

Determination of REEs in Seawater RMs (NASS-7, CASS-6, and NMIJ 7204-A) Using Online Automated Separation ICP-MS Analysis System

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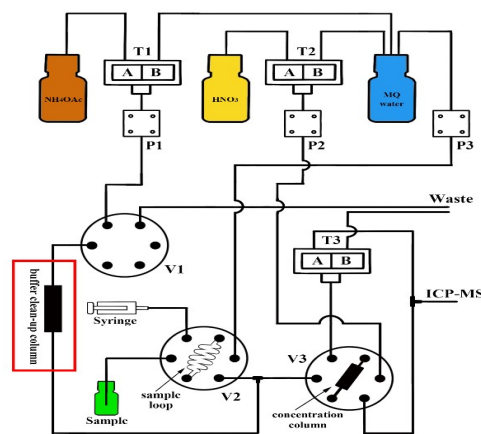
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ABSTRACT: Rare earth elements (REEs) with systematically varying properties are useful indicators of marine geochemistry. However, the accurate determination of REEs in seawater is complicated because of their low elemental concentrations, highly saline matrices, and contamination of the samples during pretreatment. Herein, we report a rapid, automated, and reliable method using a novel automated separation system (ELSPE-2 Precon) that efficiently separates seawater matrix elements and elutes preconcentrated targets directly into inductively coupled plasma-mass spectrometry (ICP-MS) online detection. The detection limits (3 s) were in the range from 0.002 (Dy) to 0.097 ng L⁻¹ (La), and the accuracy of this method was confirmed using a seawater certified reference material (NASS-6). This method was used for the long-term measurement of REEs in three new seawater reference materials (NASS-7, CASS-6, and NMIJ 7204-A) and the preferred values were provided for subsequent studies. Compared with other commercially available systems (i.e., SeaFAST™), the proposed system exhibited a higher throughput (>14 samples/h) and lower sample consumption (< 1 mL/sample).



INTRODUCTION

Rare earth elements (REEs) are an extremely coherent group in terms of (geo) chemical behavior and have become useful tracers in marine geochemistry.^{1,2} The application of REE data as geochemical fingerprints in hydrogeochemical processes includes studies on ocean circulation, rock-water interface interactions, water physical mixing, and external water input.^{3,4} However, the accurate determination of REEs in seawater remains a challenge owing to their extremely low concentration (~sub ng L⁻¹), the highly saline matrix (~3.5% NaCl), and the contamination of the samples during pretreatment.

Although the highly sensitive inductively coupled plasma mass

spectrometry (ICP-MS) is widely used for the determination of REEs and other trace elements in various samples, this technique cannot overcome the effects of coexisting high-salt matrix (i.e., 3.5% NaCl) and Ba, which leads to polyatomic mass spectral interference, instrumental drift, and suppression of the analyte signals, and clogging of the sample introduction system.⁵⁻⁸ Therefore, most previous techniques for measuring REEs in seawater before ICP-MS have required sample volumes of ~1 L and time-consuming chemical preparation techniques, such as chelating resins, solvent extraction, and co-precipitation.⁹⁻¹⁶ The most precise method for measuring REE concentrations in seawater samples is isotope dilution ICP-MS. However, this strategy is time-consuming and requires a calibrated multi-element spike and the concentrations of mono-isotopic lanthanides

cannot be determined.¹⁷⁻¹⁹

To avoid contamination of the samples during pretreatment, an online separation and/or preconcentration procedure based on flow injection with ion exchange or chelating resin separation was coupled with ICP-MS to analyze the trace REE concentrations in natural water samples.²⁰⁻²² Compared with the traditional offline separation method, the advantages of this method are automatization potential, low required sample volume, and enhanced accuracy.^{23,24} A typical commercially available automated device, seaFAST™ systems, was developed for use in the online analyses of trace elements in seawater samples.²⁴ The seaFAST™ system separates REEs and matrices (*e.g.*, alkali and alkaline earth cations and anions) using a cartridge of polymeric beads with iminodiacetic and ethylenediaminetriacetic acid functional group resins (particle size: 75 μm).²⁴ Although this device has been installed in many laboratories and is used to analyze seawater samples,²⁵⁻²⁷ its practicality is limited by its speed (<5 samples per h), bulkiness (1.5 m × 1 m × 0.6 m), and high cost (> US\$ 100 000).

Recently, we developed a novel automated separation system (ELSPE-2 Precon; detailed information can be found at www.princensci.com/en) that was preliminarily used to determine REE concentrations in river and coastal water samples.²⁸ Herein, this automated system was coupled with ICP-MS for the accurate determination of ultra-trace REEs in three new seawater RMs (NASS-7, CASS-6, and NMIJ 7204-A), all of which lacked certified REE reference values. The elimination of coexisting high-salt matrices (*e.g.*, NaCl) and Ba, which are prone to mass interference with the target, the limit of detection (LOD), accuracy, and precision were systematically evaluated. Finally, the recommended REE values in these RMs were obtained after long-term measurements.

EXPERIMENTAL

Instrumentations, reagents, and materials. The ELSPE-2 Precon separation system (Guangzhou Prin-Cen Technology Co., Ltd., Guangzhou, China) used a poly(styrene-divinylbenzene) (PS-DVB) resin (5 mm, 200 mg) with iminodiacetic (IDA) and ethyl-enediaminetriacetic (ED3A) acid functional groups (Col007 separation column) to separate the target REEs and anions, and alkali and alkaline earth cations were washed out. The system consisted of a Col007 separation column (Prin-Cen, Guangzhou, China), a Trp002 trace metal cleanup column (Prin-Cen), one syringe pump (2.5 mL), three inert 6-port valves (Prin-Cen), an eas-2A auto-sampler (Prin-Cen), and three ion chromatography pumps (Prin-Cen).²⁸ As shown in Fig. 1, the eluent was injected online into the introduction system (glass concentric nebulizer and cyclonic spray chamber) of a NexION 350D ICP-MS instrument (PerkinElmer, Waltham, MA, USA). The separation (ELSPE-2

Fig. 1 Schematic configuration of the ELSPE-2 Precon system. 1 and 3: Deionized water; 2: 5% HNO₃; 4: Ammonium acetate buffer; 5: Waste; I and II: PTEE pipes with inner diameters of ≥0.25 mm; III: Polytetrafluoroethylene pipe with a 0.5 mm inner diameter; A: Ammonium acetate pump; B: HNO₃ pump; C: Water pump; D: Syringe pump; V1, V2, and V3: six-port valves.²⁸

Table 1. Optimized parameters of the automated separation ICP-MS system

ELSPE-2 Precon system	Parameters
Mode of analysis	Online
Column resin	PS-DVB resin
Buffer	2 mol L ⁻¹ ammonium acetate, pH 5.8–6
Eluent	5% HNO ₃
Sample acidity	1% HNO ₃
Initial volume of the sample	900 μL
Sample throughput	4 min 10 s/sample
NexION™ 350D ICP-MS	
ICP RF power	1350 W
Nebulizer gas flow	0.66 L min ⁻¹
Auxiliary gas flow	1.3 L min ⁻¹
Plasma gas flow	14 L min ⁻¹
Sensitivity of 1 μg L ⁻¹ ¹¹⁵ In	> 50 000 cps
Background on mass 220	0.6 cps
Oxide formation CeO ⁺ /Ce	1.7%
Sweep	20
Reading	480
Replicates	1
Dwell time	20 ms
Internal standard	¹⁰³ Rh
Isotopes monitored	¹³⁹ La, ¹⁴⁰ Ce, ¹⁴¹ Pr, ¹⁴³ Nd, ¹⁴⁷ Sm, ¹⁵³ Eu, ¹⁵⁷ Gd, ¹⁵⁹ Tb, ¹⁶³ Dy, ¹⁶⁵ Ho, ¹⁶⁶ Er, ¹⁶⁹ Tm, ¹⁷² Yb, and ¹⁷⁵ Lu
Control software	EasySpec

Pre-con) and detection (ICP-MS) systems were simultaneously controlled using customized EasySpec software. The optimized operating parameters of the ELSPE-2 Precon and ICP-MS are listed in Table 1.

Seawater CRM NASS-6 was purchased from the National Research Council of Canada (NRC, Ottawa, Canada) to verify the accuracy of the developed method. Two new seawater RMs

Fig. 2 Schematic of the workflow of the ELSPE-2 Precon system. P1: ammonium acetate pump; P2: HNO₃ pump; P3: water pump; V1, V2, V3: six-way valves; T1, T2, T3: three-way valves. Steps: (A) Load sample on coil and clean columns; (B) Condition columns; (C) Load sample on resin and rinse matrix; (D) Rinse out buffer; (E) Elution; (F) Cycle back to the first step A. P1: ammonium acetate pump; P2: HNO₃ pump; P3: water pump; V1, V2, V3: six-way valves; T1, T2, T3: three-way valves.

(NASS-7 and CASS-6) were purchased from the NRC, and one new seawater RM (NMIJ 7204-A) was purchased from the National Metrology Institute of Japan (NMIJ, Japan). The deionized (DI) water (18.2 MΩ·cm) was obtained using a Milli-Q purification system (Millipore Sigma, Burlington, MA, USA). High-purity HNO₃ and 2 mol L⁻¹ ammonium acetate (pH 5.8–6.0) were obtained from Sinopharm Chemical Reagent (Shanghai, China) and Prin-Cen, respectively. HNO₃ was distilled twice using a custom-built PFA sub-boiling distillation system. The REE standard solutions were diluted from a 10 mg mL⁻¹ multi-REE mixed standard solution (SPEX CertiPrep, Metuchen, NJ, USA) using 5% HNO₃.

Analytical procedures. Fig. 2A–F shows a schematic of the workflow of the ELSPE-2 Precon system, and only 4 min 10 s is required to run six steps (a detailed description in Table S1) for each sample with the target REE chromatogram peaks lasting for 15–20 s. Detailed analytical procedures for the ELSPE-2 Precon system have been described in a previous study.²⁸

RESULTS AND DISCUSSION

Method development. The presence of the complex coexistence matrix (*e.g.*, high content of NaCl and Ba) is the most challenging

Table 2. Removal rates of the high-salt matrices in a typical seawater sample

Matrix	Before separation mg L ⁻¹	After separation mg L ⁻¹	Removal rate %
Na	35200	35.2	99.9
Ba*	54	0.16	99.7
Ca	526	2.10	99.6
Fe	3.2	0.02	99.4
K	287	0.57	99.8
Mg	1123	3.37	99.7
Sr	12.2	0.02	99.8
PO ₄ ³⁻	16.1	0.11	99.3
SO ₄ ²⁻	421	0.02	100
Cl	36100	72.2	99.9

* Concentration units are µg L⁻¹.

Table 3 Results of the REE concentrations in the seawater reference material NASS-6 (ng L⁻¹)

REEs	This work ^a	Zhu et al. ²⁹	Wysocka et al. ³⁰
La	11.83±1.25	11.82±0.62	10.18±1.06
Ce	5.21±0.62	6.35±0.49	3.93±0.42
Pr	1.78±0.11	1.83±0.14	1.56±0.17
Nd	6.46±0.83	7.84±0.36	6.75±0.72
Sm	1.17±0.52	1.42±0.10	1.17±0.13
Eu	0.26±0.05	0.27±0.07	0.26±0.030
Gd	1.28±0.12	1.85±0.08	1.39±0.14
Tb	0.24±0.02	0.26±0.05	0.23±0.025
Dy	1.75±0.05	1.80±0.08	1.67±0.18
Ho	0.44±0.04	0.45±0.06	0.42±0.044
Er	1.46±0.20	1.47±0.16	1.39±0.15
Tm	0.22±0.01	0.21±0.05	0.20±0.022
Yb	1.39±0.17	1.40±0.14	1.37±0.14
Lu	0.23±0.04	0.24±0.07	0.22±0.025

^a mean ± 2SD (N = 3).

Table 4 The recommended values of REEs for NASS-7, CASS-6, and NMIJ 7204-A (ng L⁻¹)

REEs	CASS-6(n=50)		NASS-7, n=44		NMIJ7204-A, n=40	
	Rec. value	2SD	Rec. value	2SD	Rec. value	2SD
La	10.32	2.38	9.93	1.21	41.67	9.15
Ce	5.87	1.81	4.09	1.23	106.97	21.86
Pr	1.46	0.44	1.5	0.28	11.06	1.92
Nd	5.94	1.75	5.69	1.25	31.06	9.18
Sm	1.05	0.49	1.02	0.31	6.15	1.54
Eu	0.32	0.13	0.26	0.07	1.32	0.24
Gd	1.87	0.65	1.48	0.32	6.92	1.39
Tb	0.22	0.07	0.23	0.07	0.99	0.21
Dy	1.26	0.56	1.49	0.37	5.72	1.19
Ho	0.35	0.12	0.42	0.09	1.11	0.23
Er	1.18	0.46	1.28	0.29	3.3	0.65
Tm	0.16	0.06	0.18	0.05	0.51	0.08
Yb	1.22	0.39	1.14	0.30	3.2	0.84
Lu	0.22	0.07	0.22	0.07	0.46	0.11

issue in accurately measuring sub-ng L⁻¹ REEs in seawater because it leads to significant signal suppression, polyatomic mass spectral interference (*i.e.*, the Eu signal is interfered with by that of BaO), instrumental drift, and clogging of the sample introduction system. In this study, an automated separation system (ELSPE-2

Precon) was used to remove high-salt matrices (*i.e.*, alkali and alkaline earth metals and anions) from seawater.

The removal rates of the coexisting matrix elements in typical seawater are listed in Table 2. The removal rates of all ions were >99.3%, and even 99.9% of Na (the most abundant element in seawater) was effectively removed. Notably, the interference of BaO with Eu is ignored because of the low Ba concentrations in seawater samples (~162 µg L⁻¹), high removal efficiency of the system (>99.3%), and low oxidation yield during ICP-MS (<2%). Thus, the removal efficiencies of the high-salt matrix and Ba within seawater using the proposed method enabled the accurate determination of sub-ng L⁻¹ REE concentrations in seawater.

Reduction of the procedural blank could improve the signal background ratio (SBR) and the method detection limit (DL). In this separation system, we found that the source of the main procedural blank is the buffer reagent (ammonium acetate). Fortunately, this can be minimized using a special purification module equipped with a trace metal clean-up Trp002 column (see Fig. 1). The background signal of the ammonium acetate used for REEs with online purification (by Trp002 column) could be decreased by 1.4- to 3.5-fold compared to that without purification.

Calibration curves were constructed using mixed REE standard solutions (1–100 ng L⁻¹), and linear correlation coefficients ($R^2 > 0.999$) were calculated for all REEs. Low DLs were obtained (0.002–0.097 ng L⁻¹), with DL defined as three times the standard deviation of the procedural blank value divided by the sensitivity (*i.e.*, the slope of the calibration curve). The accuracy of the proposed method was verified using seawater reference material NASS-6. Because no certified values of REEs were obtained from the producer (NRC), the accuracies of the NASS-6 values obtained during this study were compared with those previously reported.^{29,30} As shown in Table 3, the tested values agree with the reported reference values, which confirms the reliability of the proposed method based on this system. The short-term precision (RSD, 1 h) and long-term precision (RSD, 8 h) of the NASS-6 analysis were less than 15% (n=14) and 10% (n=110), respectively.

Analysis of three new seawater reference materials.

The proposed method was applied to measure the REE concentrations of three new seawater RMs (NASS-7, CASS-6, and NMIJ 7204-A) without certified REE values. The long-term analytical results of REEs for these RMs are shown in Fig. 3 and Fig. S1 and S2, respectively). Most of the measured values were distributed in the range of $X \pm 2$ SD, indicating the analysis results are stable. Finally, the recommended values are listed in Table 4, and we believe that these values will provide important comparative information for subsequent researchers.

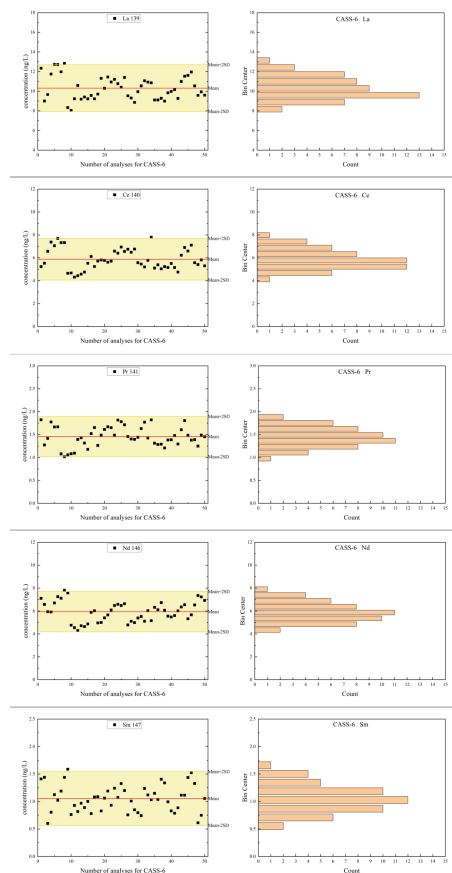


Fig. 3 Results of REEs concentration for CASS-6 from March 03, 2022 to March 21, 2023.

CONCLUSION

In this study, a rapid, automated, and reliable method using a novel automated separation and ICP-MS online analysis system was developed to measure sub-nanogram per liter levels of REEs in seawater RMs. This method was used for the long-term measurement of REEs in three new seawater reference materials (NASS-7, CASS-6, and NMIJ 7204-A). These values are expected to provide important comparative information for subsequent researchers. Compared with other commercially available systems (i.e., SeaFAST™), the proposed system exhibited a higher throughput (>14 samples/h) and lower sample consumption (<1 mL/sample).

ASSOCIATED CONTENT

Supporting information (Table S1 and Figs. S1-S2) is available at www.at-spectrosc.com/as/home.

AUTHOR INFORMATION



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Notes

The authors declare no competing financial interest.

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