

琉球大学学術リポジトリ

Determination of rare earth elements in small-volume seawater by off-line preconcentration system and inductively coupled plasma mass spectrometry

メタデータ	言語: 出版者: 琉球大学理学部 公開日: 2011-11-09 キーワード (Ja): キーワード (En): Rare earth element, seawater, preconcentration, ICP-MS, NASS-5 作成者: Le, Luong Duc, Shinjo, Ryuichi, 新城, 竜一 メールアドレス: 所属:
URL	http://hdl.handle.net/20.500.12000/22109

Determination of rare earth elements in small-volume seawater by off-line preconcentration system and inductively coupled plasma mass spectrometry

Luong Duc Le^{1,2} and Ryuichi Shinjo¹

¹ Department of Physics and Earth Sciences, University of the Ryukyus, Senbaru 1, Nishihara, Okinawa 903-0213, Japan

² Institute of Geological Sciences, Vietnam Academy of Science and Technology, 84 Chualang, Hanoi, Vietnam

Abstract

An analytical method was developed for determining rare earth element (REE) concentrations in seawater using inductively coupled plasma mass spectrometry (ICP-MS). A relatively small-volume seawater sample (25 ml) was used for chemical separation. REE concentrations in 20-fold preconcentrated solution by an off-line preconcentration system were analyzed by ICP-MS with microflow nebulizer. The recoveries were mostly higher than 95%. To assess the analytical method, REE concentrations of the North Atlantic Surface Seawater (NASS-5), a seawater certified reference material, were measured with the proposed preconcentration procedure. Results obtained in this study are consistent with those of previous studies with good precision.

Keywords: Rare earth element, seawater, preconcentration, ICP-MS, NASS-5

1. Introduction

Scientists have been increasingly interested in marine geochemistry of REEs for the last few decades, because of its usefulness as a geochemical tracer of water masses (Elderfield and Greaves, 1982; Zhang and Nozaki, 1996) and probe in understanding scavenging processes of particulate matter (Alibo and Nozaki, 1999). REE concentrations in seawater from many locations in the world-wide oceans have been reported based on a number of different methods. Because of the extremely low concentrations of REEs and the high salt content in seawater, it is still a challenging work for analyzing REEs in seawater.

In recent years, columns containing various kind of resins were utilized in on-line or off-line methods for preconcentration of REEs in seawater. Some of those methods are convenient (Willie and Sturgeon, 2001; Rahmi et al., 2007;

Zhu et al., 2009). The advantages of using those columns are effective removal of matrix elements and adequate preconcentration of REEs. In this study, we examine an effective preconcentration method for determining REE concentrations in seawater by using a syringe-driven chelating column (SDCC) and ICP-MS. To examine reliability and accuracy of the analytical method, we analyzed NASS-5, a seawater certified reference material (CRM) produced from the National Research Council of Canada (NRCC).

2. Experimental

2.1. Equipment

Preconcentration method utilized in this study largely follows the method proposed by Zhu et al. (2009). The REE separation and preconcentration system (Fig. 1) includes the 6-port manual rotation valve (TFR-6, GL Sciences Inc., Tokyo, Japan), pump (LC-10Ai, Shimadzu Corp., Kyoto, Japan) and the packed column.

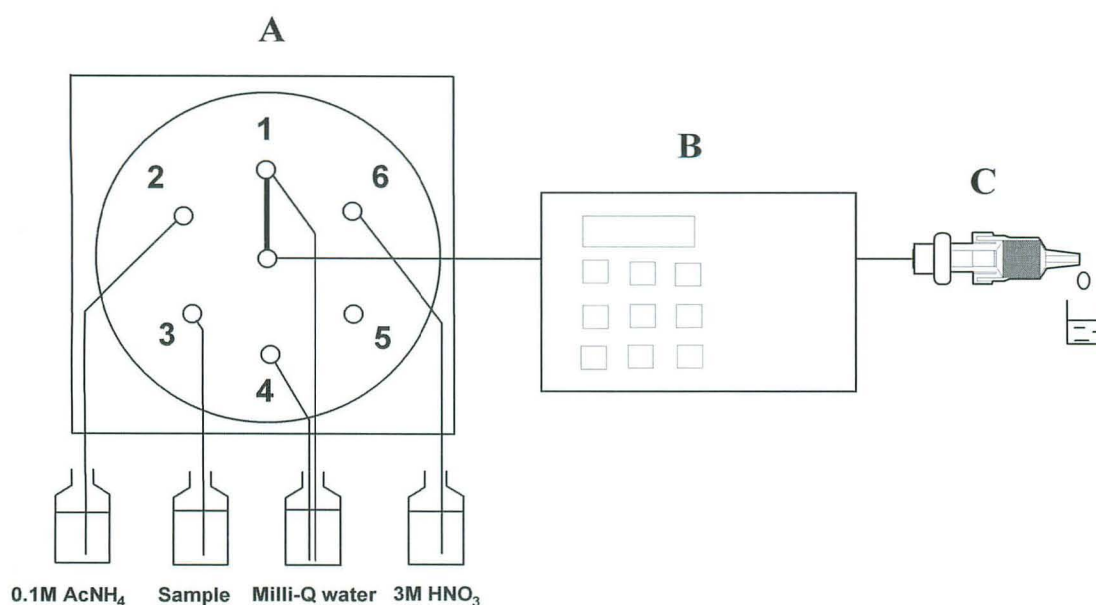


Fig. 1. Diagram of the off-line pre-concentration system. A, 6-port manual rotation valve; B, LC-10Ai pump; C, Syringe-driven chelating column. Valve positions are indicated in 1 to 6 (valve 5: position was not used).

Five ports of the rotation valve were connected to four bottles containing solutions as indicated in Fig. 1 with Teflon tubes (o.d. 1.5 mm, i.d. 0.5 mm), which were cut as short as possible to achieve high throughput measurement of REEs as suggested in Zhu et al. (2009). The central port of the valve was connected to the LC-10Ai pump using Teflon tube. All flow paths of the pump are made from metal-free materials (PEEK), thus reducing metal contamination.

Teflon tube from the pump is connected with chelating resin-packed column. The syringe-driven chelating column (SDCC) is the model of Nobias Chelate-PA1M, purchased from Hitachi High-technologies Corp (Tokyo, Japan). A compact pH meter (Twin pH meter B212; Horiba, Kyoto, Japan) was used for pH adjustment.

Quadrupole ICP-MS (HP 4500, Yokogawa Analytical Systems; now Agilent Technologies) at Department of Physics and Earth Sciences, University of the Ryukyus was used for a measurement of REEs after pre-concentration. Typical operational conditions of ICP-MS instrument are presented in Table 1.

Table 1. Operational conditions of ICP-MS.

ICP-MS	HP 4500 (Yokogawa Analytical Systems)
RF power	1.2 kW
Plasma gas flow	16 l min ⁻¹
Auxiliary gas flow rate	1 l min ⁻¹
Sample gas flow rate	0.7 l min ⁻¹
Additional gas flow rate	0.4 l min ⁻¹
Nebulizer	Microflow nebulizer
	Sample uptake rate: 0.1 ml min ⁻¹
Spray chamber	Quartz Double pass-type
Sample cone	Nickel
Skimmer cone	Nickel

2.2. Chemicals and samples

3M HNO₃ and 0.1M AcNH₄ (ammonium acetate) were prepared by dilution from concentrated solutions which were purchased from Kanto Chemicals (Tokyo, Japan). Ultrapure water (~18.3 Ω; Milli-Q water) was generated by using a Milli-Q purification system (Nihon Millipore Ltd., Tokyo).

Standard calibration solutions of 5 ppt, 50 ppt and 500 ppt REEs were prepared from three 1000 ppm standard stock solutions (Standard 1

contains La, Ce, and Pr; Standard 2, Nd, Sm, Eu, Gd and Tb; Standard 3, Dy, Ho, Er, Tm, Yb, and Lu). These standard solutions of REEs were purchased from Wako Pure Chemicals (Osaka, Japan). Indium (1 ppb) was used as an internal standard for collection of matrix effect and ICP-MS machine drift. Concomitantly, open ocean seawater certified reference material (CRM), NASS-5, was purchased from the National Research Council (Canada).

The spiked-seawater samples having the concentration of 0.1 ppb for each REE were made. After that, 25 ml spiked seawater samples were adjusted to pH 5.5 - 5.6. That pH value has been suggested to be optimum condition for the highest recovery (e.g., Zhu et al., 2009). Following the same preparation procedure, NASS-5 and blank samples were prepared after finishing of recovery tests.

All Teflon vials and bottles used in experiments were sequentially soaked in 20-times diluted TMSO solution (Tama chemicals Co., Ltd.), 1:4 HNO₃, 1:4 HCl, and Milli-Q water on a hotplate overnight at ~100°C.

2.3. Preconcentration procedure

Preconcentration procedure was performed in a clean room of the Department of Physics and Earth Sciences, University of the Ryukyus. The operational procedure of the preconcentration system is given in Table 2. The time and flow rate of each step were optimized after several recovery tests. Note that the flow rate of 2 ml min⁻¹ was used for the sample loading instead of 5 ml min⁻¹ as suggested in Zhu et al. (2009), because the obtained recoveries at 2 ml min⁻¹ were significantly higher than those at 5 ml min⁻¹.

Table 2. Operational procedure of the off-line preconcentration system.

Step	Valve position	Flow rate (ml/min)	Time (min)	Used amount (ml)	Purpose
1	1	5	2	10	Washing and regenerating system
2	6	5	2	10	Washing and regenerating system
3	1	5	4	20	Washing and regenerating system
4	2	5	2	10	Conditioning
5	3	0.5	0.1	-	Sample introduction
6	3	2	10	20	Sample loading
7	4	2	1	2	Washing and removing unwanted elements
8	4	5	2	10	Washing and removing unwanted elements
9	6	1	3	3	Elution of REEs
10	3 + Drain valve	5	2	10	Washing the Tube

In the first three steps, Milli-Q water, 3M HNO₃ and Milli-Q were subsequently introduced into the system. The purposes of these steps were washing and regenerating the SDCC prior to passing of the next sample. For pH conditioning, AcNH₄ was passed through the column in step 4. In step 5, for introducing sample to the system, the flow rate was adjusted to 0.5 ml min⁻¹ for 6 seconds. This step is set to fill tube with sample solution. After that, 20 ml sample solution was passed through the SDCC for 10

minutes at 2 ml min⁻¹ in step 6. In the next two steps, in order to wash and separate salt matrix in the SDCC, Milli-Q was passed through column. The values of flow rate and time of each step were 2 ml min⁻¹ and 1 minute for step 7 and 5 ml min⁻¹ and 2 minutes for step 8, respectively. Such different flow rates were selected to keep sample retention maximum at the beginning of washing step. In step 9, REEs were extracted from the SDCC by passing of 3M HNO₃, and REEs were collected in a Teflon vial.

Finally, the valve was rotated to position 3 and the drainage valve was opened, then washing of the sample introducing tube system was done by passing of 10 ml Milli-Q water for 2 minutes.

After being dried down on hotplate in 7 hours, all dried samples were dissolved with 1 ml of 1% HNO₃ containing 1ppb In. Vials were capped and heated on a hotplate for ~30 minutes to ensure complete dissolution. Consequently, the concentration factor of REEs was 20-fold (from 20 ml original solution to 1 ml final solution).

2.4. REE analysis by ICP-MS

The operational condition of ICP-MS is shown in Table 1. Tuning solution containing 10 ppb of Li, Y, Ce and Tl was used to optimize high sensibility and to reduce formation of oxide ion (CeO/Ce < 1.0 %) and doubly charged spe-

cies (Ce²⁺/Ce < 2.0 %) of ICP-MS system. It took 30 seconds for introducing sample, 40 seconds for stabilization, and ~140 seconds (3 times of 45-seconds measurement) for analysis. 5% HNO₃ was used to wash the sample introduction system of ICP-MS for 2 minutes prior to the measurement of the next sample.

3. Results and discussion

3.1. Recovery and blank values of REEs

Recovery tests together with blank tests were carried out using three spiked seawater samples and four blank samples. Results are given in Table 3. The detection limits were calculated by 3 times standard deviation from 4 measurements of the separately prepared procedural blank solution.

Table 3. Recovery and blank values.

Element	m/z	Recovery (%) n = 3	Procedural blank (pg ml ⁻¹) n = 4	Detection limit (pg ml ⁻¹)
Y	89	95.0 ± 1.2	0.021 ± 0.01	0.03
La	139	86.4 ± 6.2	0.114 ± 0.068	0.204
Ce	140	97.6 ± 2.8	0.235 ± 0.188	0.564
Pr	141	100.8 ± 1.3	0.013 ± 0.007	0.021
Nd	143	101.1 ± 0.9	0.029 ± 0.037	0.111
Sm	147	103.3 ± 0.6	0.006 ± 0.004	0.012
Eu	153	103.3 ± 0.7	0.004 ± 0.004	0.012
Gd	157	102.1 ± 0.3	0.002 ± 0.002	0.006
Tb	159	102.3 ± 0.5	0.001 ± 0.002	0.006
Dy	163	102.0 ± 0.4	0.006 ± 0.011	0.033
Ho	165	101.7 ± 0.4	0.0005 ± 0.001	0.003
Er	166	101.5 ± 0.3	0.006 ± 0.009	0.027
Tm	169	100.3 ± 0.6	0.001 ± 0.001	0.003
Yb	173	99.0 ± 0.5	0.004 ± 0.005	0.015
Lu	175	100.5 ± 0.5	0.002 ± 0.002	0.006

Mean ± standard deviation.

The obtained average values for recovery tests are given in Table 3. Except for La (~86.4 %), the values are in range 95 to 103 % for the other elements. Procedural blanks were insignificant, varying from 0.0005 to 0.029 pg ml⁻¹, except for La (0.114 pg ml⁻¹) and Ce (0.235 pg

ml⁻¹). Table 3 also shows that the detection limits and quantitation limits were small enough for determining trace metals in seawater, compared with previous studies (e.g., Totland et al., 1992). The results in this study indicate that the present method is accurate and reliable and can be used

in determining REE concentrations in seawater.

3.2. Analytical results of a seawater certified reference material, NASS-5

To confirm the reliability and accuracy of the analytical method presented here, twelve NASS-5 samples were analyzed. Results of

NASS-5 were obtained just after recovery corrections (only for La) and subtraction of the blank value contributions. Analytical results of REEs of NASS-5 are given in Table 4, along with the compiled values in previous studies (Willie and Sturgeon, 2001; Zhu et al., 2006; Rahmi et al., 2007; Lawrence and Kamber, 2007; Zhu et al., 2009).

Table 4. Analytical results for REEs in open ocean seawater CRM NASS-5 and reference values ($\mu\text{g ml}^{-1}$).

Element	m/z	This study n = 12	Willie and Sturgeon (2001) ^a	Zhu et al., (2006) n = 5	Rahmi et al., (2007) n = 5	Lawrence and Kamber (2007) n = 22	Zhu et al., (2009) n = 5
Y	89	21.71 ± 0.58			20.7 ± 0.7	22.0 ± 2.9	
La	139	12.44 ± 1.05	12.8 ± 1.2	11.1 ± 0.5	11.8 ± 0.4	12.19 ± 1.14	12.0 ± 0.3
Ce	140	5.13 ± 0.19	4.0 ± 0.6	4.9 ± 0.3	5.23 ± 0.05	5.72 ± 0.69	5.26 ± 0.16
Pr	141	1.98 ± 0.05	1.5 ± 0.2	1.9 ± 0.1	1.84 ± 0.06	2.09 ± 0.19	1.96 ± 0.02
Nd	143	8.13 ± 0.15	9.9 ± 1.8	6.8 ± 0.5	7.5 ± 0.1	8.43 ± 0.65	8.7 ± 0.7
Sm	147	4.68 ± 0.15	4.0 ± 0.4	4.0 ± 0.3	4.5 ± 0.3	4.74 ± 0.34	4.50 ± 0.14
Eu	153	0.31 ± 0.02	0.26 ± 0.05	0.35 ± 0.01	0.29 ± 0.02	0.33 ± 0.03	0.27 ± 0.02
Gd	157	1.84 ± 0.05	1.53 ± 0.28	2.1 ± 0.1	1.59 ± 0.08	1.83 ± 0.15	1.77 ± 0.09
Tb	159	0.27 ± 0.01	0.29 ± 0.05	0.22 ± 0.01	0.24 ± 0.02	0.27 ± 0.03	0.37 ± 0.04
Dy	163	1.87 ± 0.06	1.65 ± 0.28	1.8 ± 0.1	1.8 ± 0.2	1.82 ± 0.2	1.86 ± 0.05
Ho	165	0.48 ± 0.02	0.36 ± 0.05	0.44 ± 0.02	0.43 ± 0.02	0.47 ± 0.06	0.44 ± 0.04
Er	166	1.49 ± 0.07	1.24 ± 0.24	1.3 ± 0.1	1.36 ± 0.08	1.43 ± 0.2	1.49 ± 0.08
Tm	169	0.22 ± 0.02	0.15 ± 0.03	0.19 ± 0.02	0.18 ± 0.01	0.21 ± 0.04	0.19 ± 0.02
Yb	173	1.26 ± 0.07	1.22 ± 0.29	1.3 ± 0.1	1.13 ± 0.07	1.29 ± 0.38	1.40 ± 0.17
Lu	175	0.22 ± 0.02	0.20 ± 0.04	0.22 ± 0.02	0.20 ± 0.02	0.19 ± 0.06	0.21 ± 0.02

Mean ± standard deviation.

^a Number of measurement is unknown.

The results determined in this study show a good agreement, within analytical uncertainty, with those of previous studies. The obtained standard deviations are relatively small, indicating good external precision of the present method. These fairly good results reinforced the reliability and usefulness of the analytical method in this study.

Conclusion

An off-line preconcentration system using SDCCs (Nobias-chelate-PAIM) was developed for determining REE concentrations in seawater. Recovery yields are ~100%, except for La (86%). Results of REEs in NASS-5, determined by developed method, agree well with those of

previous studies, indicating the reliability and good accuracy of the developed method. Moreover, the present method is very efficient because of the use of small-volume seawater sample (25 ml) in preconcentration procedure compared with the other methods. In addition, the preconcentration system is convenient and easily operated.

Acknowledgements

L.D.L gratefully thanks Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) for providing scholarship during 2 years of master course under the Okinawa International Marine Science Program at the University of the Ryukyus. We thank Yanbei Zhu for his kind suggestion in using

preconcentration system. L.D.L also thanks Daniel Meshesha for his assistance in washing bottles.

References

- Alibo, D.S. and Nozaki, Y. (1999) Rare earth elements in seawater: Particle association, shale-normalization, and Ce oxidation. *Geochim. Cosmochim. Acta*, 63, 363-372.
- Alibo, D.S. and Nozaki, Y. (2004) Dissolved rare earth elements in the eastern Indian Ocean: Chemical tracers of the water masses. *Deep-Sea Res. Part I: Oceanographic Research Papers*, 51, 559 - 576.
- Bai, L.L. and Zhang, J. (2008) Clarifying the structure of water masses in East China Sea using low-volume seawater measurement with rare earth elements. *Adv. Geosci.*, 18, 169-180.
- Lawrence, M.G. and Kamber, B.S. (2007) Rare earth element concentrations in the Natural Water Reference Materials (NWRM) NASS-5, CASS-4 and SLEW-3. *Geostandards and Geoanalytical Research*, 31, 95-103.
- Nozaki, Y. (2001) Rare earth elements and their isotopes in the oceans. A derivate of *Encyclopedia of Ocean Sciences*, 2nd edition, 39-51. Academic Press, Elsevier.
- Rahmi, D., Zhu, Y., Fujimori, E., Umemura, T., Haraguchi, H. (2007) Multielement determination of trace metals in seawater by ICP-MS with aid of down-sized chelating resin-packed minicolumn for preconcentration. *Talanta*, 72, 600-606.
- Totland, M., Jarvis, Ian. and Jarvis, K.E. (1992) An assessment of dissolution techniques for the analysis of geological samples by plasma spectrometry. *Chem. Geol.*, 95, 35-62.
- Wang, Z.L. and Yamada, M. (2007) Geochemistry of dissolved rare earth elements in the Equatorial Pacific Ocean. *Environ. Geol.*, 52, 779-787.
- Willie, S.N. and Sturgeon, R.E. (2001) Determination of transition and rare earth elements in seawater by flow injection inductively coupled plasma time-of-flight mass spectrometry. *Spectrochim. Acta Part B*, 56, 1707-1716.
- Zhang, J. and Nozaki, Y. (1996) Rare earth elements and yttrium in seawater: ICP-MS determinations in the East Caroline, Coral Sea, and South Fiji basins of the western South Pacific Ocean. *Geochim. Cosmochim. Acta*, 60, 4631-4644.
- Zhu, Y., Itoh, A., Fujimori, E., Umemura, T., Haraguchi, H. (2006) Determination of rare earth elements in seawater by ICP-MS after preconcentration with a chelating resin-packed minicolumn. *J. Alloys Comp.*, 408-412, 985-988.
- Zhu, Y., Umemura, T., Haraguchi, H., Inagaki, K., Chiba, K. (2009) Determination of REEs in seawater by ICP-MS after on-line preconcentration using a syringe-driven chelating column. *Talanta*, 78, 891-895.