FULL PAPER
JAAS
www.rsc.org/jaas

Determination of trace elements in filtered suspended marine particulate material by sector field HR-ICP-MS

Jay T. Cullen, M. Paul Field and Robert M. Sherrell*

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

Received 18th May 2001, Accepted 30th July 2001
First published as an Advance Article on the web 15th October 2001

Quantification of particulate (> 0.45 μm) and dissolved (< 0.45 μm) trace elements in seawater is imperative for understanding geochemical cycling in the marine environment. Suspended particulate trace element concentrations are typically < 10% of total element concentrations in seawater. To overcome analytical difficulties associated with low analyte concentrations, it is common to filter large volumes (tens to thousands of litres) of seawater. We report a novel method for the rapid quantification of Al (324 ppb), P (159 ppb), V (2.02 ppb), Cr (2.85 ppb), Mn (22.3 ppb), Fe (304 ppb), Co (0.129 ppb), Ni (0.817 ppb), Cu (1.68 ppb), Zn (3.25 ppb), Mo (0.264 ppb), Ag (0.079 ppb), Cd (0.029 ppb), Ba (3.54 ppb), Pb (1.13 ppb) and U (0.053 ppb) in digest solutions of suspended matter, filtered from 0.2 to 5.0 L of seawater. Filter digest solutions, consisting of a complex matrix of filter residue, sea salt, dissolved solids and strong acids, are analyzed on the ELEMENT, a high resolution, inductively coupled plasma mass spectrometer (Finnigan-MAT, Bremen, Germany). High sensitivity ($> 1 \times 10^6$ counts s^{-1} ppb^{-1} In; with shielded torch) combined with low flow rates (μFlow nebulizer, Elemental Scientific) provide excellent absolute detection limits (0.4 to 720 pg depending on the element). A resolution of 300 (low resolution) is appropriate for interference-free high mass analytes of interest (Ag, Cd, Pb, Ba and U), whereas 4300 (medium resolution) is sufficient to resolve all plasma-, water- and matrix-based polyatomic interferences on low mass analytes (Al, P and first row transition metals). The precision of the method is better than ±4% for most analytes. Accuracy could not be determined conventionally using a certified reference material (not available), but was estimated from spiked samples to be < ±4% when calculated using a standard additions curve and < ±10% for most elements if using an external standard curve.

Introduction

The vertical and horizontal distributions of many dissolved trace elements in the ocean are controlled by their interaction with particulate material suspended in the water column. Oceanic particulate material is dominated by the organic and inorganic residues of surface-dwelling organisms, with smaller contributions from lithogenic minerals, authigenic oxides, cosmic dust and anthropogenic particulate phases.[1–4] Great progress has been made over the last 30 years in techniques for seawater sampling and analysis, affording the community a fundamental understanding of the concentration and distribution of many dissolved trace elements in the ocean. Determining the distributions of particulate trace elements, although a requisite for investigating the marine biogeochemical cycles of the elements, is more difficult because particulate elemental concentrations are usually an order of magnitude lower than dissolved concentrations.[2,5–9] Perhaps because of low analyte concentrations and the potential for sample contamination, few high quality data sets of particulate trace elements in the ocean have been reported.

The trace element composition of marine particulate material is difficult to determine for a number of practical reasons. First, the concentrations of particulate matter in oceanic waters can be exceedingly low, requiring either processing of large volumes or the analytical challenge of working with small sample sizes. Second, techniques relying on sensitive analytical methods may be compromised by blanks associated with the filter material. Finally, sample contamination from the ship, investigator, sampling apparatus and reagents can compromise attempts to determine particulate trace element concentrations. Earlier studies that dealt successfully with these issues collected large samples, and determined a small set of elements using less sensitive and less efficient graphite furnace atomic absorption techniques.[8,10,11]

Here we describe a novel method suited for the rapid determination of a suite of bioactive trace elements and P (as a measure of biomass) in digests of small samples (*e.g.*, 0.2 L filtered seawater, about 60 μg dry weight) of marine particulate material. The method exploits the low detection limits and resolving power of HR-ICP-MS (ELEMENT, Finnigan MAT, Bremen, Germany) and is optimized for analyzing small, size-fractionated, particulate samples collected as described previously.[12] With modifications, this method is particularly suitable for small samples and low analyte concentrations.

Experimental

Reagents and materials

Trace metal-clean 32 M hydrofluoric acid (HF; Baseline, SeaStar Chemical Inc.) and 16 M nitric acid (HNO_3; Baseline, SeaStar Chemical Inc.) were used for all digestion procedures. Deionized, distilled water (ddH_2O) was prepared from deionized water by passing through finishing deionizing columns and glass distillation apparatus (Barnstead, Iowa, USA). The primary standards (10 ppm) were purchased from High-Purity Standards (Charleston, South Carolina, USA) and used to make working standard mixtures in ultrapure 10% HNO_3 (v/v). Preparation of standards and samples in 10% HNO_3 matched the acid matrix and minimized dilution of particle digest solutions.

All materials and apparatus used for sampling were of polypropylene, polyethylene, or polystyrene and were leached in 1 M HCl (Baker trace metal grade) at 60 °C for at least 24 h prior to use. Teflon digestion vials (15 mL screw-cap; Savillex,

DOI: 10.1039/b104398f

Minnetonka, MN, USA) were cleaned by boiling in *aqua regia* for 4 h, by rinsing with ddH$_2$O, and by sealed refluxing of 1 mL of 16 M (Baker reagent grade) HNO$_3$ on a hotplate set at 120 °C for an additional 4 h. Following acid leaches or boiling steps, all materials were rinsed thoroughly (5 times) with ddH$_2$O and left to dry in an HEPA filtered Class 100 laminar flow bench (Enviroco, Albuquerque, NM, USA).

Sample preparation

Size-fractionated particulate samples were collected on acid-washed filters and handled using established, trace element clean methodology.[12] Filter materials were selected to maximize flow rate and volume before clogging, with seawater passing sequentially through a stack of two 47 mm filters [5 μm Poretics polycarbonate (PC), then 0.45 μm Gelman Supor polysulfone (PS)] held in a polypropylene in-line filter holder.[12] Filters were stored at -20 °C prior to digestion in a sealed vial, using a mixture of 950 μL HNO$_3$ (16 M) and 50 μL HF (32 M), on a hotplate at 120 °C for 4 h. Although this procedure leaves the filter material partially digested, resultant solutions are visibly clear, and complete digestion of solids is assumed for this strong acid mixture, consistent with previous work on marine particles in this and other laboratories.[2,4,10,11] Loss of analyte to insoluble phases, formed during sample dissolution (*e.g.*, CaF$_2$), is a concern for HF-containing digests, but we assume that the small quantities of particulate material per acid volume mean that the digest solutions remain below the solubility product for such solids. In addition to fluorides, digests containing residual seawater Cl may form insoluble complexes with Ag. However, at typical particulate Ag concentrations, all the Ag will form soluble species.[13] Changes in particle quantity, the fraction of biogenic calcium, or the acid mixture from those described here and previously[12] might require that such issues be re-evaluated. After cooling, samples were prepared for analysis by adding 100 μL of the digest to 100 μL of an internal standard solution (10 ppb In in 10% HNO$_3$ v/v) and diluting with ddH$_2$O to a final volume of 1.1 mL, yielding a final acid strength of 10% HNO$_3$ (v/v). Maintaining a constant acid strength of 10% across samples, standards and rinse solutions avoids the development of time-dependent (5–20 min) sensitivity transients associated with changes in acid strength.[14] Unused filters and empty vials were processed as samples to determine trace element blanks associated with filter media and the digestion procedure, respectively. Note: hydrofluoric and nitric acids are hazardous. Appropriate safety precautions should be adopted after consulting Material Safety Data Sheets.

Standardization

A multi-element standard was prepared gravimetrically in 10% HNO$_3$ (v/v) from 10 ppm single element standards to realize concentration ranges typical of surface ocean marine particulate material digests. We make multi-element standards at target concentrations between 5 and 10 times greater than elements in the sample solutions. Since the composition of marine particulate material (terrestrial : phytoplankton : oxides) varies with location and defines the elemental ratios in the samples, it is important to have a number of multi-element stock standards which span the expected range sample composition. An internal standard of 10 ppb In was prepared in 10% HNO$_3$ (v/v) and 100 μL were added to all solutions yielding a final concentration of 1 ppb In. The six point external standard curve was prepared by serial dilutions of the multi-element standard. Similarly, three point standard additions were prepared by adding varying amounts of the multi-element standard to the sample matrix.

Instrumentation

The magnetic sector inductively coupled plasma mass spectrometer (ELEMENT, Finnigan MAT, Bremen, Germany) has three resolution [$R = M\ (\Delta M)^{-1}$ at 10% peak height] settings: low resolution (LR where $R = 300$), medium resolution (MR where $R = 4300$), and high resolution (HR where $R = 9300$). The concept, features and performance of the ELEMENT are described elsewhere.[15,16] To minimize dilution factors and enhance absolute detection limits, a PFA free aspirating nebulizer was used (μFlow-100; Elemental Scientific, Omaha, NE, USA). The nebulizer was fitted to a Scott double-bypass spray chamber using a PFA end cap (Elemental Scientific, Omaha, NE, USA). Additional argon gas was then introduced to the sample aerosol through a second port on the end cap. This configuration allowed independent optimization of the nebulizer and injection flow rates, thereby improving aerosol formation and reducing deposition of drops that re-aspirated from the nebulizer tip. This sample introduction system reduced both the blank and noise associated with aerosol formation. The sensitivity was enhanced approximately 10-fold when using a shielded torch, as here, compared to an unshielded configuration.[17] Detailed operating parameters, including the mass spectrometer scan settings, are given in Table 1.

Results and discussion

Calculation of results

To calculate the concentration of Al, P, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ag, Cd, Ba, Pb and U in unknown samples, external calibration curves were constructed from serial dilutions of a multi-element standard before each analytical run. Additionally, three point standard additions were made to every 5th sample. Raw intensities were normalized to the initial sensitivity for In in each resolution. Counts were corrected for instrument blank and slopes for the external standard curve, and standard additions were computed for all elements (counts s^{-1} ppb^{-1}). We routinely found correlation coefficients of $r = 0.9999$ for 3 to 6 point external calibration and standard additions curves. Unknown samples were quantified by dividing In-normalized intensities by the slope of the standard curve. To evaluate potential matrix effects, concentrations, calculated using the external standard curve and the standard

Table 1 Operating parameters

Tune parameters		
ELEMENT (Finnigan MAT) with CD-1		
Gas flow	L min^{-1}	
Sample	0.8	
Additional	0.3	
Auxilliary	1	
Cool	13	
Sample uptake	45 s	
Sample wash	60 s	
Sample flow rate	100 μL min^{-1}	
Rf power	1350 W	
Aquisition parameters		
Resolution	Low	Medium
Mass window (%)	10	150
Samples/Peak	100	30
Sample time/ms	3	5
Segment time/ms	30	225
Evaluation parameters		
Resolution	Low	Medium
Search window (%)	10	100
Integration window (%)	100	50
Integration type	Average	Average
Runs	3	3
Passes	15	8

additions method, were compared. Sample concentrations were then corrected for filter blanks,[12] yielding final particulate element concentrations on the filters. The average concentration calculated from two isotopes of the same element was taken when the difference was <2%. Occasionally poorer agreement was observed in very low concentration samples; in these cases the more abundant isotope was selected because of superior counting statistics.

Precision

The analytical precision of the method was evaluated using marine particulate samples collected from the Mid-Atlantic Bight off the coast of New Jersey, USA. Two filter digests, one polycarbonate (PC) and one polysulfone (PS), were analyzed thirteen times during a 24 h period (Table 2). Minimal variation in sensitivity throughout the run was observed in both LR and MR. The first 13 analyses (PC digest) indicated an initial LR In sensitivity of 1840000 counts s^{-1}, which gradually decreased to 1770000 counts s^{-1}, representing approximately 6% drift (Fig. 1). Continued analysis of the PS sample indicated no continued decrease in LR sensitivity, but rather a ±1% deviation about the mean sensitivity of 1770000 counts s^{-1}. Since the PS samples have a significantly greater matrix component than the PC samples, the initial 6% loss in sensitivity is interpreted as instrumental and not matrix related.

The precision obtained for the PC and PS filter digests is similar, ranging from approximately 1.0% for the best elements to 7.9% for ^{111}Cd in both sample types (Table 2). The relatively poor precision for ^{111}Cd is attributed to low count rates in the sample, which indicate theoretical counting errors of ±9% (1σ). Since these experiments, the total ion counting time on ^{111}Cd has been increased from 0.3 to 3.0 s, thereby improving theoretical counting statistics to <3%. One noticeable outlier was ^{60}Ni with precisions ranging between 16 and 50%. The poor data quality for Ni was due to a high Ni blank from the sampler and skimmer cones that decreased exponentially throughout the run as the cones become coated with oxides. If the first 4 of the 13 PC analyses were omitted, the precision was better than 10%. Ni contribution from the cones, although less variable during the later PS filter analysis, resulted in a relative standard deviation of 16%. This is attributed to 4-fold lower Ni concentration in the PS size fraction for this sample. Ni precision was improved for routine sample analysis by periodic blank determination, less frequent cleaning of cones, conditioning of the cones with a dilute seawater solution or, if necessary, switching to Pt or Al cones.[18]

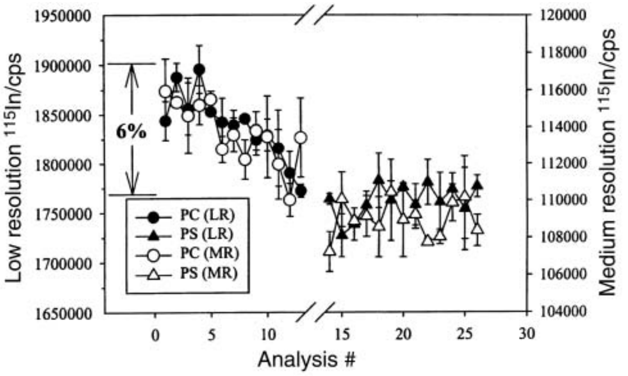

Fig. 1 Variability of ^{115}In sensitivity (1 ppb) in PC and PS filter matrices for low (solid symbol) and medium (open symbol) resolution over a typical 7 h analytical run. Error bars represent RSD (1σ). The break in the x-axis represents the approximate 2 h hiatus necessary to prepare a new sample set and recommence analysis.

Normalization to ^{115}In has little effect on the precision of the data for both sample matrix types (Table 2). This may be due to minimal instrument drift over a typical day of analysis (12–18 h); the total was generally less than 5%, or ±2.5% about the mean. When the error associated with the In correction is propagated (final fractional standard deviation $=[(\mathrm{stdev/mean})^2+(\mathrm{stdev/mean})^2]^{1/2}$) it is similar to that of the uncorrected data. If the drift were greater, as seen in other sample types, we would anticipate a significant improvement in precision upon internal standard normalization.

Accuracy

No appropriate certified reference material for suspended marine particulate samples is commercially available. The accuracy of the method was, therefore, measured by the recovery of a multi-element solution added to digests of both PC and PS matrices. The digestion of filters results in a complex

Table 2 Precision for analysis of marine particulates collected on two different filter materials ($n=13$)

	Polycarbonate (5 μm poresize)					Polysulfone (0.45 μm poresize)				
	No drift correction		In normalized			No drift correction		In normalized		
Element	ppb[a]	%RSD (1σ)	ppb[a]	%RSD (1σ)	Counting statistics %RSD	ppb[a]	%RSD (1σ)	ppb[a]	%RSD (1σ)	Counting statistics %RSD
^{27}Al	889	1.7	906	1.4	0.1	324	0.9	319	1.2	0.2
^{31}P	182	2.3	185	3.3	0.8	159	1.2	156	1.2	1.0
^{51}V	5.45	2.5	5.56	3.5	1.5	2.02	1.1	1.99	1.4	2.6
^{52}Cr	5.83	1.9	5.95	3.0	1.1	2.85	1.0	2.80	0.9	1.7
^{55}Mn	49.0	1.6	50.0	2.6	0.3	22.3	1.8	21.9	1.9	0.5
^{56}Fe	1340	1.5	1370	2.6	0.1	304	3.5	300	3.2	0.2
^{59}Co	0.449	1.4	0.46	2.3	3.5	0.129	3.2	0.127	3.3	6.8
^{60}Ni	3.04	51	3.09	50[b]	2.8	0.817	16	0.804	16[c]	5.9
^{63}Cu	2.78	1.8	2.84	2.8	1.9	1.68	1.7	1.65	1.4	2.5
^{65}Cu	2.79	1.8	2.85	2.8	2.7	1.63	1.1	1.61	1.5	3.8
^{64}Zn	8.48	1.1	8.65	1.7	2.1	3.25	2.0	3.20	1.8	3.7
^{66}Zn	8.68	2.6	8.85	3.6	2.8	3.38	2.5	3.33	2.8	4.8
^{98}Mo	0.178	2.4	0.180	2.8	2.8	0.264	2.3	0.264	2.3	2.3
^{109}Ag	0.147	1.5	0.148	1.9	1.3	0.079	1.6	0.079	1.7	1.9
^{111}Cd	0.024	7.9	0.024	7.9	9.6	0.029	7.9	0.029	7.6	9.0
^{138}Ba	12.1	1.0	12.1	1.4	0.1	3.54	1.2	3.55	1.3	0.2
^{208}Pb	3.64	1.9	3.67	1.3	0.2	1.13	1.3	1.13	1.2	0.4
^{238}U	0.089	2.6	0.089	3.3	2.5	0.053	2.4	0.053	2.7	3.2

[a] Concentration as analyzed. [b] Excluding the first four analyses actual RSD(%) = 9.6. See text for details. [c] Excluding the first four analyses actual RSD(%) = 6.6. See text for details.

Table 3 Comparison of known spike concentrations determined by an external standard curve and a standard additions curve

Element	Known concentration (ppb)	Ext. std. det. ($n=5$)	% Diff.[a]	Std. add. det. ($n=5$)	% Diff.[a]
Polycarbonate					
Al	19.7	19.9	0.9	20.5	3.9
P	213	239	11.8	215	0.9
V	1.71	1.74	2.1	1.75	2.3
Cr	1.76	1.84	4.2	1.77	0.6
Mn	10.9	11.3	3.0	11.0	0.6
Fe	35.7	36.9	3.4	35.7	0.1
Co	0.723	0.737	1.8	0.741	2.5
Ni	3.56	3.43	−3.5	3.56	0.1
Cu	3.59	3.66	1.9	3.62	0.7
Zn	3.56	3.59	1.1	3.82	7.5
Mo	7.43	7.66	3.1	7.54	1.6
Ag	0.373	0.381	2.1	0.378	1.5
Cd	1.76	1.76	0.0	1.80	2.5
Ba	1.76	1.67	−5.4	1.80	2.1
Pb	0.173	0.163	−5.9	0.177	2.5
U	0.403	0.374	−7.1	0.403	0.0
Polysulfone					
Al	19.7	19.6	−0.5	20.9	5.7
P	213	218	2.1	218	2.1
V	1.71	1.71	0.4	1.72	0.8
Cr	1.76	1.65	−6.4	1.80	2.3
Mn	10.9	10.3	−5.8	11.2	1.9
Fe	35.7	32.7	−8.3	35.7	0.1
Co	0.723	0.692	−4.3	0.737	1.8
Ni	3.56	3.22	−9.5	3.62	1.9
Cu	3.59	3.20	−11	3.61	0.6
Zn	3.56	3.57	0.4	3.67	3.1
Mo	7.43	7.25	−2.3	7.66	3.1
Ag	0.373	0.317	−15	0.387	3.8
Cd	1.76	1.64	−6.5	1.81	3.3
Ba	1.76	1.74	−1.1	1.79	1.7
Pb	0.173	0.163	−5.5	0.174	0.9
U	0.403	0.395	−1.9	0.401	−0.4

[a] Calculated %diff. = (determined − known)/known × 100.

matrix of high total dissolved solids consisting mainly of filter residue, sea-salt, particulate sample and mineral acids, which can affect instrument sensitivity. To evaluate the potential matrix effects on the accuracy, five samples of each matrix type were prepared with an addition of the multi-element standard. Both an external calibration and standard additions curve (Table 3) were then used to quantify recovery of the multi-element spike.

In both PC and PS sample matrices, external standardization (acid matrix only) is accurate to $<\pm15\%$ for all elements of interest and $<\pm10\%$ for most (Table 3). There is an under-determination of the spike concentration (as indicated by negative numbers) for most elements in the PS matrix. These data suggest an overall suppression across the mass range that is not appropriately corrected for by In normalization (Table 3). Most notable discrepancies between the spiked and determined values are evident for Fe (−8.3%), Ni (−9.5%), Cu (−11%) and Ag (−15%). Unlike the PS matrix, the recovery of the spike concentration in the PC matrix does not exhibit a consistent negative offset. Rather, most of the determined values fall within the precision of the data. The largest discrepancies were observed for P (+12%), Pb (−5.9%) and U (−7.1%). The sensitivity of P, a poor ionizer, was enhanced relative to the metals. The approximate 10% enhancement was observed on five subsequent analysis dates, suggesting that the phenomenon is not related to individual samples or tune parameters. In the PC matrix, P was over-determined by +12% and in the PS matrix, where most metals are suppressed, it was over-determined by +2.1%. A preferential seawater matrix enhancement of light elements using HR-ICP-MS has been reported.[19] An increase in electron density in the central channel results in an increase in ambipolar diffusion of low mass elements to hotter zones of the plasma. Since low first ionization (<8 eV) potential elements experience greater than 90% ionization efficiency it is likely that only poor ionizers (P = 33% ionization[20]) will experience increased ionization in the hotter region. Because of low mass and a high first ionization potential (10.5 eV), P would be a likely candidate for such an effect, possibly explaining its observed matrix enhancement. Regardless of the mechanism it is clear that small ($<10\%$) matrix enhancements and suppressions, not corrected by In normalization, occur for a number of elements.

Quantification of the multi-element spike by applying the slope of one three-point standard additions curve yields an accuracy of $\pm4\%$ for all elements except Zn (PC, $\pm7.5\%$) and Al (PS, $\pm5.7\%$; Table 3). All determined concentrations were calculated from two analyses (determined = spiked sample − sample), and therefore have associated propagated errors. Even with error propagation, our determined values fall within or approach the precision of the data. It is clear from these results that the small matrix suppressions and enhancements discussed above are compensated for by a standard additions curve. In summary, external standards provide accuracy at about the $\pm10\%$ level, whereas the standard additions method yields the most accurate ($\pm4\%$) results, approaching the precision ($\pm4\%$) of the data for all elements. Based on these results we recommend the use of standard additions curves for the highest quality data.

Detection limits and blanks

Detection limits were calculated as three times the standard deviation (3σ; $n=10$) of the acid blank (Table 4). The best detection limits were observed for high isotope abundance, easily ionized, high mass elements (>100 amu) with low blanks and no interferences. Elements (such as U, 40 ppq; Table 4) that meet these criteria typically exhibit excellent detection limits ranging from <10 to 10s of ppq.[21] Poorer detection limits were evident for elements with high first ionization potentials, low masses, numerous interferences and potential blank problems. For example, a combination of reduced sensitivity due to poor ionization, requirement of MR, poor ion transmission and high blanks resulted in P having the highest detection limit of 72 ppt (Table 4). Fortunately, low mass elements exhibiting poorer detection limits are typically found at high concentrations ($>$ppb) in most surface water particles.[7] A free aspirating micro-flow PFA nebulizer operating at a flow rate of 100 μL min^{-1} requires only 500 μL of sample for an analysis. Such small sample volumes translate to excellent absolute detection limits ranging from 0.4 to 720 pg for U and P, respectively (Table 4).

The instrument blank ranged in concentration from 0.01 ppt for U to 352 ppt for P and is not a significant (less than a 4%) correction for most elements determined in typical marine particulate samples collected on both filter types off the coast of New Jersey (Table 4). The Ag blank was large relative to sample concentrations (15% PC to 28% PS; Table 4), however, the blank was stable (as indicated by low detection limits) minimizing error associated with the correction. The contribution of Ni from the cones may also be a significant fraction (up to 8%) of the total Ni measured in the sample. If we use the detection limit (3σ of the blank) as an approximation of the error associated with blank correction we see that the uncertainty of blank correction ($<3\%$) for all elements in typical samples is similar to the precision ($<4\%$) and accuracy ($<4\%$) of the data.

Depending on particle composition and concentration, a minimum acceptable filtration volume can be estimated: however, when doing so, it is important to take into consideration blanks associated with selected filter media. Filter blanks are the most important component of the total

Table 4 Detection limits and blanks determined on 10% HNO_3 (v/v)

				Blank correction as % of sample		Detection limit as % of sample	
Element	DL (ppt)	Abs. DL/pg per filter	Blank (ppt)	Polycarbonate	Polysulfone	Polycarbonate	Polysulfone
Al	43	430	310	0.03	0.10	0.005	0.01
P	72	721	350	0.19	0.22	0.04	0.05
V	1.7	16.6	1.8	0.03	0.09	0.03	0.08
Cr	2.1	20.9	6.7	0.12	0.24	0.04	0.07
Mn	1.6	16.3	2.1	0.00	0.01	0.003	0.01
Fe	35	353	95	0.01	0.03	0.003	0.01
Co	0.84	8.36	1.2	0.26	0.90	0.19	0.65
Ni	11	109	56	1.8	6.9	0.36	1.3
Cu	27	265	52	1.9	3.1	0.95	1.6
Zn	24	238	56	0.66	1.7	0.28	0.73
Mo	1.2	11.8	2.3	1.3	0.87	0.66	0.45
Ag	2.5	24.8	22	15	28	1.7	3.1
Cd	0.4	4.31	0.1	0.44	0.37	1.8	1.5
Ba	3.4	34.3	5.4	0.04	0.15	0.03	0.10
Pb	0.58	5.77	1.9	0.05	0.17	0.02	0.05
U	0.04	0.355	0.01	0.01	0.01	0.04	0.07

uncertainty of the blank correction.[12] A summary ($n=10$) of filter blank data taken from Cullen and Sherrell[12] (1999) indicated a larger blank associated with PS than with PC filters (Table 5). Samples with relatively low particulate metal concentrations collected on PC filters have less than a ±3.2% blank correction for all elements, whereas samples collected on the paired PS filters may require up to 25% blank correction for some elements (Zn = 25% and Cd = 17%; Table 5). This result depends, of course, on the size fractionation of elements in the sample investigated. As a result, the uncertainty in the filter blank (1σ), expressed as a percent relative standard deviation of the sample, is very small (<1%) for PC filters and may be as high as ±7.6% for PS filters. This uncertainty when propagated with the sample uncertainty ($S_{tot} = (S_1^2 + S_2^2)^{1/2}$; where S_1 = analytical error and S_2 = error associated with filter blank; Table 5) does not contribute to the error associated with determination of particulate metal concentrations on PC filters, but does increase the error associated with PS filters. The propagated error is greatest for Zn, demonstrating a sample precision of ±1.8% and a filter blank corrected precision of ±8.7%. Overall, the error magnification is small for most elements (%RSDs less than ±5%; Table 5), and is quite acceptable for interpretation of this sample type.

Table 5 Polycarbonate and polysulfone filter blanks (n = 10) and total error associated with filter blank correction of a representative sample

Element	Abs. DL/ ng	Filter blank (ppt)[a]	Blank correction (%)	S_1 (%RSD)[b]	S_2 (%RSD)	S_{tot} (%RSD)
Polycarbonate						
Al	18.0	1364	0.2	1.4	0.002	1.4
P	8.7	1364	0.7	3.3	0.004	3.3
V	—	—	—	3.5		3.5
Cr	—	—	—	3.0		3.0
Mn	0.44	35.6	0.1	2.6	0.0002	2.6
Fe	19.3	1344	0.1	2.6	0.0004	2.6
Co	0.04	3.9	0.9	2.3	0.02	2.3
Ni	—	—	—	50		50
Cu	1.5	92.1	3.2	2.8	0.48	3.3
Zn	1.7	162	1.9	1.7	0.06	1.8
Mo	—	—	—	2.8		2.8
Ag	0.01	3.6	2.0	1.9	0.03	1.9
Cd	0.03	4.5	3.0	7.9	0.04	7.9
Ba	—	—	—	1.4		1.4
Pb	—	—	—	1.3		1.3
U	0.01	0.6	0.0	3.3	0.02	3.3
Polysulfone						
Al	33.6	3510	1	1.2	0.05	1.3
P	96.7	5890	4	1.2	1.2	2.4
V		—	—	1.4		1.4
Cr		—	—	0.9		0.9
Mn	1.1	151	1	1.9	0.007	1.9
Fe	40.5	3136	1	3.2	0.03	3.2
Co	0.1	8.9	7	3.3	0.93	4.3
Ni	—	—	—	16		16
Cu	1.4	116	7	1.4	1.7	3.1
Zn	8.2	798	25	1.8	6.9	8.7
Mo	—	—		2.3		2.3
Ag	0.04	4.6	2	1.7	0.60	2.3
Cd	0.16	13.5	17	7.6	0.75	8.4
Ba	—	—	—	1.3		1.3
Pb	—	—	—	1.2		1.2
U	0.09	3.8	0	2.7	3.38	6.0

[a] From Cullen and Sherrell (1999, ref. 12). [b] See Table 4.

Conclusions

A simple, multi-element method for the determination of a suite of trace elements (Al, P, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ag, Cd, Ba, Pb and U) in marine particulate material using sector field HR-ICP-MS is presented. The inclusion of P in the method allows estimation of biomass-normalized metal concentrations in phytoplankton-dominated surface ocean samples. This is the first method described for ICP-MS analysis of small samples of this type (equivalent of <0.5 L filtered seawater; 100 µL of particle digest solution), and replaces our much less efficient approach using graphite furnace atomic absorption spectrophotometry.[2,4] The precision (<4%) and accuracy (<4% using a matrix matched standard curve) of the method allow resolution of small geochemical gradients in natural samples and high-precision measurements of inter-element ratios that can reveal geochemical mechanisms governing element distributions. For example, the dependencies of Cd/P ratios in natural phytoplankton samples have been investigated using this method.[22] With minor modifications, the technique used here is appropriate for a wide range of environmental particles sampled on filters, including freshwater particles, cultured plankton, atmospheric aerosols, and indoor dusts.

Acknowledgements

This work was supported by grants to R.M.S. from NSF (OCE 9720692) and NOAA/CMER. The equipment used was purchased with support from NSF (ARI 9601668) and Rutgers University. We thank two anonymous reviewers whose helpful comments improved the manuscript.

References

1 R. Collier and J. Edmond, *Prog. Oceanogr.*, 1984, **13**, 113.

2 R. M. Sherrell and E. A. Boyle, *Earth Planet. Sci. Lett.*, 1992, **111**, 155.

3 J. R. Donat and K. W. Bruland, in *Trace Elements in Natural Waters*, ed. B. Salbu and E. Steinnes, CRC Press, Boca Raton, 1995.

4 R. M. Sherrell, M. P. Field and Y. Gao, *Deep-Sea Res.*, 1998, **45**, 733.

5 J. H. Martin and G. A. Knauer, *Earth Planet. Sci. Lett.*, 1986.

6 K. W. Bruland, G. A. Knauer and J. H. Martin, *Limnol. Oceanogr.*, 1978, **23**, 618.

7 J. K. B. Bishop, R. W. Collier, D. R. Ketten and J. M. Edmond, *Deep-Sea Res.*, 1980, **27A**, 615.

8 K. W. Bruland, K. J. Orians and J. P. Cowen, *Geochim. Cosmochim. Acta*, 1994, **58**, 3171.

9 W. M. Landing and K. W. Bruland, *Geochim. Cosmochim. Acta*, 1987, **51**, 29.

10 E. Helmers, *Mar. Chem.*, 1996, **53**, 51.

11 J. Kuss and K. Kremling, *Mar. Chem.*, 1998, **68**, 71.

12 J. T. Cullen and R. M. Sherrell, *Mar. Chem.*, 1999, **67**, 233.

13 J. R. Reinfelder and S. I. Chang, *Environ. Sci. Technol.*, 1999, **33**, 1860.

14 I. I. Stewart and J. W. Olesik, *J. Anal. At. Spectrom.*, 1998, **13**, 843.

15 I. Feldmann, W. Tittes, N. Jakubowski, D. Stuewer and U. Gieβmann, *J. Anal. At. Spectrom.*, 1994, **9**, 1007.

16 U. Gieβmann and U. Greb, *Fresenius' J. Anal. Chem.*, 1994, **350**, 186.

17 P. K. Appelblad, I. Rodushkin and D. C. Baxter, *J. Anal. At. Spectrom.*, 2000, **15**, 359.

18 M. P. Field, J. T. Cullen and R. M. Sherrell, *J. Anal. At. Spectrom.*, 1999, **14**, 1425.

19 I. Rodushkin, T. Ruth and D. Klockare, *J. Anal. At. Spectrom.*, 1998, **13**, 159.

20 K. E. Jarvis, A. L. Gray and R. S. Houk, *Handbook of Inductively Coupled Plasma Mass Spectrometry*, Chapman and Hall, New York, 1992.

21 M. P. Field and R. M. Sherrell, *Anal. Chem.*, 1998, **70**, 4480.

22 J. T. Cullen, T. W. Lane, F. M. M. Morel and R. M. Sherrell, *Nature*, 1999, **402**, 165.