These nebulizers were compared at sample gas flow rates of 0.8 L min^{-1}. The T-1 and the µFlow nebulizers self-aspirate at flow rates of 50 and 100 µL min^{-1}, respectively. Although both can aspirate 10% seawater, only the µFlow will not clog during routine daily analysis of seawater (at 10%) and will consistently restart after air has filled the uptake capillary. The T-1 is unable to sustain aspiration of 20% seawater for extended periods of time (>30 min). In general, the µFlow is better able to tolerate high total dissolved solids samples such as diluted seawater, and does not lose aspiration owing to higher flow resistance induced by air bubbles.

The MCN-6000 desolvating system provides several advantages for the direct analysis of seawater. (1) A clogged nebulizer can be removed and cleaned easily, without shutting down the plasma or affecting the tuning parameters. (2) Desolvating the aerosol significantly reduces oxides (two orders of magnitude) and enhances the sensitivity 10-fold above normal spray chamber, unshielded torch operating conditions.[33] Previously, molybdenum oxide interferences (Mo = 9 ppb, Cd = 0.03 ppb in seawater) prevented the direct determination of Cd in seawater.[8] Using the MCN-6000, MoO^+ interferences are sufficiently reduced to allow the accurate determination of Cd (0.005% ^{95}Mo produces 3 cps from $^{95}Mo\ ^{16}O^+$ at ^{111}Cd for diluted seawater). (3) Our experiments with direct aspiration of seawater in a Scott double bypass spray chamber resulted in the rapid deposition of major element oxides on the cones and attendant decrease in sensitivity. Lower oxide formation in the plasma achieved through desolvation also reduces oxide deposition on the cones, thereby providing extended hours of operation without the need for cone cleaning and without the associated decrease in sensitivity. For optimum results it is important to clean the cones thoroughly at the beginning of each day. Refractory oxides which build up on cones are not easily removed with common cone cleaning solutions (water, dilute nitric acid, Citranox, weak bases). However, we have found that a strong reducer (hydroxylamine hydrochloride in 35% acetic acid) works very well for this purpose.

For the standard spray chamber configuration, operation of the CD-1 in the shielded torch position results in a 10-fold enhancement in sensitivity relative to a standard spray chamber configuration (1 ppb In solution in 5% HNO_3). However, when operated with the MCN-6000, the CD-1 gives only a 2–3-fold increase in sensitivity, yielding a combined approximate 20–30-fold increase in sensitivity relative to unshielded spray chamber introduction.

Sources of contamination. Historically, blanks associated with sample collection have hindered the accurate determination of trace metals in natural seawater.[34] In the analytical laboratory, similar problems arise, particularly for metals which are abundant in terrestrial dust, laboratory and instrument materials, and anthropogenic aerosols, relative to typical dissolved seawater concentrations (*e.g.* Fe, Ni, Zn, Cu, and Pb). Our higher sensitivity combined with low analyte concentrations (in 10-fold diluted seawater) make blank control the single most important obstacle to the success of the method. In the following, we address blank issues with respect to sample introduction.

Blanks may have a source within the materials of the sample introduction system or may result from memory retained from previous sample introduction. Nickel blanks derived from Ni cones were eliminated by using Al cones, which remained dedicated to seawater analysis. After thorough cleaning, aspirating air indicated that no measurable blank (<20 cps) was associated with the Teflon spray chamber, desolvating membrane, sample carrier tube or torch. Aspirating various blank solutions (10% HNO_3, 10% HCl, 1% HF, 1% SSSW, and ddH_2O) indicated that significant blanks can be associated with the nebulizer uptake capillary. Signal spikes which wash out slowly, and result from the introduction of a different acid or acid strength, are attributed to the uptake tubing. These blanks may result from adsorption and desorption of trace metals on the Teflon uptake tubing or complexation by natural organic ligands which then bind metals to the tubing walls. We have noticed these problems specifically in our micronebulizers, implicating a source related to high surface area to sample volume. Uptake tubing blanks were reduced by the following steps: (1) rigorous cleaning (alternating 10% HNO_3, 10% HCl, 1–5% HF flushed through off-line); (2) occasional cleaning with acetone or H_2O_2 to remove organics; (3) exclusive use of a dedicated nebulizer for seawater analysis; (4) alternated aspiration of clean acids (10% HNO_3, 10% HCl, 1–5% HF) while the instrument warms up; and (5) limited aspiration of solutions containing high concentrations of the analytes.

Random intensity spikes during aspiration of a single solution are a result of reaspiration occurring in the tip of the nebulizer or in the heated spray chamber (if droplets accumulate). It is important to ensure that the system is completely heated and dry before beginning sample aspiration. After approximately 2 h we often find the tip of the nebulizer is wet (shorter time for the μFlow) and the spray chamber has accumulated droplets. Reaspiration of the droplets results in signal spikes which are most evident for Pb and Fe. To minimize this problem, the sample gas flow is heated to 80–90 °C. Heated by the Ar, the T-1 tip does not serve as a point of condensation and no drops accumulate in the spray chamber, but heated Ar is not as effective at the higher flow rates of the μFlow nebulizer. Under these conditions we have run the T-1 for 72 h without encountering reaspiration problems. In ongoing experiments, we have had success running the μFlow for 8 h, avoiding reaspiration effects by tipping the MCN-6000 on its side so that the spray chamber is horizontal.

To account accurately for blanks (the largest sources of uncertainty for accuracy), which may vary slightly depending on the solution aspirated (10% HNO_3, 10% HCl, 1% HF, 1% SSSW, or ddH_2O), it is best to match the blank solution to the samples. For this purpose, we have adopted SSSW with naturally low analyte concentrations and diluted it 100-fold (10-fold more than samples) in 10% HNO_3. Based on published metal concentrations for this region,[2] the resultant solution should contain analyte metals at <1% of coastal values. We have found that 1% SSSW can desorb blank from the sample introduction system that simple acids do not remove. Therefore, to quantify the instrument blank accurately, it is important to use 1% SSSW or a similar sample-matched matrix for blank determination and final cleaning before sample analysis.

Plasma conditions. Fundamental design features of the mass spectrometer result in sensitivity variations as a function of mass, resolving power, and ionization efficiency. Altering the ion source by varying plasma conditions affects sensitivity and stability, thereby influencing precision, accuracy, and detection limits. The CD-1 option allows the plasma to be operated at a significantly lower forward power (750 W) than conventional operating parameters (1350 W). To determine optimum plasma conditions we investigated forward powers of 750, 1100 and 1350 W using the T-1 nebulizer in the MCN-6000 with the CD-1 in place. At each forward power, matrix effects on sensitivity and mass bias relative to Sr (potential internal standard; see Standardization section below) were examined to determine optimum dilutions for seawater analysis. To do this, we spiked 10% HNO_3 and SSSW at 1, 5, 10, and 20% dilutions with a mixture of the analytes of interest. These solutions were then analyzed at each plasma condition, first after tuning in a 10% HNO_3 matrix, then after tuning in a 10% SSSW matrix. In each case, the tuning procedure consisted of optimizing sensitivity for the matrix at each forward power, and required only focus lens adjustment. The adjustment was greater between matrices at lower forward power. Between forward power adjustments, it was necessary to increase the nitrogen flow on the MCN-6000 (750 W = 0 mL min^{-1}, 1100 W = 8 mL min^{-1}, 1350 W = 14 mL min^{-1}) and then adjust the focus lens.

To illustrate the effect of the matrix on sensitivity at each plasma condition, we plotted Mn, Cu, Zn, and Cd sensitivity for each solution relative to that obtained for spiked 10% HNO_3 (Fig. 1). Also plotted were the sensitivities, relative to that obtained in 10% HNO_3, for all five dilutions of seawater when the instrument was tuned on the 10% SSSW matrix. Suppression of analyte sensitivity due to matrix occurs at all forward powers but is greatest at lower power (750 W). The sensitivity for 10% SSSW is always greater if the instrument is tuned on that matrix rather than on the 10% HNO_3 matrix. Elements with high ionization potentials, such as Zn and Cd, experience a larger matrix suppression from 0% SSSW to 1% SSSW than easily ionized elements such as Mn and Cu. The degree of suppression, although greater with increasing matrix, is similar for all four elements. Optimum sensitivity and minimum matrix effects are observed at forward powers at or above 1100 W when tuned on a 10% SSSW matrix.

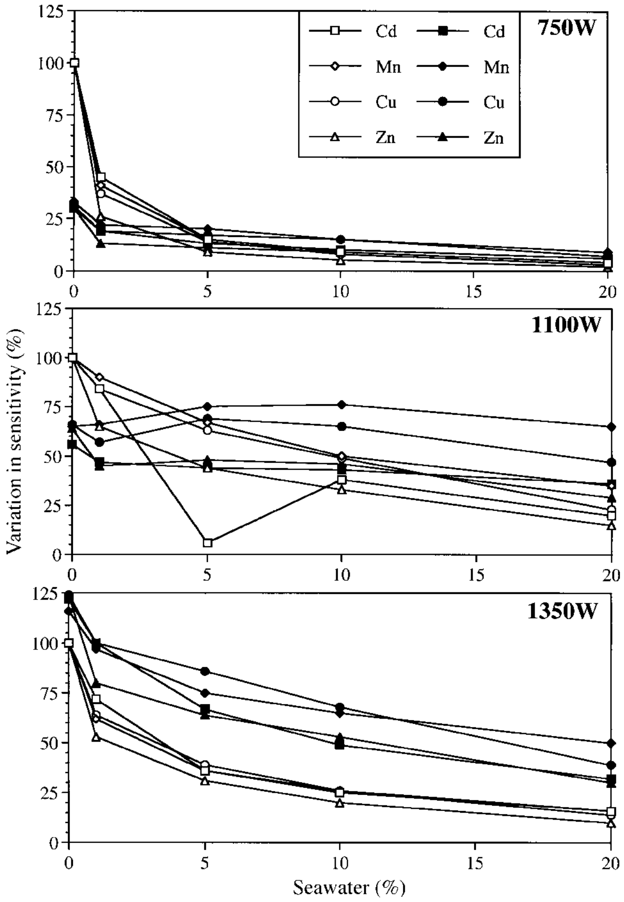

Fig. 1 Effect of tuning solution matrix and forward power on matrix-dependent sensitivity suppression. Tuning was performed either on 0% SSSW (open symbols) or 10% SSSW (closed symbols) in 10% HNO_3. Plasma forward power was 750, 1100, or 1350 W. Data for four representative metals are plotted as percentage difference relative to the sensitivity obtained for 0% SSSW when this matrix was used for tuning. At 1100 W, anomalous nebulizer clogging occurred after the 1% SSSW was run in the 10% SSSW tuning mode (closed symbols). This suggested that a decrease in nebulizer flow rate was responsible for the anomalously low sensitivity observed for all metals at 0% and 1% SSSW in this experiment. A small change in nebulizer flow rate is also probably responsible for the apparent sensitivity enhancement at 1350 W for 0% SSSW under the 10% SSSW tuning condition.

The accuracy of the results depends strongly on appropriate internal standardization for all elements of interest, particularly when determining appropriate blank subtraction on solutions with very different matrices. Strontium, a major conservative ion in seawater, can be calculated accurately (<0.1%) from salinity measured by conductivity at the time of sample collection. To investigate the efficacy of Sr as an internal standard for seawater matrices, we determined the consistency

Table 2 Variability of Sr/element ratios with varying seawater dilutions calculated as RSD (%) for 1, 5, 10, and 20% seawater solutions

	Tuned on spiked 10% HNO_3			Tuned on spiked 10% SSSW		
Element	750 W	1100 W	1350 W	750 W	1100 W	1350 W
Low resolution—						
Cd	39.4	48.5	10.0	23.4	9.9	5.4
Pb[a]	68.7	92.6	40.3	54.3	45.7	49.3
Medium resolution—						
V	6.0	5.9	8.1	5.6	4.6	0.7
Cr	15.0	7.2	4.0	7.6	3.2	7.8
Mn	16.2	7.0	2.1	11.6	2.4	4.1
Fe	23.9	5.8	5.8	17.3	2.1	1.8
Co	23.8	13.4	7.6	11.8	1.7	3.5
Ni	23.9	12.3	9.1	14.1	1.9	2.6
Cu	26.3	15.8	7.0	11.7	6.1	6.5
Zn	37.6	20.0	11.3	19.2	4.6	3.5

[a] Sr/Pb ratios were unstable owing to the high Pb blank on the day of the experiment.

on the Sr/element ratios for 1, 5, 10, and 20% spiked SSSW at the aforementioned forward powers (Table 2). Strontium/element ratios are most constant at greater forward powers whether tuned on 10% HNO_3 or on 10% SSSW matrix. At lower forward powers, poor ionizers (Cd and Zn) have less consistent Sr/element ratios than more easily ionized elements (Mn and Cu). At higher powers, however, the Sr/element uniformity over the complete range (1–20%) of matrices is better than $\pm 10\%$ for all elements and $\pm 5\%$ for most (Table 2). These results indicate that tuning on 10% SSSW improves the uniformity of Sr/element ratios at all forward powers investigated, and forward powers of $\geqslant 1100$ W exhibit the most stable ratios for all matrices.

The above findings indicate that optimum plasma conditions for maximum sensitivity, appropriate internal standardization, and accurate blank correction are obtained by tuning on 10% SSSW at forward power > 1100 W.

Detection limits and blanks

Detection limits are expressed as three times the standard deviation of the noise as determined in 1% SSSW (Table 3). At the sensitivities realized by the new method (T-1 = 800 000 cps ppb^{-1} and μFlow = 1 200 000 cps ppb^{-1} at ^{86}Sr), the detection limits are strongly influenced by the blank control. When both nebulizers are cleaned with an identical procedure, the μFlow has lower blanks, most notably for Fe (2 ×), Cu (2 ×), Zn (4 ×), and Pb (10 ×). This may be a result of cleaner materials used in construction or the absence of an encapsulated steel support for the sample probe of the μFlow. Indeed, Fe blanks can be observed to increase in an acid solution if the steel portion of the T-1 probe is left submerged for several minutes, despite encapsulation in Teflon. With the μFlow, $<12\%$ blank correction is necessary for CASS-3 and higher range coastal (New Jersey) samples for all elements except Cr (32%). For the lowest New Jersey coastal samples the blank correction is less than 30% for all elements except Cr (98%). The lower blank with the μFlow relative to the T-1 does not improve the detection limit for Fe, but those for Cu, Zn and Pb were improved approximately two-fold. For CASS-3 and high New Jersey coastal samples, all analytes of interest are present at 10 times the detection limits and many at least 50 times the detection limits (Table 3). These low detection limits and stable low blanks should allow for the accurate and precise determination (possibly with the exception of Cr) of the selected suite of trace metals in our study area. However, the method would be inappropriate for the determination of trace metals at levels much below our lowest samples, as for some elements (*e.g.* Zn, Cd) in open ocean surface waters.

Standardization

The intensities for elements of interest in both LR and MR are corrected for sensitivity variations by normalization to Sr. Blanks are determined from normalized 1% SSSW and subtracted as intensities before calculation of concentrations. Concentrations are then calculated by dividing the normalized intensities by the slope of a three point standard addition to

Table 3 Detection limits and blanks (ppt) determined on 1% SSSW (10 m)

		T-1		μFlow		Concentration (10 × dilution)		Blank correction (%) (μFlow)		Sample/detection limit	
Element	Isotope	Blank	DL	Blank	DL	CASS-3	NJ Coast	CASS-3	NJ Coast	CASS-3	NJ Coast
Low resolution—											
Cd	111	0.4	0.5	0.3	0.2	3.0	2–4	9.2	13.8	13	9
Pb	208	0.8	0.1	0.1	0.02	1.2	0.3–1.6	7.7	30.7	53	13
Medium resolution—											
V[a]	51			23.3	11.5	126	113–135	18.5	20.6	11	10
Cr	52	3.4	0.8	2.9	0.7	9.2	3.0–1.3	32.0	98.1	13	4
Mn	55	0.6	0.2	1.4	0.9	251	25.0–320	0.6	5.7	266	26
Fe	56	28.8	3.6	14.5	4.7	126	52.0–110	11.5	27.9	27	11
Co	59	0.1	0.1	0.1	0.1	4.1	1.0–4.0	2.0	8.1	39	10
Ni	58	2.0	1.1	1.6	0.5	38.6	15–40	4.3	11.0	71	28
Cu	63	11.0	1.4	4.2	1.2	51.7	16–52	8.2	26.4	43	13
Cu	65	10.4	2.4	4.0	1.1	51.7	16–52	7.8	25.2	49	15
Zn	64	14.5	7.1	8.1	2.3	124	28–140	6.6	29.1	54	12
Zn	66	11.6	4.2	2.9	1.9	124	28–140	2.4	10.5	65	15

[a] V was not determined using the T-1 nebulizer. Value for CASS-3 not certified but taken from Rodushkin and Ruth.[8] Acid blank (10%) used for V because 1% SSSW contributes approximately 10% of coastal values due to natural concentration.

Table 4 Precision and accuracy using a T-1 microconcentric nebulizer for analysis of CASS-3 standard coastal seawater [concentrations in ppb ± standard deviation (2σ)]

Element[a]	Typical cps	Determined 14 November 1998 ($n=4$)	Determined 6 January 1999 ($n=3$)	Certified
Cr	275	0.112 ± 0.014	0.101 ± 0.031	0.092 ± 0.010
Mn	6529	2.832 ± 0.246	2.710 ± 0.379	2.510 ± 0.360
Fe	3038	1.352 ± 0.078	1.404 ± 0.337	1.260 ± 0.170
Co	106	0.050 ± 0.005	0.045 ± 0.003	0.041 ± 0.009
Ni	404	0.409 ± 0.095	0.385 ± 0.078	0.386 ± 0.060
Cu	643	0.464 ± 0.140	0.482 ± 0.058	0.517 ± 0.060
Zn	656	1.288 ± 0.198	1.214 ± 0.132	1.240 ± 0.250
Cd	319	0.034 ± 0.006	0.029 ± 0.006	0.030 ± 0.005
Pb	924	0.010 ± 0.002	0.012 ± 0.003	0.012 ± 0.004

[a] V was not determined in CASS-3.

either CASS-3 or to one sample from an analytical batch (depending on the experiment).

Precision and accuracy

To assess the precision and accuracy of the method during two separate experiments, we analyzed CASS-3, a coastal seawater standard reference material collected 500 m off the coast of Nova Scotia, Canada (Table 4). The earlier data (14 November 1998) were obtained during the initial development of the method, whereas the later data (6 January 1999) represent maturity of the method. With the exception of Cr in the first data set, both determinations agree with the certified CASS-3 values within the 2σ confidence limits. It is worth noting, however, that the later data, representing the established method, demonstrate better agreement with certified values (most metals within 1σ). Replicate determinations on both dates indicate a precision similar to that certified for CASS-3 (Table 4). The precision (1σ) for the later date is 3–10% for V, Mn, Co, Ni, Cu, Zn, and Cd, 12% for Fe and Pb, and 15% for Cr.

Application to coastal waters off southern New Jersey

Any new method for seawater analysis should be shown to generate reproducible data for natural samples which follow spatial trends consistent with known oceanographic physical processes. We analyzed in duplicate a series of 0.45 μm filtered seawater samples collected along an inshore–offshore transect extending 32 km ESE from Little Egg Inlet in southern New Jersey, USA.

The precision of the measurements is evident from the duplicate analyses, which are within the precision determined by multiple analyses of CASS-3 (Table 4; Fig. 2). In addition, the smooth spatial trends decrease monotonically offshore (Fig. 2), consistent with previous trends for shelf waters in this region.[1] Elevated concentrations for Fe and Pb in the offshore sample are very reproducible and probably represent contamination during sampling, rather than analytical problems. The concentrations at the offshore stations agree well with the few previous measurements of mid-shelf metal concentrations,[3,34] but the trends for inner-shelf waters have not been documented previously. Nearshore concentration maxima are in the range observed previously at greater distances from shore and at higher salinities on the European shelf.[4,6]

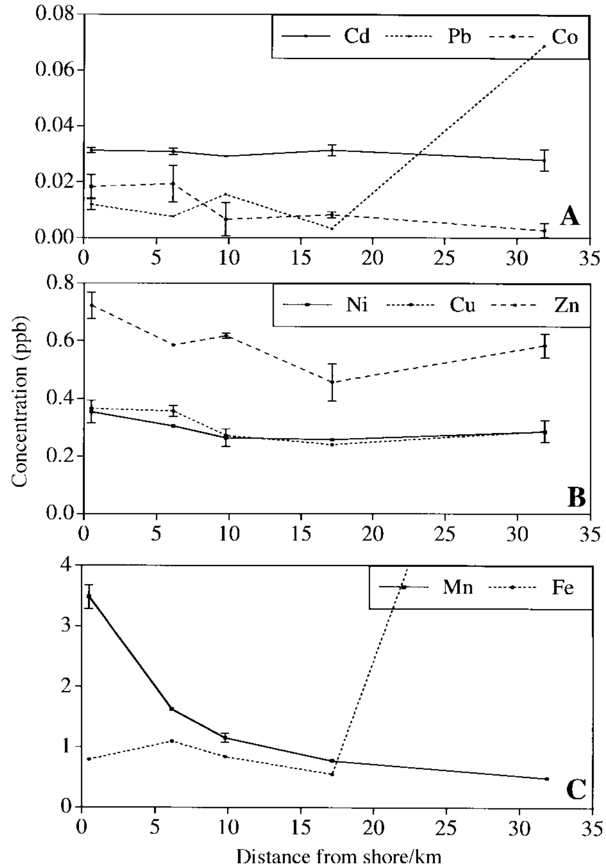

Fig. 2 Inshore–offshore trends of dissolved (<0.45 μm) seawater metals between 0.5 and 33 km from the southern New Jersey coast on 19 June, 1995. All samples were collected using trace-metal clean techniques at ~2 m off the bottom (bottom depth 8–30 m), and were analyzed in duplicate. Error bars represent ranges about the mean for duplicate analyses (some smaller than symbol size). The most offshore sample was probably contaminated during sampling for Fe, Pb, and possibly Zn.

Conclusions

We have demonstrated a new method for the direct analysis of coastal seawater which is rapid, precise, and accurate. The performance characteristics suggest its utility for a broader range of analytes and for other types of natural waters. At typical seawater concentrations not influenced by gross anthropogenic inputs,[35–37] we estimate that the method has sufficient sensitivity for potential determination of Al, P, Si, Ti, Sb, and possibly rare earth elements. An important aspect of the method is that, unlike previous methods, sensitivity variations can be normalized for a broad range of metals using only one (in this case natural) internal standard. Although the detection limits are not sufficient for the determination of many of these elements in open ocean seawater, V, Mn, and Cu could be determined in open ocean surface waters and V, Ni, Cu, Zn and Cd could be determined in deep or recently upwelled open ocean waters. Most estuarine waters could be analysed for all

10 elements, as long as the salinity is known and Sr is proven conservative. Similarly, fresh water detection limits should be at least 10 times lower, since no dilution would be required, and signal suppression due to the sea-salt matrix would be eliminated. For fresh water, an internal standard other than Sr may be desirable since the Sr level varies widely in continental waters; the method should work equally well with added In as an internal standard, as long as the total range of matrices within a sample set is not so large that mass bias suffers matrix-driven variability. The same caveat also applies for applications to brines and hydrothermal solutions. In its present form, the method requires that salinity (and therefore Sr) either be known for each sample or vary over the sample set within an interval which is smaller than the measurement precision for the analytes. Because salinity distributions in the ocean are sufficiently well known that salinity can be estimated to within 3% for most locations, this is not a severe limitation. Finally, because such small sample volumes are required (50 μL; less for fewer elements), the method lends itself to sample-limited applications such as sediment porewaters, biological fluids of small organisms, and samples from *in situ* micro-scale autonomous samplers.

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