Magnetic Sector ICPMS with Desolvating Micronebulization: Interference-Free Subpicogram Determination of Rare Earth Elements in Natural Samples

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A new method has been developed combining desolvating micronebulization with magnetic sector inductively coupled plasma mass spectrometry (ICPMS) for the analysis of all 14 stable rare earth elements (REEs) in small samples of marine particulate matter. Application is demonstrated for REEs in suspended particles from a deep ocean hydrothermal vent plume and a geological reference material. A 100-fold reduction in oxide formation, relative to standard nebulizer−spray chamber sample introduction, makes oxide interference correction negligible, even for samples that are very enriched in Ba and light REEs. Enriched isotopes for one light and one heavy REE (^{145}Nd and ^{171}Yb) are used as both isotope dilution and internal standards, providing determination of all the REEs in one analysis. This standardization scheme eliminates the need for multimass drift correction used previously to achieve acceptable accuracy with external standardization techniques. Instead, the method exploits capabilities for accurate and precise determination of isotope ratios, a principal strength of ICPMS, and the mass-independent sensitivity of electric field scans on our double-focusing instrument. We demonstrate overall precision of $\leq$2% (1σ) and accuracy better than 6% for all the REEs (except Er = 8.7%), based on comparison to recommended values for USGS certified reference material BHVO-1 (basalt). This performance is similar to that obtained by full isotope dilution mass spectrometric techniques, but the new method is far simpler, requires 5 min sample^{-1}, and avoids interferences introduced by complex mixtures of enriched isotopes. Sensitivity of $(1.2-1.4) \times 10^6$ counts s^{-1} ppb^{-1} and background intensities of 2−60 counts s^{-1} provide excellent detection limits of 1−40 ppq, a 100-fold improvement on established ICPMS methods. The low sample introduction rate (100 μL min^{-1}) allows unprecedented absolute detection limits of 1−20 fg.

The rare earth elements (REEs) comprise a coherent series of elements possessing generally similar chemical properties. Thus, to a first approximation, the trivalent REEs are transported through the environment as a group. However, a systematic decrease in ionic radii as inner 4f electrons are filled with increasing atomic number (the "lanthanide contraction") leads to systematic differences in the elements' chemical properties, resulting in fractionation along the series during reaction and transport in the natural environment. Because this property generates characteristic relative abundance patterns for the REEs which reflect chemical processes in the natural environment, the REEs comprise a good model for understanding the relationship between fundamental properties of elements and their geochemical behavior in the marine environment.[1,2]

Inductively coupled plasma mass spectrometry (ICPMS) has the potential to be an ideal tool for precise, accurate, and rapid determination of REEs, and much effort has been expended recently within the geological community to optimize multielement ICPMS techniques.[3] However, published methods have optimized accuracy using cumbersome schemes to correct for polyatomic oxide interferences and for instrumental drift between samples and standards. Drift can be corrected as a curvilinear function of mass by running external drift monitors at frequent intervals[4] or as a linear function of mass using internal drift correctors.[5,6] More recently, enriched isotopes have been used as internal standards for drift correction.[3] Corrections must also be made for interferences of metal oxides (MO$^+$) on M + 16 analytes, incorporating variability of oxide production with time and matrix.[5−7] The middle REEs (MREEs) are complicated by many oxide interferences. Most prevalent among these is the interference of ^{135}Ba^{16}O$^+$ on ^{151}Eu, of ^{137}Ba^{16}O$^+$ on ^{153}Eu, and of the light REE (LREE) oxides on the MREEs.[6,7] Corrections for these oxide interferences are often made externally and may introduce additional uncertainties for the MREEs.

The determination of REEs in seawater or suspended oceanic particles is an especially challenging goal, complicated by limited sample, low concentrations, and difficult matrixes (e.g., Na, Ca,

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Mg, Si, Al, Cl, and digested filter material). A number of analytical methods have been used to determine the REEs in marine samples, including instrumental neutron activation analysis (INNA),[8] isotope dilution thermal ionization mass spectrometry (ID-TIMS),[9,10] and quadrupole ICPMS.[11] Only ID-TIMS and ICPMS are sufficiently sensitive to determine REEs on practical sample sizes of open ocean particulate matter, which occurs in suspension at a dry weight concentration of $5-100$ μg L^{-1}. ID-TIMS methods, while notable for high precision, are hindered by limited multielement capability, slow sample throughput, requirements for extensive sample preparation, and inability to determine the monoisotopic REEs (^{141}Pr, ^{159}Tb, ^{165}Ho, and ^{169}Tm). Alternative microsampling methods for ICPMS, such as direct injection nebulization (DIN) and electrothermal vaporization (ETV), may be used to reduce absolute detection limits and minimize oxide interferences. However, DIN is characterized by high oxide production at sensitivity similar to that of conventional nebulization,[12] and ETV generates transient signals which limit the number of elements per analysis and the precision of the measurements.[13,14]

Given the analytical difficulty, oceanic data for REE distributions are still relatively sparse, and the marine geochemistry of the REEs is not thoroughly understood.[2] One impediment to progress has been the difficulty of analysis; REEs are present in seawater at nanogram per liter concentrations, and the open ocean particulate fraction is just a few percent of the total.[15] As a further challenge, interpretable fractionations among the REEs can be rather subtle and may be resolvable only if analytical precision is better than 5%, a level of performance not typically achieved for trace metal analysis of seawater.[15] Principal among the outstanding geochemical questions are the magnitude and fractionation associated with diffusive flux from sediments into the ocean, the nature of dissolved REE adsorption/desorption reactions with a range of natural oceanic particle types, and the role of hydrothermal vent systems in regulating the oceanic residence time of the REEs.[2,15-17]

In this work, we used a microconcentric desolvating nebulizer (MCN-6000, CETAC Corp., Omaha, NB) to improve substantially the absolute detection limits of magnetic sector ICPMS by achieving analyses on sample volumes of $\sim$100 μL at $\sim$10-fold increase in sensitivity. A novel but simple internal standardization method was developed and used in combination with mass bias tuning to achieve overall precision similar to that of ID-TIMS methods ($<\pm3\%$[10]), with greatly simplified interference correction

(none) and drastically reduced analysis time. The key aspects which make the method possible are improved sensitivity, low oxide production, and mass-independent sensitivity at a single magnet setting.

EXPERIMENTAL SECTION

Reagents and Materials. Trace metal clean 32 N hydrofluoric acid (HF; Ultrex grade, J.T. Baker, Phillipsburg, NJ) and clean 16 N nitric acid (HNO_3), prepared by double subboiling distillation of reagent grade acid in a Teflon still, were used for digestion procedures. Deionized distilled water (ddH_2O) was prepared from house deionized water using finishing deionizing columns and glass distillation. Primary standards (1000 μg mL^{-1}) used to make working standard mixtures in 2% HNO_3 (v/v) were purchased from High-Purity Standards (Charleston, SC), and enriched isotopes (^{145}Nd and ^{171}Yb) were purchased from Oak Ridge National Laboratories (Oak Ridge, TN). Users should be warned that HF and HNO_3 are highly corrosive acids and should be handled with extreme caution.

Polypropylene and polyethylene materials and apparatus used for sample handling were leached in 1 N (reagent grade) HCl at 60 °C for 12 h. Teflon digestion vials were cleaned by sealed refluxing of 1 mL of 16 N (reagent grade) HNO_3 on a hotplate for 4 h, rinsing, and then boiling in 33% aqua regia for 2 h. Following acid leaching, all containers are rinsed thoroughly (5×) with ddH_2O.

Marine Particulate Samples. Particulate samples were collected from the neutrally buoyant hydrothermal plume in the vicinity of hydrothermal vent L at 9°46′ N above the East Pacific Rise during hydrowire casts from the R/V Atlantis II, Voyage 132 during April 3−27, 1996. The rotating automatic pump for particulate inorganics determination (RAPPID[18]), a battery-powered large-volume in situ filtration system, was used to collect samples on 0.45-μm pore size Millipore HA filters (142-mm diameter). Filtered volumes varied from 700 to 1530 L for the 20 samples collected. After brief application of mild vacuum to the filter holder to remove most residual seawater (while avoiding filter rinsing), filters were folded in half and immediately frozen. In the laboratory on shore, a representative subsample for REE analyses was cut from the frozen filters using a polycarbonate template and a stainless steel scalpel on an acid-cleaned acrylic cutting board. This subsample, representing 14.8% of the total particulate mass (by area; approximately 1 mg) and containing a similar mass of residual sea salt, was digested in 980 μL of HNO_3 and 20 μL of HF (concentrated acids) in closed 15-mL Teflon screw-cap vials (Savillex, Minnetonka, MN) on a hotplate for 4 h at $\sim$100 °C. This refluxing solution completely digested both the particulate and filter material. After cooling, digest solutions were diluted to 4 mL with distilled deionized water in preparation for rare earth analysis.

Standard Rock Reference Material BHVO-1. The certified reference material BHVO-1 (basalt) was digested by Dr. Jenish Jain at Notre Dame University for an interlaboratory comparison using a procedure modified from that of Xie et al.[19] In brief, 50

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mg of sample powder was digested in 2 mL of HNO_3 and 2 mL of HF in a screw-cap Teflon vial (Savillex) at 100 °C. The HF/HNO_3 mixture was then evaporated to dryness, and the residue was taken into solution in 2 mL of concentrated HNO_3. The solution was dried, redissolved a second time in 2 mL of concentrated HNO_3, and dried again. The two nitric acid treatments ensured complete conversion of fluorides to nitrates. Finally, the residue was taken up in 2 mL of concentrated HNO_3, transferred to a 125-mL bottle, and diluted gravimetrically with water to ~100 mL to give a final total dissolved solids of <0.1%. The entire procedure was carried out under clean laboratory conditions (class 1000).

Standardization. The Nd and Yb concentrations for unknowns were calculated by isotope dilution from determined $^{145}Nd/^{143}Nd$ and $^{171}Yb/^{173}Yb$ ratios. The enriched isotope signal intensities were also used as internal standards for determination of the rest of the REEs (see Calculation of Concentrations, below). Nd and Yb spikes used for isotope dilution are enriched above natural as follows: $^{145}Nd = 91.58\%$, $^{143}Nd = 0.64\%$, $^{171}Yb = 95.07\%$, and $^{173}Yb = 0.74\%$ (Oak Ridge National Laboratory lot determination). Concentrations of working spike solutions were determined using natural Nd and Yb standard solutions for reverse isotope dilution. These natural Nd and Yb standards were spiked with natural Sm and Er to correct mass bias in the determined Nd and Yb isotope ratios, allowing ratio accuracy near the determined ratio precision of 0.05% (1σ). Because the concentrations of stock Nd and Yb standards are certified accurate to ±0.3%, this uncertainty sets the limit on the accuracy of the determined concentrations of the enriched isotope spike solutions.

The isotope dilution target ratio for spiked to reference isotope was determined as a compromise between minimizing the error magnification factor and minimizing measurement uncertainties which increase as ratios deviate from 1:1. The optimal ratio for the lowest error magnification factor, determined as the geometric mean of spiked and reference isotope ratio, was 14:1 for Nd and 11:1 for Yb.[20] To minimize possible inaccuracies associated with measuring such large ratios (e.g., dead time correction), and to prevent Nd spike signal intensities beyond the pulse counting range, a target ratio of 6:1 (spiked to reference isotope) was chosen. However, a 7-fold deviation from the target ratio would increase the error magnification factor by only a small amount, e.g., from the minimum of 1.3 to 2.0 for Nd. This provides generous spiking latitude (factor of 49) without significantly sacrificing precision of the calculated concentrations. Marine particulates are generally enriched in light REEs relative to chondritic patterns (similar to shales) and have a Nd/Yb molar ratio of ~5.[16] To accommodate this average composition, a mixed spike working solution of enriched ^{145}Nd (9.36 ppb) and ^{171}Yb (2.20 ppb) in 2% HNO_3 was prepared. For the particulate matter samples, a 100-μL aliquot of this spike solution was mixed with 100 μL of the 4-mL digest solution and diluted to 1000 μL with 2% HNO_3, a dilution which targets maximum REE concentrations of 1 ppb for our sample set. The BVHO-1 digest was also diluted and spiked (gravimetrically) at the same ratios.

Instrumentation. A low-flow desolvating nebulizer (MCN-6000; CETAC Corp., Omaha, NB) was used for sample introduction to an ELEMENT magnetic sector inductively coupled plasma

mass spectrometer (also known as high resolution, or HR-ICPMS; Finnigan MAT, Bremen, Germany). The MCN-6000 consists of a microautosampler (ASX-100) attached to a self-aspirating Teflon capillary microconcentric nebulizer MCN-100 (type T-1) fitted into a heated, vertically mounted single-pass Teflon spray chamber. Following aspiration, the sample aerosol passes through ~2 m of heated Teflon desolvating membrane mounted within a housing through which dry sweep gas is passed. After desolvation, the Ar sample gas is mixed with a small amount of N_2, which assists in sample transport and reduction of oxide production in the plasma. The MCN-100 operates at a free aspiration rate of ~100 μL min^{-1}, which varies with sample viscosity and, to some extent, with sample gas flow rate.

The ELEMENT is a sector field double-focusing mass spectrometer with reverse Neir−Johnson geometry.[21,22] Although the instrument was operated in low resolution ($M/\Delta M = 300$) for this application, medium- and high-resolution settings (nominally 3000 and 7500) can be selected. The mass spectrometer can be operated in B-scan (magnetic), E-scan (electric), and Synchro-Scan (combined magnetic and electric) modes.[21,22] The REEs vary in mass up to ~25% above La. Although the geometry of the instrument allows this mass range to be scanned electrostatically, the control software sets a limit of 17% above magnet set mass. This restriction avoids excessive decreases in ion transmission associated with the low acceleration potential necessary for very broad E-scans. As a result, one complete scan of the REEs consists of one magnet jump and two E-Scans. Operating conditions for both the MCN-6000 and the ELEMENT are outlined in Table 1. During methods development, several isotopes were determined for some elements to demonstrate agreement and absence of interferences; these could be eliminated in future applications. As implemented here, the method requires ~5 min sample^{-1} (~500 μL), including sample uptake and acid rinse.

RESULTS AND DISCUSSION
Mass-Dependent Sensitivity. Because our method uses only one internal standard for each E-scan element group, minimization of mass bias within each group is desired for optimal accuracy of all REE determinations. Although the inherent total mass bias of the ELEMENT is toward increasing ion transmission with mass, this trend is nearly balanced by decreasing ion transmission with decreasing acceleration voltage during E-scans. To further minimize final effective mass bias, the focus offset parameter is tuned to maintain the focal depth of the low-resolution lenses at the plane of the entrance slit while the acceleration voltage is varied during E-scans. When tuned appropriately, the REEs, which have similar first ionization potentials (5.3−6.25 eV), exhibit nearly flat response curves (as counts s^{-1} ppb^{-1}) at each magnet mass setting (Figure 1). In principle, the standardization method could work with any well-defined and stable dependence of sensitivity on mass, e.g., a linear function of nonzero slope. We were able to tune the instrument to approximately zero slope; nonoptimized tuning gave nonlinear sensitivity−mass relationships (Figure 1). By comparing mass bias over a range of focus offset settings (5−45 V), we determined that the minimum mass bias for our mass spectrometer is achieved at a setting of 5 V (Figure

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Table 1. Operating Parameters

Tune Parameters

ELEMENT (Finnigan MAT)		MCN-6000 (CETAC)	
sample gas flow	0.93 L min^{-1}	sweep gas flow	4.3 L min^{-1}
auxiliary	1 L min^{-1}	sweep gas temp	175 °C
cool	14 L min^{-1}	spray chamber temp	75 °C
		nitrogen flow	0.014 L min^{-1}

Aquisition Parameters / Evaluation Parameters

Aquisition Parameters		Evaluation Parameters	
mass window	5%	search window	100%
samples/peak	400	integration window	100%
sample time	2 ms	integration type	average
segment time^a	40 ms	runs	3
detection mode	counting	passes	50
resolution	low		

Scan Parameters

magnet settling time	100 ms		50 ms
magnet mass	137		158

element	isotope	element	isotope
Ba^b	137	Gd	158
La	139	Gd	160
Ce	140	Tb	159
Pr	141	Dy	163
Nd	143	Ho	165
Nd	145	Er	166
Nd	146	Er	167
Sm	147	Tm	169
Sm	149	Yb	171
Eu	151	Yb	172
Eu	153	Yb	173
Gd	155	Lu	175
Gd	157		

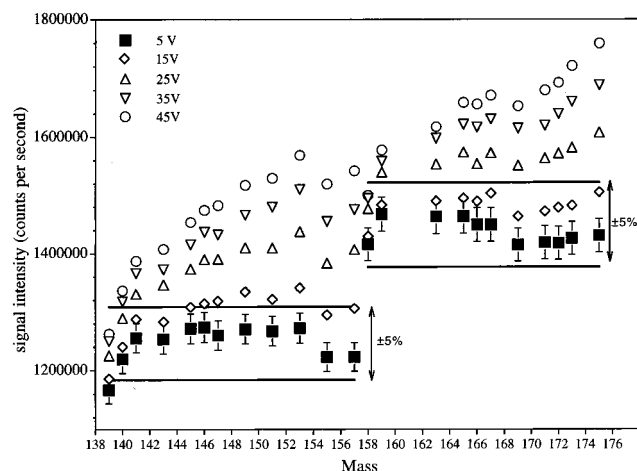^{a} Segment time is time per isotope per pass. ^{b} Measured in analog mode.

Figure 1. Signal intensity vs mass for a 1 ppb mixed REE solution (corrected to elemental concentration using isotope abundances) for focus offset settings of 5, 15, 25, and 45 V. Note that the flattest response is obtained at 5 V; all REEs except La fall within ±5% of mean intensity for each magnet setting. Mass bias increases and becomes more nonlinear at higher focus offsets. Conservative analytical precision of ±2% is plotted as error bars shown for focus offset used in analytical runs.

1). We observed minimal variations in sensitivity ($<\pm2\%$, 1σ, with the exception of La, Ce, and Gd) at this offset using a 1 ppb mixed-REE tuning solution (Figure 1). Slightly lower sensitivity for La, Ce, and Gd (5−9%), relative to those for the other REEs,

Table 2. Oxide Formation and Associated Interferences with Meinhard Type-C vs MCN-6000 Desolvating Nebulizer on Finnigan MAT ELEMENT

	Meinhard^a		MCN-6000	
oxide formed	BaO, 0.5%	CeO, 1.0%	BaO, 0.0008%	CeO, 0.01%
analyte	^{153}Eu	^{156}Gd	^{153}Eu	^{156}Gd
interference	^{137}Ba^{16}O$^+$	^{140}Ce^{16}O$^+$	^{137}Ba^{16}O$^+$	^{140}Ce^{16}O$^+$
	Correction (%)			
BHVO-1	7.55	53.37	0.01	0.48
marine particulates^b	344.2	19.98	0.57	0.17

^{a} Reference 25. ^{b} Calculated for a sample from 2500 m depth in the eastern tropical North Pacific.

may be attributed to the formation of doubly charged species.[23] Sensitivity is nearly invariant with mass at each magnet setting, but it steps up at the higher magnet mass because maximum acceleration voltage is used at the beginning of the second E-scan (^{158}Gd; Figure 1). Overall sensitivity is excellent, at >1 million counts s^{-1} ppb^{-1}. This is roughly 10 times higher than we were able to achieve with a standard Meinhard concentric nebulizer on a Scott double-pass spray chamber. Apparently, comparable improvements in sensitivity are not are not achieved with the MCN-6000 on a quadrupole instrument (VG PQ2+; Richard Mortlock, personal communication).

Negligible Oxide Interference. Suspended marine particulate samples contain abundant barium and LREE enrichments relative to the MREEs and HREEs.[16,24] Typical metal oxide production observed with Meinhard or V-groove conventional pneumatic nebulizers mounted on a standard Scott double-pass spray chamber are around 0.5% for BaO$^+$ and 1% for LREEO$^+$, resulting in significant interferences on the MREEs[25,26] (Table 2). Desolvating nebulization using the MCN-6000 generates a dry aerosol and suppresses oxide production by approximately 2 orders of magnitude, thereby greatly reducing interferences[27] (Table 2). All potential oxide interferences are reduced to <1% of analyte signal, negligible for our desired accuracy. Removing oxide correction from the calculation scheme eliminates the need to determine oxide interferences externally and improves accuracy by removing error propagation associated with this correction. Ba is monitored in analog mode to ensure that barium oxide corrections are negligible for each sample.

Memory and Wash Out. Memory effects are caused typically by signal enhancements from previous sample material remaining in the tubing, nebulizer, spray chamber, torch, and sampler and skimmer cones. Rare earths are not memory-prone elements, and system retention/release not a common problem in their determination. However, it is reasonable to suggest that the large surface areas associated with desolvation combined with low flow rates might increase memory problems for the MCN-6000. Washout tests show that the REE signal returns to background in less than 1 min after switching uptake from a 1 ppb REE solution to a 2% HNO$_3$ rinse, demonstrating no short-term washout

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Table 3. REEs Determined by This Study ($n = 5$) Compared to Other Recommended and Determined Values for Certified Reference Material BHVO-1 (ppm)

			Govindaraju (1994)[28]		Xie et al. (1994)[19]		Cheatham et al. (1993)[4]		Hofmann[a]		Eggins et al. (1997)[3]	
REE	this study	%RSD	recommended	%diff[b]	ICPMS[c]	%diff[b]	ID-TIMS[d]	%diff[b]	ID-TIMS[d]	%diff[b]	preferred[e]	%diff[b]
La	15.1	1.06	15.8	−4.5	16.0	−5.7	15.7	−4.1	15.4	−2.0	15.5	−2.7
Ce	37.0	1.33	39.0	−5.2	39.3	−5.9	37.8	−2.1	38.1	−2.9	38.0	−2.7
Pr	5.61	1.13	5.70	−1.6	5.60	0.2	5.40	3.9			5.45	2.9
Nd	26.0	0.75	25.2	3.3	24.6	5.8	24.8	4.9	24.7	5.4	24.7	5.4
Sm	6.35	0.97	6.20	2.5	6.01	5.7	6.10	4.2	6.13	3.6	6.17	3.0
Eu	2.15	0.44	2.06	4.2	2.14	0.3	1.98	8.4	2.09	2.7	2.06	4.2
Gd	6.35	0.73	6.40	−0.8	6.55	−3.1	6.56	−3.2	6.31	0.6	6.22	2.0
Tb	0.957	0.87	0.960	−0.3	0.895	6.9	1.020	−6.2			0.950	0.7
Dy	5.48	0.81	5.20	5.3	5.37	2.0	5.37	2.0	5.33	2.7	5.25	4.3
Ho	1.01	0.73	0.990	2.1	0.958	5.5	1.01	0.1			1.00	1.1
Er	2.61	0.65	2.40	8.7	2.56	1.9	2.38	9.6	2.56	1.9	2.56	1.9
Tm	0.339	0.62	0.330	2.8	0.331	2.5	0.330	2.8				
Yb	2.00	1.68	2.02	−1.1	2.01	−0.6	2.01	−0.6	2.01	−0.6	1.98	0.9
Lu	0.275	1.24	0.291	−5.5	0.288	−4.5	0.290	−5.1	0.275	0.0	0.278	−1.1

[a] A. Hofmann, preliminary data, personal communication (1998). [b] %diff = (this study − compared value)/this study × 100. Negative numbers indicate our determined value is lower. [c] ICPMS = inductively coupled plasma mass spectrometry. [d] ID-TIMS = isotope dilution thermal ionization mass spectrometry. [e] Preferred = compilation of preferred values selected by author.

effects. Based on this result, a 2% HNO_3 rinse was adopted and used between every sample in our analytical runs. The sample introduction system may accumulate elevated La and Ce blanks after extended use and should be rinsed manually on a regular basis (once a week).

Calculation of Concentrations. Samples spiked with enriched ^{145}Nd and ^{171}Yb were analyzed for Ba and the full suite of REEs as outlined in Table 1. Corrections for deadtime are performed transparently in the software on the basis of a predetermined deadtime value for the detector. Potential variations in mass bias for low and high magnet settings are monitored using $^{147}Sm/^{149}Sm$ and $^{166}Er/^{167}Er$, respectively. With proper tuning, however, the mass bias calculated from these Sm and Er isotope ratios falls within the precision of the determined ratio (usually less than ±0.2%/amu), demonstrating no measurable mass bias at the selected focus offset of 5 V. Consequently, Nd and Yb concentrations are simply calculated from intensities using the standard ID equation.[20]

Once natural Nd and Yb concentrations are calculated, sensitivity (counts s^{-1} ppb^{-1}) is determined for total ^{145}Nd and ^{171}Yb (spike plus small contribution from natural Nd and Yb in sample). Because mass bias within each REE group is negligible, the sensitivity for ^{145}Nd and ^{171}Yb is used directly to calculate the concentrations of ^{139}La to ^{157}Gd and ^{158}Gd to ^{175}Lu, respectively. The method is designed so that determined Gd isotopes span the magnet jump; ^{155}Gd and ^{157}Gd are at the end of the low-mass E-Scan, and ^{158}Gd is at the beginning of the high-mass E-scan (Figure 1). Concentrations calculated from ^{155}Gd, ^{157}Gd, and ^{158}Gd agree to <1%, attesting to the legitimacy of the concentration calculation method and the absence of a standardization discontinuity across the magnet jump. Concentrations of elements for which multiple isotopes are determined are calculated from the mean of the abundance-corrected intensities for each isotope. As discussed above, no oxide or drift corrections are necessary.

Precision and Accuracy. In this method, elemental concentrations are calculated from determined isotope and elemental ratios, which always show better precision than do absolute intensities. Rapid scanning allows the determination of precise

Table 4. Comparison of This Method with Standard Additions Determination of REEs in 20 Marine Particulate Samples

	sample range	
element	concn (pg L^{-1})[a]	diff ± SD ($n = 20$) (%)[b]
La	50.7−245	−5.80 ± 1.3
Ce	121−200	−1.90 ± 1.4
Pr	10.3−60.0	1.98 ± 1.1
Nd	41.8−260	
Sm	9.00−59.2	3.09 ± 1.4
Eu	2.24−6.1	3.31 ± 1.2
Gd	9.42−69.0	−0.89 ± 1.7
Tb	1.41−10.6	1.03 ± 1.1
Dy	9.33−69.9	0.47 ± 1.6
Ho	2.11−5.0	0.95 ± 1.0
Er	6.65−44.7	0.37 ± 1.4
Tm	0.974−6.46	−2.15 ± 1.0
Yb	6.97−41.2	
Lu	1.08−6.02	−1.28 ± 1.2

[a] Expressed per volume seawater. [b] diff = (determined by this method − determined by standard additions)/determined by this method × 100. Negative numbers indicate this method gives lower value. SD = 1 standard deviation of %diff for 20 samples.

(<1%, 1σ) ratios for elements spanning a large mass spectrum. Analyses of BHVO-1 demonstrate that precision is always better than 2% (1σ) and often better than 1% (Table 3). The data in Table 3 were collected from five individually spiked aliquots of a BHVO-1 digest and represent overall procedural precision comprising gravimetric, analytical, and isotope dilution error magnification. Elements for which two or more isotopes were analyzed (Sm, Gd, Eu, Er) were determined individually for each isotope, and concentrations calculated for each element agreed to within 0.6% for each analytical run.

Determining the accuracy of this method as it applies to suspended particulate marine matter is difficult because there is no recognized deep ocean particulate reference material. We therefore determined accuracy by analyzing a well-known certified reference material (BHVO-1; Table 3) and by comparing concentrations determined for marine particulate digests with

values determined on the same solutions by standard addition (Table 4).

BHVO-1, a Hawaiian tholeite certified reference material, is very different from marine particulate material with respect to matrix, REE concentration, and REE fractionation pattern. As a result, our standard Nd/Yb spike ratios were necessarily not optimized. Despite the compositional differences from marine particulate matter, we selected BHVO-1 as a means of testing the accuracy of this method for the following reasons: (1) it is easily digested compared to granites and shales, (2) homogeneity of the standard is good, due to its fine grained nature, and (3) published analyses of the standard are extensive and include ID-TIMS determinations. Rather than tailor-make optimized spikes for the BHVO-1 REE pattern, we used our standard spike mixture, described above, to demonstrate the robust nature of the method. If analytical requirements called for optimized determination of samples with a wide range of REE patterns, tailored spikes could be made by simply altering the Nd/Yb ratio of the spike solution and adjusting the spike/sample mixture. For BHVO-1, our determined values differ from recommended values by less than 5% for Pr, Nd, Sm, Eu, Gd, Tb, Ho, and Tm and by <10% for the remainder of the REEs[28] (Table 3). While this agreement is acceptably good, we note that comparison of our data with the more precise ID-TIMS values for BHVO-1 (preliminary data, A. Hofmann, personal communication, 1998) demonstrates agreement of better than 3% for all REEs except Nd (5.4%) and Sm (3.65%; Table 3). Agreement is also very good with the compiled data of Eggins et al.[3] Comparison with Cheatham's ID-TIMS values[4] shows more variability, with 5–10% differences for Eu, Er, and Lu.

As an independent measure of the accuracy of our method, we compared REE concentrations obtained by this method to those obtained by single spike standard additions for 20 individual marine particulate samples (natural Ba in sample used to drift correct between sample and spiked sample pairs). The two methods gave results that differed by ≤2% for all the REEs except La (5.8%), Sm (3.1%), and Eu (3.3%) (Table 4). The mean difference for most of the REEs was less than the standard deviation of the difference ($n = 20$), indicating no measurable discrepancy between concentrations determined by the new method versus standard additions. Differences appear to be insignificant at the 1σ level for six of the REEs but still do not exceed 3.3%, except for La, which is 5.8% lower by the new method than by standard additions. The 5.8% underestimate of the La concentration recalls the similar 4.5% underdetermination of the BHVO-1 recommended value (Table 3), suggesting that a correction for doubly charged species formation may be required. However, La concentrations by the new method agree within 2% with the recent ID-TIMS value for BHVO-1 (preliminary data, A. Hofmann, personal communication, 1998) and within 3% of Eggins's recent compilation of preferred values.[3] Because Hofmann's values are the most precise yet claimed for BHVO-1 (0.2–1.6% SD for eight separate digestions), we conclude that our La value is correct within our stated precision, and that previous determinations of La in BHVO-1, including those used for the recommended value, may be flawed. We suspect that our high standard additions value may be inaccurate because La standard

(28) Govindaraju, K. *Geostand. Newsl.* **1994**, *18*, 1, 15, 16.

Table 5. Detection Limits Determined in 2% HNO₃

element	blank (counts s⁻¹)	blank (fg/g)	DL (fg/g)	absolute DL (fg) (0.5 mL)
La	61	70	18	9
Ce	71	88	15	7
Pr	13	14	7	4
Nd	6	54	29	15
Sm	5	32	26	13
Eu	1	3	2	1
Gd	6	46	41	21
Tb	9	8	4	2
Dy	3	10	8	4
Ho	1	1	1	1
Er	1	5	4	2
Tm	3	3	2	1
Yb	1	6	10	5
Lu	2	2	2	1

added was too small to be optimal, a compromise necessary to avoid exceeding the range of pulse-counting signal detection for the more abundant REEs.

Limits of Detection and Blanks. Limits of detection presented in Table 5 are defined as 3 times the standard deviation of 10 acquisitions of a blank solution (2% HNO₃). Sensitivity is determined from five acquisitions of a 1 ppb mixed REE standard. The 10-fold enhancement in sensitivity over conventional nebulization provides detection limits at ≤41 ppq for the LREEs and <10 ppq for the HREEs (Table 5). Our blank levels (clean 2% HNO₃) are very good, ranging from 1 ppq for Ho to 88 ppq for Ce (Table 5). For our analytical runs, 2% HNO₃ blanks interspersed with samples have always been <1% of the sample signal. This sensitivity and low blank, combined with 100 μL min⁻¹ sample flow rates, yield absolute detection limits at the femtogram level (Table 5). Comparison with recent multielement techniques using quadrupole ICPMS with standard 1 mL min⁻¹ sample nebulization shows improvement in detection limit by >100-fold and in absolute detection limit by 1000-fold. Such low detection limits are a great advantage, for example, in the analysis of REE in biogenic particles from the surface ocean, which have very low REE content (e.g., 0.02–30 pg (kg of seawater)⁻¹ [16].

SUMMARY AND CONCLUSION

The use of ICPMS for the analysis of trace elements in geological materials is well established, and application to seawater and marine particle analysis is growing.[29] For example, a number of methods for the determination of REEs in rocks using conventional pneumatic nebulization and quadrupole ICPMS have been reported.[3,4,6] These methods use a combination of internal standards combined with external standard reference materials to obtain precision at the 1–3% level and accuracy which is usually better than ±8%. Our method, developed for the analysis of marine samples, demonstrates similar precision (<2%) and better accuracy (<6%) for the REEs. The new method also enjoys the following advantages for determination of REEs in oceanic samples; (1) high sample throughput (12 h⁻¹), (2) greatly superior detection limits, (3) freedom from oxide and drift correction, and (4) freedom from a requirement for standardization using similar certified reference material.

(29) McLaren, J. W.; Lam, J. W. H.; Berman, S. S.; Akatsuka, K.; Azeredo, M. A. *J. Anal. At. Spectrom.* **1993**, *8*, 279–286.

Results obtained with the new method are in very good agreement with published concentrations for the standard reference basalt BVHO-1 and also agree with a standard additions method when both methods were applied to a set of 20 digests of particulate samples from a deep ocean hydrothermal vent plume. The new method can be described as a hybrid isotope dilution/internal standardization method and has several important advantages over standard additions, including a simple spiking procedure, a reduced preparation time, a single analysis per sample, an increased sample throughput by a factor of 2−3, no limitations on spike/sample ratio imposed by pulse counting intensity limits for the abundant LREEs, and an improvement of precision by avoiding errors associated with monitoring and correcting for instrument drift. Because matrix simplification is generally unnecessary, spiking is simple, the REEs can be analyzed as a group in minutes per sample, and the method is vastly simpler and faster than ID-TIMS, while providing similar precision and accuracy for all the REEs, including the four monoisotopic elements.

Importantly, this method also has detection limits which improve on previous techniques by >2 orders of magnitude. It is therefore well suited to analysis of samples with low REE content and is relatively immune to problems associated with complicated matrices. We envision its applicability to improved methods of seawater analysis, to analysis of continental freshwaters, and to determination of severely REE-depleted rocks. This first demonstration of utility (oceanic particles on filters) indicates successful REE determination for a sample type which is characterized by limited sample, high total dissolved solids, and high ratios of Ba and LREE to the MREE. The sensitivity of the method provides very good precision even at low REE abundances, allowing resolution of subtle changes in intra-REE fractionation in most kinds of natural samples.