

Preconcentration and Purification of Rare Earth Elements in Natural Waters Using Silica-Immobilized 8-Hydroxyquinoline and a Supported Organophosphorus Extractant

Bradley K. Esser,* Alan Volpe, Jacqueline M. Kenneally, and David K. Smith

Nuclear Chemistry Division, L-232, Lawrence Livermore National Laboratory, Livermore, California 94550

8-Hydroxyquinoline immobilized on silica gel (silica-8HQ) and RE-Spec, a supported organophosphorus extractant, were used to preconcentrate and purify rare earth elements (REEs) from natural waters prior to their determination by isotope-dilution inductively coupled plasma mass spectrometry (ID-ICPMS). Preconcentration onto silica-8HQ is applicable to a wide range of trace metals, making it suitable for multielement ID-ICPMS studies. The silica-8HQ, RE-Spec technique concentrates REEs from 1 L or less of water into 1 mL of salt-free 0.1% nitric acid. The technique is rapid and has high REE yields (>80%) and low REE blanks (<2–6 pg). In addition, Ba separation is high, allowing determination of La and Eu by ID— ≤ 300 pg of Ba is present in the final concentrates of sample solutions initially containing >4 μ g of Ba.

We report a preconcentration and purification chemistry for the determination of rare earth elements (REEs) in natural waters by isotope-dilution inductively coupled plasma mass spectrometry (ID-ICPMS). The sensitivity and multielement measurement capability of the ICPMS are ideally suited to the determination of dissolved metals, which are present at extremely low concentrations in natural waters. Furthermore, the ability to measure isotopic ratios accurately at the 0.1–1% level using ICPMS makes isotope dilution a practical approach to precise and accurate trace metal determination. The principal advantages of isotope dilution compared to calibration of signal intensity are twofold—first, reproducible chemical yields are not necessary during sample preconcentration or processing, and second, corrections for changes in signal intensity associated with differences in sample matrix or instrument drift are not necessary.

Preconcentration techniques currently in use for low-level REE determination include coprecipitation with iron hydroxide,^{1,2} ion exchange with Chelex 100,^{3,4} and solvent extraction with bis(2-ethylhexyl) hydrogen phosphate/2-ethylhexyl dihydrogen phosphate (HDEHP/H₂MEHP).^{5,6} Coprecipitation with Fe(OH)₃ requires an additional separation step (usually cation-exchange chromatography) to remove Mg, Ca, and Fe before analysis. Chelation with Chelex 100 requires removal of Ca and Mg by careful washing with ammonium

acetate or by cation- and anion-exchange chromatography prior to elution of REEs. Neither technique provides good separation between REEs and Ba without additional chromatography, and separation of the REEs from Ba is required in ID-ICPMS because of isobaric interferences between the REEs and Ba and barium oxide. Complexation with HDEHP/H₂MEHP does not require removal of alkaline earths, but its utility in preconcentrating trace metals from natural waters has been demonstrated only for REEs. Taking full advantage of the multielement capability of ICPMS requires a preconcentration scheme which is applicable to a wide range of transition and other trace metals.

The technique we describe preconcentrates and purifies REEs from 1 L or less of natural water by adsorption onto silica-immobilized 8-hydroxyquinoline (silica-8HQ) and then further purifies REEs from Ba using a lanthanide-selective organophosphorus extractant. Previous studies have demonstrated that adsorption onto silica-8HQ is an efficient and low-blank method for preconcentrating transition metals from seawater for determination by ICPMS.^{7–11} We have used this technique in our laboratory to determine Cr, Ni, Cu, Zn, Mo, Cd, Te, Pb, Hg, Th, and U concentrations in seawater and in saline groundwater by ID-ICPMS. In the interest of combining REE studies with other trace metal studies, we expanded the silica-8HQ technique to include REEs.

The behavior of REEs on silica-8HQ is largely unknown.¹² However, aqueous-phase formation constants for trivalent REE oxinates in 50% (v/v) dioxane are high ($\log K_1 = 8.5$ – 9.0),¹³ and recoveries of aqueous middle to heavy REEs by complexation with oxine and adsorption onto activated carbon are good (88–99%).¹⁴ These previous studies justified an investigation, reported here, of the behavior of seawater-, groundwater-, and river water-equilibrated REEs on silica-8HQ.

The need for greater purification of REEs from Ba prompted development of a second separation chemistry downstream from the silica-8HQ chemistry. Recently, RE-

- (1) Greaves, M. J.; Elderfield, H.; Klinkhammer, G. P. *Anal. Chim. Acta* **1989**, *218*, 265–280.
- (2) Piepgras, D. J.; Jacobsen, S. B. *Geochim. Cosmochim. Acta* **1992**, *56*, 1851–1862.
- (3) De Baar, H. J. W.; Bacon, M. P.; Brewer, P. G. *Geochim. Cosmochim. Acta* **1985**, *49*, 1943–1959.
- (4) Möller, P.; Dulski, P.; Luck, J. *Spectrochim. Acta* **1992**, *47B*, 1379–1387.
- (5) Shabani, M. B.; Akagi, T.; Shimizu, H.; Masuda, A. *Anal. Chem.* **1990**, *63*, 2709–2714.
- (6) Shabani, M. B.; Akagi, T.; Masuda, A. *Anal. Chem.* **1992**, *64*, 737–743.

- (7) Akatsuka, K.; McLaren, J. W.; Lam, J. W.; Berman, S. S. *J. Anal. At. Spectrom.* **1992**, *7*, 889–894.
- (8) Watanabe, H.; Goto, K.; Taguchi, S.; McLaren, J. W.; Berman, S. S.; Russell, D. S. *Anal. Chem.* **1981**, *53*, 738–739.
- (9) Beauchemin, D.; McLaren, J. W.; Mykytiuk, A. P.; Berman, S. S. *J. Anal. At. Spectrom.* **1988**, *3*, 305–308.
- (10) Sturgeon, R. E.; Berman, S. S.; Willie, S. N.; Desaulniers, J. A. H. *Anal. Chem.* **1981**, *53*, 2337–2340.
- (11) McLaren, J. W.; Mykytiuk, A. P.; Willie, S. N.; Berman, S. S. *Anal. Chem.* **1985**, *57*, 2907–2911.
- (12) Jezorek, J. R.; Freiser, J. *Anal. Chem.* **1979**, *51*, 366–373.
- (13) Gupta, R. D.; Manku, G. S.; Bhat, A. N.; Jain, B. D. *Aust. J. Chem.* **1970**, *23*, 1387–1395.
- (14) Vanderborght, B. M.; Van Grieken, R. E. *Anal. Chem.* **1977**, *49*, 311–316.

Spec, a supported organophosphorus extractant selective for lanthanides and transuranic actinides,^{15,16} has become commercially available. The extractant is 1 M octyl(phenyl)-(N,N-diisobutylcarbamoyl)methylphosphine oxide (CMPO) in tributyl phosphate (TBP). The RE-spec resin is a 40% (by weight) loading of 1 M CMPO/TBP onto Amberchrome CG-71ms resin. The extractant in RE-Spec is similar to the extractant used in TRU-Spec.¹⁶

RE-Spec was developed to have better selectivity toward heavy REEs, which are poorly adsorbed by TRU-Spec. In both resins, metals are adsorbed in 2–6 N nitric acid and eluted in dilute nitric acid. Their specificity indicates that good separation between Ba and the REEs is possible. Information on the behavior of REEs on RE-Spec or TRU-Spec resins is limited. The second goal of our study was to determine the effect of nitric acid normality on the retention of REEs and Ba by RE-Spec. To our knowledge, this is the first study describing REE behavior on RE-Spec.

The low-temperature aqueous geochemistry of REEs is a field of increasing interest. REEs are geochemically coherent, having a number of chemical properties which are simple functions of atomic number. And, while most REEs are strictly trivalent under natural conditions, Ce and Eu exhibit variable valency in response to changes in oxidation state. These characteristics allow variations in REE patterns, including Ce and Eu anomalies, to be attributed quantitatively to specific geochemical processes. To demonstrate the applicability of our technique to natural waters, we have determined REE patterns by ID-ICPMS on a number of North Pacific seawater and Nevada Test Site groundwater samples.

EXPERIMENTAL SECTION

Reagents. The measurement of REEs at trace and ultratrace concentrations in natural waters requires high-purity reagents, rigorously cleaned labware, and a particle-free environment. All cleaning operations and sample and reagent chemistries were carried out in a class 100 clean room equipped with vented laminar flow hoods.

Nitric acid, hydrochloric acid, and ammonium hydroxide purified by subboiling distillation in quartz stills were obtained commercially (Seastar Chemicals, Seattle, WA). Normality of the concentrated acids was determined by titration. Reagent water was further purified to 18 M Ω in a four-bowl Milli-Q system water purification system (Millipore Corp., Bedford, MA). MQ-water and sample solutions were adjusted to pH 8 or 8.5 by addition of high-purity ammonium hydroxide and nitric acid.

REE Standards. The REE, Ba, and Cs standard solutions were obtained from Spex Industries (Edison, NJ). The Spex REE solution used, ICPMS-1, is a multielement standard containing equal concentrations (by weight) of each of the 14 naturally occurring REEs. We used two Spex Ba solutions—a single-element Ba standard and a multielement standard, ICPMS-2, containing equal concentrations of Ba, Cs, and several other elements. Dilutions of these standard solution were made with MQ-water and high-purity acids. All isotopically enriched REE spikes (¹³⁸La, ¹⁴²Ce, ¹⁴⁸Nd, ¹⁴⁷Sm,

¹⁵³Eu, ¹⁵⁵Gd, ¹⁶⁷Er, ¹⁷⁵Yb) were obtained from Oak Ridge National Laboratory.

Silica-Immobilized 8-Hydroxyquinoline and RE-Spec Columns. Silica gel (LC Porasil B, 37–55- μ m particle size, 125-Å pore size; Waters Associates Inc., Milford, MA) was rinsed with 50% concentrated nitric acid, 50% concentrated hydrochloric acid, and MQ-water before use. 8-Hydroxyquinoline, triethylamine, and (3-aminopropyl)triethoxysilane were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used as received. Silica-8HQ was prepared as described by Hill¹⁷ from the above reagents. The immobilized functional group synthesized in this procedure is phenylazo-8HQ.¹² Resin was stored in MQ-water and protected from light.

Columns for silica-8HQ were constructed from quartz glass tubing (14 mm i.d.) bonded with silicone cement to a Teflon resin reservoir in which resin was supported by a porous Teflon frit (20- μ m pore size). This column held 2 mL of Porasil 8HQ and 10 mL of sample solution and was connected to the sample solution reservoir, a 1-L Teflon separatory funnel, with Teflon tubing and a silicone stopper. Flow rate was controlled by the separatory funnel stopcock.

The ~2 mL of silica-8HQ in each column was initially cleaned with 100 mL of 2.0 M HCl/0.5 M HNO₃, 750–1000 mL of MQ-water adjusted to pH 8, 20–25 mL of MQ water, 20–25 mL of 1.0 M HCl/0.1 M HNO₃, 20–25 mL of 2.0 M HCl/0.5 M HNO₃, and 20–25 mL of MQ-water. Subsequently, resin was cleaned after each use with 20–25 mL of 2.0 M HCl/0.5 M HNO₃ and 20–25 mL of MQ-water and stored in the column with ~5 mL of MQ-water.

RE-Spec chromatographic extraction resin was obtained from Eichrom Industries, Inc. (Darien, IL). The resin was rinsed several times in MQ-water and stored in MQ-water. The 100- μ L columns used in the RE-Spec separation chemistry were crafted out of heat-shrink Teflon tubing and a polyethylene frit. The columns were stored in dilute nitric acid between uses.

Sample Solutions. Natural water sample solutions include coastal seawater collected from Half Moon Bay (California), surface North Pacific seawater collected off Kauai (Hawaii), river water collected from the Merced River at Vernal Falls (California), and well and spring waters collected at the Nevada Test Site (NTS). The geochemistry and hydrology of the NTS springs are described in Smith et al.¹⁸ Unfiltered North Pacific seawater was acidified to pH \leq 2 with high-purity nitric acid soon after collection. The remaining samples were filtered through 0.45- μ m Supor filters (Gelman Sciences) and then acidified to pH \leq 2. To facilitate calibration of the column chemistries, we added Ba, Cs, and REEs to several aliquots from these waters. Standard solution was weighed into a clean Teflon or high-density polyethylene (HDPE) bottle with acidified and filtered sample solution. The two solutions were homogenized by shaking and equilibrated by heating for at least 48 h.

Silica-Immobilized 8-Hydroxyquinoline Chemistry. To examine the behavior of REEs on silica-8HQ, we equilibrated 10 μ g of each REE with 1-L aliquots of filtered Half Moon

(15) Dietz, M. L.; Horowitz, E. P. *Appl. Radiat. Isotopes* **1992**, *43*, 1093–1101.
(16) Horowitz, E. P.; Dietz, M. L.; Nelson, D. M.; LaRosa, J. J.; Fairman, W. D. *Anal. Chim. Acta* **1990**, *238*, 263–271.

(17) Hill, J. M. *J. Chromatogr.* **1973**, *76*, 455–458.

(18) Smith, D. K.; Gerlach, D. C.; McKinnis, W. B.; Nimz, G. J. *Hydrochemistry of selected springs and wells at the Nevada Test Site: geology and trace element analysis*. Lawrence Livermore National Laboratory, 1991.

Bay seawater, Merced River water, and Nevada Test Site groundwater. Sample and standard solutions were equilibrated by heating at 70–80 °C for 48 h in 1-L Teflon bottles. The silica gel and column apparatus (including the 1-L separatory funnel) were preconditioned by passing through the column 50 mL of 2.0 M HCl/0.5 M HNO₃, 150 mL of MQ-H₂O, and ~50 mL of pH 8.5 water to produce an eluent pH of ≥8.

Immediately before transferring the REE-equilibrated sample solution to the separatory funnel, sample solution acidity was adjusted to pH 8 by addition of high-purity ammonium hydroxide. As the sample solution passed through the column, aliquots were taken to determine pH and, for the river water and groundwater, REE concentration. Seawater sample eluent pHs, initially less than 5, climbed to 8 after 100–150 mL. The spring water eluent evolved from an initial pH of 4–5 to 8 in less than 50 mL. Average flow rates for the three samples were 2.1–2.4 mL/min; total processing time was ~3.5 h.

After all the sample solution had passed through the column, the column was detached from the separatory funnel and placed on a column stand. The silica-8HQ was washed with 10 mL of MQ-water, during which eluent pH rose to 9 and the eluent acquired a pink color. Then, 1.0 M HCl/0.1 M HNO₃ was passed through the column until an abrupt pH change from basic to acidic was observed after ~1.2–1.5 mL. This volume is assumed to represent the pore volume of the resin bed and corresponds to a resin porosity of 60–75%. Another ~10 mL of 1.0 M HCl/0.1 M HNO₃ was passed through the silica-8HQ to elute the REEs. Finally, the column was cleaned with 10 mL of 2.0 M HCl/0.5 M HNO₃.

RE-Spec Chemistry. We performed two experiments with RE-spec resin. The first experiment addressed the effect of nitric acid normality on the retention of REEs, Cs, and Ba. Synthetic sample solutions were prepared by dissolving 160 ng of each REE and 200 ng of Ba and of Cs in 2, 4, or 6 N nitric acid. A 100-μL Teflon column was rinsed with MQ-water, and ~100 μL of fresh RE-Spec resin was slurried into the column with water. One free column volume (FCV) of RE-Spec resin is 65–75% of the bed volume. In the first run, the resin was conditioned with ~15 FCV of 2 N nitric acid. Sample solution (20 FCV of 2 N nitric acid) was loaded onto the resin, which was then washed with 20 FCV of the 2 N nitric acid. Finally, REEs were eluted in 20 FCV of 0.015 N nitric acid. The 4 and 6 N nitric acid runs proceeded analogously. For REEs, the total for all collected fractions was within ~10% of the quantity in the original sample solution.

By use of the data from the first experiment, the RE-Spec protocol was standardized to conditioning, loading, and washing with 15 FCV of 6 N nitric acid in each step, and eluting REEs with 15 FCV of 0.0015 N nitric acid. Note that 15 FCV are ~10 bed volumes of 1 mL. In the second experiment, this protocol was tested with Half Moon Bay coastal seawater processed through silica-8HQ. We evaporated to dryness a 50% aliquot of the 1.0 M HCl/0.5 M HNO₃ fraction from the silica-8HQ column chemistry and then dissolved the residue in 1000 μL of 6 N nitric acid, which was then loaded onto a 100-μL column of RE-spec. The column was washed with 1000 μL of 6 N nitric acid and stripped with

1000 μL of 0.015 N nitric acid. All solutions were added in 500-μL increments. Load, wash, and collect fractions were collected and analyzed.

REE Blank Determination. REE reagent blanks were determined by isotope dilution on 250 mL of MQ-water and on 250 mL of 1.0 M HCl/0.1 M HNO₃. These solutions were spiked with a multielement solution of isotopically enriched REEs and evaporated to dryness. The residues were dissolved in 10 mL of 1% HNO₃ and were analyzed by ICPMS. Procedural blanks for the silica-8HQ chemistry and for the silica-8HQ + RE-Spec chemistry were also determined by isotope dilution. Replicate (*n* = 10) procedural blanks for both silica-8HQ and combined silica-8HQ + RE-Spec chemistries were below the detection limits of the ICPMS as determined from background counts plus three standard deviations on 10 mL of 1% HNO₃.

Natural Waters. To evaluate the technique on natural waters containing low concentrations of REEs, we processed three replicates of North Pacific surface seawater collected off Kauai, HI, and five spring waters collected from the Nevada Test Site. Acidified aliquots of these solutions were weighed and then spiked and equilibrated with a mixed solution of isotopically enriched REEs; concentrations were determined by isotope dilution. The Kauai aliquots were ~1 L in volume; the spring water aliquots were ~200 mL. The samples were processed as described in the previous two sections; 6 N HNO₃ was used in the RE-Spec purification step.

Instrumentation and Measurements. All analyses were by ICPMS. Developmental work was done on a VG Plasma Quad PQ2. In the developmental work, sample solution concentrations were determined by calibrating peak intensities acquired in scan mode with REE standard solutions. An In and Pb internal standard was added to each sample solution to monitor changes in response due to solution matrix effects and instrumental drift. External REE sensitivity standards and replicate sample analysis indicate that reproducibility was ≤6%. We determined REE concentrations in North Pacific seawater samples and Nevada Test Site groundwaters by isotope dilution. For these samples, isotope ratios were acquired in peak jump mode on a Finnigan MAT SOLA.

RESULTS AND DISCUSSION

REE Behavior on Silica-Immobilized 8-Hydroxyquinoline Columns. Retention by silica-8HQ resin of REEs equilibrated with Half Moon Bay coastal seawater is uniform at 90–93% with the exception of La (Figure 1). La retention is lower at 52%. Of the fraction retained by silica-8HQ, 90–98% is eluted in the collect fraction.

Freshwater results are variable (Figure 1). While REEs equilibrated with Nevada Test Site groundwater are retained by silica-8HQ to an extent comparable to coastal seawater, REEs equilibrated with Merced River water (MR) show clear signs of breakthrough. Retention of Merced River-equilibrated REEs is 42% for La and 25–30% for the remaining REEs. Analyses of postcolumn MR sample solution aliquots confirm that the balance of the REEs are in the pH 8 sample solution washed through the silica-8HQ column. Semiquantitative analyses show low retention of Sc, Y, and Th in addition to the lanthanides.

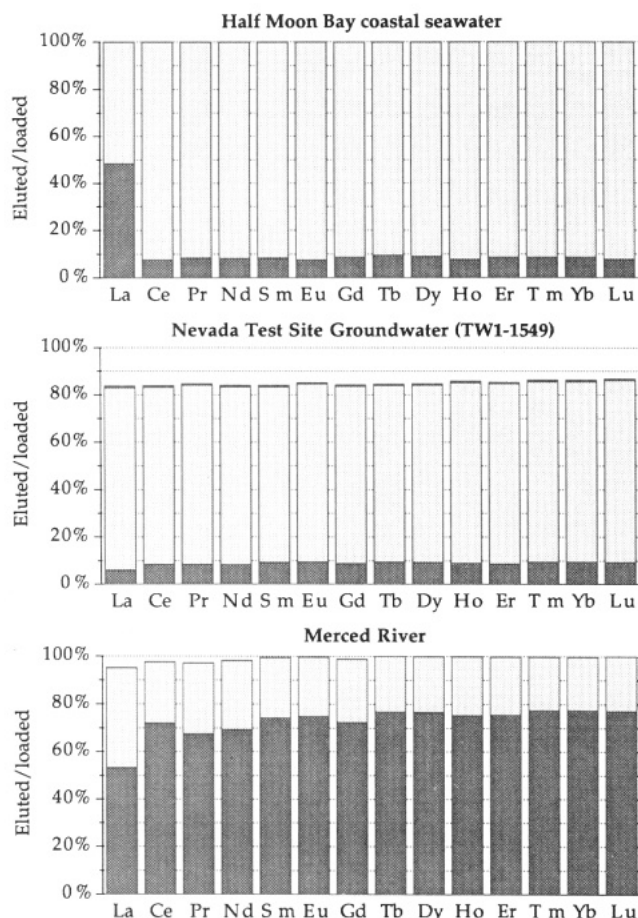


Figure 1. Elution behavior of REEs on a silica-8HQ as a function of sample solution matrix: Half Moon Bay coastal seawater, Merced River water, and Nevada Test Site groundwater. Shown for each element is the fraction eluted (%) during loading with 1 L of sample solution and washing with 10 mL of water (dark gray stipple), stripping with 11–12 mL of 1.0 M HCl/0.1 M HNO₃ (light gray stipple), and cleaning with 10 mL of 2.0 M HCl/0.5 M HNO₃ (black shading). The fraction eluted during loading was determined by mass balance for HMB coastal seawater and by direct measurement for the river and groundwaters.

In contrast, retention of all REEs (including La) equilibrated with TW1-1549 NTS groundwater is 81–84% (Figure 1). Only 2–3% of the REEs are found in the pH 8 sample solution after passing through the silica-8HQ column, leaving unaccounted 13–16% of the initially equilibrated metal. Semiquantitative analyses show high retention of Mn, Zn, Y, and Th.

The low retention of Merced River-equilibrated REEs is probably not due to competition with alkaline earth metals or other transition metals. The 800 g of Merced River water passed through the silica-8HQ column contained ~3 mmol of transition metals, while the 750 g of NTS groundwater processed contained ~6 μ mol. The groundwater and the coastal seawater also contain higher concentrations of alkali and alkaline earth metals than does the river water.

We suggest three explanations for variable REE retention from river water. First, a non-metal constituent of the river water, perhaps dissolved organic matter, may progressively occupy active sites on the silica-8HQ, reducing the effective capacity of the column and creating the conditions for breakthrough. A second possibility is that dissolved complexing ligands in river water may compete for dissolved REEs. Merced River water has lower carbonate alkalinity than NTS

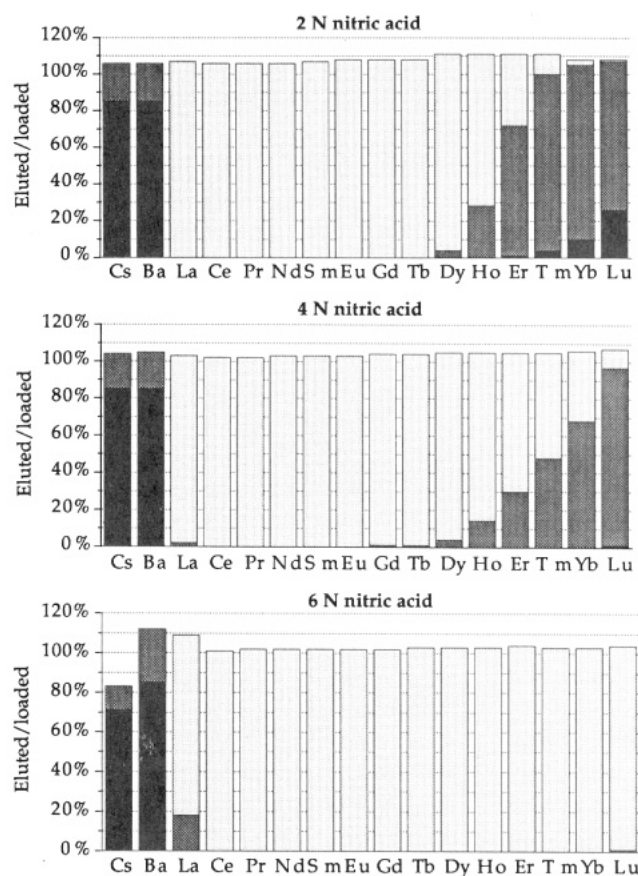


Figure 2. Elution behavior of REEs on a RE-Spec column as a function of nitric acid normality. Shown for each element is the fraction eluted (%) during loading with 15 FCVs of 2, 4, or 6 N nitric acid (black shading), washing with 25 FCVs of the same normality acid (dark gray stipple), and stripping with 25 FCVs of 0.015 N nitric acid (light gray stipple).

groundwater and much lower chloride ion concentration than HMB coastal seawater, indicating that carbonate and chloride, the major inorganic REE complexing ligands in seawater, are not responsible for the low riverine REE recovery. A final possibility is that Fe-rich colloids in the river water sample may form at pH 8, effectively scavenge REEs and Th, and pass through the column. A large component of the naturally occurring REEs in river waters is in colloidal form.¹⁹

REE Behavior on RE-Spec Columns. Retention of La and of the heavy REEs by Re-Spec resin is sensitive to the normality of nitric acid used to load the sample solution and wash the column (Figure 2). Loading and washing with 2 N nitric acid results in fractional elution, which increases with atomic number, of REEs heavier than Dy, culminating in near-total elution of Yb and Lu. In 4 N nitric acid, although fractional elution is still observed, the portion eluted for each element is smaller. In 6 N nitric acid, heavy REEs are not eluted. REEs lighter than Dy, with the exception of La, are not significantly eluted in 2, 4, or 6 N nitric acid. Lanthanum is a special case in that elution appears to increase with nitric acid normality over the range 2–6 N, a trend opposite to that observed in heavy REEs.

Once loaded onto RE-Spec resin, all REEs are eluted in 10 FCVs of 0.015 N nitric acid. This stripping is fractional and corresponds to the pattern discussed above—La and the

(19) Sholkovitz, E. R. *Earth Planet. Sci. Lett.* **1992**, *114*, 77–84.

heavy REEs elute before the light and middle REEs (e.g., 95% of the Lu and only 46% of the Pr are stripped off in the first 5 FCVs of 0.015 N nitric acid after loading and washing in 6 N nitric acid).

The retention of REEs in 6 N nitric acid by RE-spec resin is not significantly affected by initial preconcentration on silica-8HQ. In the second experiment, in which 1-L aliquots of coastal seawater were processed sequentially through the silica-8HQ and RE-Spec columns, no significant REE loss (<3–5%) occurs during RE-Spec loading in 6 N nitric acid, and recovery in dilute nitric acid is near-quantitative.

In all experiments in this study, less than 20 nmol of REEs was loaded onto 100 μ L of resin, accounting for less than 0.5% of the estimated capacity. RE-Spec and TRU-Spec resins have similar capacities—the capacity of the TRU-Spec is \sim 40 μ mol/mL resin. Suggested maximum loading is 10–20% of this value.

Preconcentration and Reduction of Salts. Low REE concentrations in natural waters require a trace metal preconcentration step. In the REE mass region, ICPMS detection limits are on the order of 0.3–0.5 pg/mL, while REE concentrations in deep seawater are 0.1–4 pg/mL with surface concentrations a factor of 5 lower.²⁰ In our procedure, the reduction in sample volume from 1 L to 1 mL corresponds to a preconcentration factor of 1000, assuming quantitative yield. In actual practice, where the sample solution is brought back up to 5–10 mL, preconcentration factors are 50–200.

To be effective, preconcentration of trace metals must be accompanied by reduction in the salt content of the analyte solution. The optimal matrix for nebulization ICPMS is 1% nitric acid with less than 0.2% total dissolved solids. Seawater has 3.5% total dissolved solids. Several observations suggest that the sequential silica-8HQ and RE-Spec column chemistries considerably reduce the salt content of the sample solutions introduced to the ICPMS. These observations include the good Ba and Cs separations (discussed below), semiquantitative determinations of sample solution Na and Mg before and after the silica-8HQ column chemistry, the extremely clean evaporation residues of the postcolumn REE aliquots, and visual inspection of the ICPMS sample and skimmer cones after running. We also note that elemental sensitivity on the ICPMS as monitored by internal In and Pb standards does not change significantly between REE standard solutions and postcolumn sample solutions.

Ba/REE Separation. The concentration of Ba in seawater, \sim 4–20 ng/mL, is high relative to REE concentrations and poses a potential isobaric interference on the major isotope of La and oxide interferences on both isotopes of Eu. Seawater $^{138}\text{Ba}/^{138}\text{La}$ ratios ($>10^3$) and $^{135}\text{Ba}/^{151}\text{Eu}$ and $^{137}\text{Ba}/^{153}\text{Eu}$ ratios ($>10^4$) preclude the use of isotope dilution to determine La and Eu without rigorous separation from Ba.

Ba, La, and Ce levels, and $^{138}\text{Ba}/^{139}\text{La}$ and $^{135}\text{Ba}/^{153}\text{Eu}$ ratios, before and after the silica-8HQ and RE-Spec column chemistries, are reported in Table 1. Total Ba in coastal HMB seawater is reduced by a factor of 300–400 by passage through silica-8HQ. Subsequent passage through RE-Spec results in an initial to final Ba ratio of $\geq 14\,000$ –50 000 and a Ba load of ≤ 100 –300 pg. Triplicate runs with 1-L aliquots of North

Table 1. Ba/REE Separations on Silica-8HQ and RE-Spec Columns

	mass (ng)			molar ratio	
	Ba ^a	La	Eu	$^{138}\text{Ba}/^{139}\text{La}$	$^{135}\text{Ba}/^{153}\text{Eu}$
Half Moon Bay D					
sample	4010	10120	10120	0.3	0.1
silica-8HQ collect	11	4880	8940	0.0016	0.0003
Half Moon Bay A					
sample	4590	240	160	14	7
silica-8HQ collect	11	170	120	0.05	0.02
RE-Spec collect	0.3	170	130	0.0014	0.0006
Half Moon Bay B					
sample	4960	250	160	14	7
silica-8HQ collect	14	150	120	0.07	0.03
RE-Spec collect	0.09	140	120	0.0005	0.0002
Half Moon Bay C					
sample	4460	92	5	35	212
silica-8HQ collect	15	62	4	0.18	0.87
RE-Spec collect	0.15	48	4	0.0023	0.0095
TW1 (1549)					
sample	11390	10010	10010	0.8	0.3
silica-8HQ collect	78	6390	6270	0.009	0.003
Merced River					
sample	1700	9950	9950	0.12	0.04
silica-8HQ collect	15	3710	2170	0.003	0.002

^a Half Moon Bay values estimated by assuming 4390 ng of Ba/kg

Pacific surface seawater collected near Kauai, in which better counting statistics were obtained over the Ba mass region, resulted in final Ba loads of less than 30 pg, approximately equal to the reagent blank in 10 mL of MQ-water (20–40 pg of Ba). The initial to final Ba ratio for Kauai samples is $\geq 150\,000$.

Barium oxide corrections in postcolumn analyte solutions are insignificant. Measured BaO/Ba ratios for the ICPMS running conditions used in this study are \sim 0.4%. For a typical open ocean surface seawater, the $^{135}\text{Ba}^{16}\text{O}/^{151}\text{Eu}$ intensity ratio will be \sim 0.20 in the silica-8HQ collect fraction and less than 0.003 in the RE-Spec collect fraction. Isobaric interferences of ^{138}Ba on spike + sample ^{138}La in postchemistry solutions are significant. $^{138}\text{Ba}/^{139}\text{La}$ ratios in postchemistry seawater analyte solutions are ≤ 0.002 , as compared to natural and spike $^{138}\text{La}/^{139}\text{La}$ ratios of 0.0009 and 0.076, respectively. If the sample solution is spiked such that the La ID ratio is 0.008 (the geometric mean), the Ba correction is significant yet tenable since $^{138}\text{Ba}/^{139}\text{Ba}$ is known and $^{138}\text{Ba}/^{139}\text{La}$ can be measured precisely. Although the size of this correction can be reduced by “overspiking”, we are presently having a more enriched La spike ($^{138}\text{La} > 90\%$) produced which should largely eliminate the need for a Ba correction.

Procedural and Reagent Blanks. Procedural REE blanks are less than the ICPMS detection limits for REEs (2–6 pg in 10 mL of 1% HNO₃; Table 2). For REEs other than Eu, blanks are less than 2% of the REEs present in 1 L of typical surface seawater (Table 2). For Eu, the blank value is less than 6%. Since surface seawater is more depleted in REEs than deep seawater or coastal seawater, and much more depleted than river water or groundwater, and since the analytical precision at these levels is 3–5%, blank values are adequate for the determination of REEs in 1 L of natural water by ID-ICPMS after preconcentration by silica-8HQ and RE-Spec column chemistries.

(20) Bertram, C. J.; Elderfield, H. *Geochim. Cosmochim. Acta* **1993**, *57*, 1957–1986.

Table 2. REE Blanks and Limits of Detection

element	SSW ^a (pg/kg)	MQ-H ₂ O (pg/mL)	acid ^b (pg/mL)	LOD ^c (pg/mL)	blank/SSW ^d (%)
La	1220	0.06	0.17	0.56	<0.5
Ce	350	0.09	0.26	0.49	<1.4
Nd	960	<0.03	0.12	0.33	<0.3
Sm	210	0.07	0.11	0.35	<1.7
Eu	60	0.06	<0.10	0.33	<5.5
Gd	380	<0.02	0.14	0.29	<0.8
Er	480	0.08	<0.10	0.26	<0.5
Yb	430	<0.02	0.12	0.23	<0.5

^a SSW, Surface seawater from the southwestern Indian Ocean.¹ All values except Ce are zero-silica values from REE/Si correlations. The Ce value is from the subsurface minimum in the Mascarene Basin. ^b Acid, 1.0 M HCl/0.1 M HNO₃. Acid and water blanks determined on 250 mL of solution. ^c LOD, limit of detection at 3 SD level in 10 mL of 1% nitric acid. ^d Blank/SSW, procedural blank in analyses of 1 kg of surface seawater, assuming 100% chemical yield through silica-8HQ and RE-Spec chemistry, and blank values less than the ICPMS LOD. See text.

Table 3. Reproducibility of Ba and REE Analyses in Three Separate Preconcentrations of 1 L of Kauai Seawater to 10 mL^a

element	1	2	3	mean	RSD (%)
Ba	4.48	4.49	4.33	4.43	2
La	1.37	1.26	1.35	1.33	4
Ce	1.72	2.04	1.93	1.90	9
Nd	1.56	1.73	1.63	1.64	5
Sm	0.54	0.64	0.61	0.60	9
Eu	0.15	0.13	0.14	0.14	7
Gd	0.72	0.68	0.73	0.71	4
Er	0.49	0.50	0.42	0.47	9
Yb	0.47	0.41	0.39	0.42	10

^a Ba concentrations in nanograms per milliliter; REE concentrations in picograms per milliliter. All concentrations determined by ID-ICPMS.

Natural Samples. Kauai surface seawater has the low REE concentrations (0.14–1.90 pg/mL; Table 3) typical for open ocean surface waters.²¹ For three 1-L replicates, reproducibility is 4–10% RSD and, except for Ce, is within a factor of 2 of the precision of the individual measurements (3–7% RSD). The larger discrepancy for Ce (precision 3%, reproducibility 9%) may arise from incomplete equilibration of enriched and natural Ce and reflect the existence of two oxidation states for Ce in natural waters. The measured REE concentrations are within the range for Pacific surface seawater.^{2,6} The Kauai REE pattern normalized against North American Shale Composite²² also shows the characteristic features of seawater—a negative Ce anomaly and heavy REE enrichment.²¹

The NTS spring waters have much higher REE concentrations than seawater (Table 4). These high and variable concentrations (e.g., 46–849 pg of La/mL) are typical for river water and groundwater.^{23,24} The most distinctive feature of the spring water REE patterns, when normalized against North American Shale Composite (NASC),²² is a negative Eu anomaly of uniform magnitude despite a 30-fold variation in Eu concentration. This anomaly is consistent with derivation of NTS spring water REEs from silicic tuffs. These Tertiary

Table 4. REE Concentrations in Nevada Test Site Spring Waters^a

element	White Rock	Tippipah	Topapah	Tub	Cane
La	849 ± 25	371 ± 8	188 ± 12	73 ± 10	46 ± 9
Ce	2230 ± 10	1005 ± 11	582 ± 4	239 ± 3	32 ± 1
Nd	1760 ± 20	457 ± 6	272 ± 2	70 ± 2	87 ± 1
Sm	405 ± 7	128 ± 1	78 ± 2	18 ± 1	25 ± 1
Eu	32.0 ± 1.0	12.0 ± 1.0	7.0 ± 0.2	1.0 ± 0.4	1.0 ± 0.3
Dy	355 ± 6	161 ± 4	101 ± 1	25 ± 2	37 ± 1
Er	163 ± 2	67 ± 1	57 ± 1	14 ± 1	22 ± 1
Yb	180 ± 3	60 ± 3	56 ± 1	14 ± 1	22 ± 1

^a REE concentrations in picograms per milliliter. Concentrations were determined by ID-ICPMS on 200-mL filtered aliquots. Uncertainties are 1 SE from variance in replicate isotope ratio determinations.

tuffs, which are a dominant lithology of the perched aquifers which supply water to the springs, also exhibit NASC-normalized negative Eu anomalies.¹⁸

CONCLUSIONS

This study is the first systematic investigation of the behavior of REEs on 8-hydroxyquinoline immobilized on silica gel and on a recently synthesized supported organophosphorus extractant, RE-Spec. Used sequentially, 2 mL of silica-8HQ and 100 μ L of RE-Spec are sufficient to preconcentrate and purify REEs from 200 mL of groundwater or 1000 mL of seawater.

The one great advantage of silica-8HQ is its selectivity for transition metals and lanthanides over alkali and alkaline earth metals. As a consequence, no special chemistry is needed to separate Mg and Ca, as is the case for Fe(OH)₃ coprecipitation and Chelex 100 ion chromatography. Furthermore, the salinity of the REE fraction is considerably reduced, so that solutions may be run by ICPMS. In contrast to extraction with HDEHP/H₂MEHP, silica-8HQ preconcentrates a wide range of trace metals, eliminating the need for multiple preconcentration chemistries in multielement studies. Recovery of REEs from NTS groundwater is uniform at 81–84%; recovery from coastal seawater is 90–93% for all REEs except La (52%). Barium is reduced in coastal seawater by a factor of 300–400.

Retention of Merced River-equilibrated REEs onto silica-8HQ is low (42% La, 25–30% remaining REEs). River water REE concentrations²⁴ are sufficiently high that if isotopic equilibration between the sample and spike REEs occurs before loading the silica-8HQ column, low chemical yields through the column will not affect the accuracy of the concentration determinations. However, since we do not know the mechanism responsible for the poor recovery, we can only speculate about the accuracy of river water REE determinations by this method.

The RE-Spec chemistry separates any residual Ba from the silica-8HQ REE fraction. In Kauai open ocean seawater samples, Ba in the final REE fraction is ≤ 30 pg as compared to 4.3×10^6 pg in the initial 1 L of sample solution. With loading and conditioning in 6 N nitric acid and eluting in 1 mL of 0.015 N nitric acid, recovery of REEs is near-quantitative, except for La, which is a bit lower. Prior passage

(21) Elderfield, H. *Philos. Trans. R. Soc. London A* **1988**, 325, 105–126.

(22) Taylor, S. R.; McLennan, S. M. *The Continental Crust: Its Composition and Evolution*; Blackwell Scientific Publications: Cambridge, MA, 1985.

(23) Banner, J. L.; Hanson, G. N.; Meyers, W. J. *J. Sediment. Petrol.* **1988**, 58, 415–433.

(24) Goldstein, S. J.; Jacobsen, S. B. *Earth Planet. Sci. Lett.* **1988**, 89, 35–47.

of solutions through a silica-8HQ column does not affect these yields. For ICPMS analysis, elution of REEs in dilute nitric acid is a significant benefit.

REE blanks for the total procedure are currently below our detection limits (2–6 pg) and, except for Ce, are less than 2% of the expected REE load in 1 L of open ocean surface seawater. The blank for Ce is $\leq 5\%$. These low blanks are made possible by the small amounts of resin used and the high-purity mineral acids used in loading, washing, and eluting the columns.

To demonstrate the utility of the procedure on natural water samples, we determined the REE concentrations by isotope dilution of three replicate samples of Kauai surface seawater and of five different Nevada Test Site spring waters. Concentrations and REE patterns obtained were geochemically reasonable. Reproducibility of the Kauai determinations is 5–10% RSD and is not significantly worse than the uncertainty in the individual replicates. This precision is

adequate for the construction of geochemically informative normalized REE patterns.

ACKNOWLEDGMENT

This research was funded by a Laboratory Directed Research and Development grant to the Isotope Hydrology program of the Nuclear Chemistry Division, Lawrence Livermore National Laboratory. The work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48. We acknowledge the helpful reviews by two anonymous reviewers whose comments substantially improved the manuscript.

Received for review October 5, 1993. Accepted January 26, 1994.*

* Abstract published in *Advance ACS Abstracts*, March 15, 1994.