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LA-ICP-MS of rare earth elements concentrated in cation-exchange resin particles for origin attribution of uranium ore concentrate

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ABSTRACT

Rare earth elements (REE) concentrated on cation-exchange resin particles were measured with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to obtain chondrite-normalized REE plots. The sensitivity of REE increased in ascending order of the atomic number, according to the sensitivity trend in pneumatic nebulization ICP-MS (PN-ICP-MS). The signal intensities of REE were nearly proportional to the concentrations of REE in the immersion solution used for particle-preparation. Minimum measurable concentration calculated from the net signals of REE was approximately 1 ng/g corresponding to 0.1 ng in the particle-preparation solution. In LA analysis, formation of oxide and hydroxide of the light REE and Ba which causes spectral interferences in the heavy REE measurement was effectively attenuated due to the solvent-free measurement capability, compared to conventional PN-ICP-MS. To evaluate the applicability of the proposed method, the REE-adsorbed particles prepared by immersing them in a U-bearing solution (commercially available U standard solution) were measured with LA-ICP-MS. Aside from the LA analysis, each concentration of REE in the same U standard solution was determined with conventional PN-ICP-MS after separating REE by cation-exchange chromatography. The concentrations of REE were ranging from 0.04 (Pr) to 1.08 (Dy) µg/g-U. The chondrite-normalized plot obtained through LA-ICP-MS analysis of the U standard sample exhibited close agreement with that obtained through the PN-ICP-MS of the REE-separated solution within the uncertainties.

1. Introduction

Nuclear forensic analysis plays an important role in nuclear counter-terrorism and counter-proliferation. There has been an increasing concern about smuggling of interdicted nuclear materials that could be altered into nuclear weapons. Uranium ore concentrate (UOC), which is better known as yellow cake, draws special attention owing to its high concentration of U, ease of distribution, and fungibility [1]. For specifying the trafficking route, the identification of the geographic origin of UOC is an effective approach. Accumulation of forensic signatures on the material origin derived from laboratory-based analysis, for example, U age determination, isotope ratio analysis, morphological observation, and impurity analysis is the key to achieve a credible attribution of UOC, resulting in the enhancement of nuclear security measures.

Impurities in UOCs, such as, Fe [2], Sr [3], Pb [3], and rare earth elements (REE) [4–6], which exhibit inherent characteristics of UOC have been determined for origin attribution of UOCs. Chondrite-normalized REE plots obtained through the impurity REE abundances can be one of the helpful predictive indicators for the source origin of the UOC. Owing to their similar chemical properties based on the stable oxidation state of +3 with the exceptions of Ce and Eu, REE behave as a coherent group over some geological or industrial processes.

Inductively coupled plasma mass spectrometry (ICP-MS) has been one of the leading techniques for acquiring chondrite-normalized REE plots which require simultaneous detection of 14 elements or more at trace or ultratrace levels. However, the spectral interference caused by isobars and isobaric molecules is a major problem in ICP-MS analysis [4,7]. The interfering species in REE measurement are roughly classified into three types: (1) plasma-based polyatomic species associated with Sr, Zr, and Mo, (2) oxides and hydroxides of the light REE, and (3) hydride, oxide and hydroxide of Ba.

The plasma-based polyatomic species, such as $^{95}Mo^{40}Ar^{16}O^+$, $^{88}Sr^{40}Ar^{16}O^+$ $^{90}Zr^{40}Ar^{16}O^1H^+$, $^{88}Sr^{40}Ar^{16}O^1H^+$, and $^{100}Mo^{40}Ar^+$, may interfere with ^{151}Eu, ^{144}Nd, ^{147}Sm, ^{145}Nd, and ^{140}Ce. However, REE are less subjected to such plasma-based polyatomic species due to generally low abundances of Sr, Zr, and Mo [8] and the instability of the formed species. In the case of the sample which contains unusually high amounts of Sr, Zr, and Mo (six or more

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orders of magnitude higher than REE), the removal of them or the suppression of the formation of the plasma-based polyatomic species is necessary.

With regard to the second group, the light REE may interfere on the heavy REE, forming some oxides, for example, $^{139}La^{16}O$ and $^{143}Nd^{16}O$, which have the nominal mass of ^{155}Gd and ^{159}Tb, respectively. Light REE oxides such as those of Ce, La, and Pr [9] have high dissociation energy and may cause interferences in the measurement of the heavier REE. The interferences associated with the light REE are more problematic than those of the plasma-based polyatomic species. Chemical separation of the light REE from the heavy REE with sufficiently high recoveries for all REE is difficult because of the similarity of their chemical properties.

The third group of polyatomic ions, hydrides, oxides and hydroxides of Ba are known to cause interferences in the measurements of Eu and Gd. As Ba is likely accompanied by the other alkaline earth metals, the determination of REE in samples with high contents of alkaline earth metals can be hampered from the interferences caused by Ba.

To eliminate the above described interferences, coexisting elements are chemically separated by solid phase extraction in column packed with commercial resins such as TRU® [4–6], UTEVA® [2], Ln® [10] or TODGA® [11]. These resins lead to the effective removal of U along with the coexisting elements in UOCs and sufficiently low limits of detection (LoD) in the pg per g range. The removal of the interfering elements is the key to realize a reliable determination. However, the separation procedure is time-consuming.

Laser ablation (LA) ICP-MS is a promising technique with a benefit of simple sample preparation. The LA system enables solid sample introduction to ICP-MS by ablating and evaporating fragments of the solid sample surface, generating fine particles to be directly transported to the ICP torch. The LA technique provides spatially resolved detection of trace elements with LoDs in the ng per g range or below. Various substrates including organic materials [12,13] have been applied to LA-ICP-MS.

In LA, quantitative analysis by LA-ICP-MS is still problematic due to the lack of standards. The preferential vaporization of volatile elements during ablation causes time-dependent sensitivity change as the depth of the crater increases [14,15]. The degree of such elemental fractionation is, in general, affected by sample matrix. Consequently, complete matrix-matching between a sample and a standard is essential for the determination of the concentrations, which makes the accurate and precise determination more difficult than that with solution nebulization ICP-MS (PN-ICP-MS). As for the analysis of chondrite-normalized REE plots of UOC samples, since only the relative relationships in their abundances are required, raw signal corrections are expected to be much simpler than that for quantitative analysis.

Table 1
Operating conditions of ICP-MS (iCAP Q) for PN- and LA-ICP-MS

Common plasma settings	
RF power	1550 W
Plasma gas flow rate	14.0 L/min
Auxiliary gas flow rate	0.80 L/min
Solution nebulization conditions	
Nebulizer gas flow rate	0.80 L/min
Dwell time	0.3 s
No. replicate	5
Laser ablation conditions	
Laser ablation device	NWR 213
Wave length	213 nm
Carrier He gas flow rate	0.75 mL/min
Nebulizer gas flow rate	0.80 L/min
Laser energy fluence	1.2 J/cm^2
Output energy	35%
Pulse repetition rate	10 Hz
Ablation pattern	Spot scan
Spot diameter	100 μm
Dwell time	0.01 s
Measured isotopes	
^{23}Na, ^{24}Mg, ^{88}Sr, ^{91}Zr, ^{95}Mo, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{143}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{171}Yb, ^{175}Lu, ^{234}U	

Another practical advantage in LA-ICP-MS is that mass spectra of heavy REE are lower susceptible to the interferences caused by the oxides and hydroxides of the light REE. Formation of such oxide ions during measurement is estimated to be much less than that in PN-ICP-MS owing to the capability of solvent-free sample introduction. LA-ICP-MS is advantageous over conventional PN-ICP-MS in alleviating the interferences and minimizing the sample preparation procedure. However, the concentrations of REE in UOC may be lower than the LoD for quadrupole ICP-MS. This indicates that direct measurement of REE in UOC is difficult without any preconcentration procedure.

The objective of this study is the development of an LA-ICP-MS method for accurate analysis of REE in U-bearing solution. The proposed approach is based on the preliminary pre-concentration of REE on commercially available strong acid cation-exchange (SCX) resin particles. REE show strong affinity to the cation-exchange group (sulfonic acid group) in dilute acid media. The distribution coefficient of the SCX resin for REE in 0.1 M HNO_3 is more than 10000, while those of U and Ba, which are major interfering components in REE detection, are about 5000 and 660, respectively [16]. Therefore, roughly selective adsorption of REE on SCX resin particles is expected, enabling the separation from interfering sample constituents. Finally, the REE containing particles were analyzed with LA-ICPMS using optimized ablation conditions. U standard solution including unknown amounts of REE was used to check the accuracy, comparing the resultant chondrite-normalized REE plots with that obtained through conventional PN-ICP-MS of REE-separated solution.

2. Experimental

2.1. Reagents

Multi-element standard solutions including fifteen rare earth elements (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, 10 mg/L in 5%(v/v) HNO_3, Agilent technologies), alkaline metal-mix standard solution (250 mg-Li/L, 1,000 mg-Na/L, and 10,000 mg-K/L in dilute HNO_3, Merck & Co., Inc.,), alkaline earth metal-mix standard solution (Mg, Ca, Sr, and Ba, 1000 mg/L in dilute HNO_3, Merck & Co., Inc.,), U standard solution (10,000 mg/L in 5% (v/v) HNO_3, SPEX CertiPrep, Inc.), were used to prepare the model sample solution and standard solutions for ICP-MS. Nitric acid used for dilution was of analytical grade and used without any further purification.

2.2. Instrumentation

All the measurements were conducted with quadrupole ICP-MS (iCAP Qc, Thermo Fisher Scientific Inc.). Sample introduction for PN-ICP-MS measurements was performed employing a peltier-cooled spray chamber equipped with a concentric quartz glass nebulizer. The final solutions for PN-ICP-MS were prepared by diluting with 1% (v/v) HNO_3. The operation conditions of ICP-MS are summarized in Table 1. The uncertainty of each measurement was set to be twice the standard deviation (SD) of five repeated measurements. The relative standard deviation (RSD) was calculated using averaged signals and corresponding SD. The instrument was tuned with multi-element standard solution before starting measurements and the sensitivity was set to be ranging from 200 to 300 kcps/ ng mL^{-1} at mass ^{115}In. The formation of oxide ions (^{140}Ce^{16}O/^{140}Ce) and doubly charged ions (^{137}Ba^{2+}/^{137}Ba) were adjusted not to exceed 2% and 3%, respectively. The NWR 213 laser system (Nd: YAG deep UV 213 nm based laser ablation system) provided by ESI's New Wave Research Division was directly attached to the torch of iCAP Q via PTFE tube. Synthetic standard reference material (SRM) 612 silicate glass provided by National Institute of Standards and Technology (NIST) was used for the tuning of the LA conditions. The blank signals observed in LA-ICP-MS originating from noble gasses (Ar, Kr, and Xe) were subtracted from raw signals.

2.3. Preparation and LA-ICP-MS analysis of REE-adsorbed particles

An analytical grade strong acid cation-exchange (SCX) resin with a crosslinkage of 8% and a wet bead size ranging from 63 to 150 μm (AG 50W-X8 resin) supplied by Bio-Rad Laboratories, Inc., was employed as an adsorbent for REE. The REE-adsorbed particles were prepared by batchwise adsorption. The resin particles were washed with 40%(v/v) and 1%(v/v) HNO_3 prior to immersion. The REE-including solutions with various concentrations were prepared by diluting the commercially available REE standard solution with 1%(v/v) HNO_3. The prewashed particles were immersed in the REE solutions for 1 hour. Then, the particles were picked up from the solution and dried under an IR lamp immediately after picked up from the solution and washed with ultrapure water. The resultant REE-adsorbed particles were spread out on a double-sided tape attached to the surface of a plastic dish to form a flat surface. Fig. 1 summarizes sample pretreatment procedures for LA-ICP-MS analysis. Prepared samples were investigated using spot ablation mode. Laser parameters were optimized to provide controlled ablation conditions without complete destruction of the particles. The instrumental parameters are given in Table 1. Data acquisition was performed using Thermo´s Qtegra software (v. 1.5.1189.31). For signal evaluation integrated counts were calculated for regions where stable signals were attained. Corresponding gas-blank signals were subtracted from each integrated count.

2.4. Separation of REE with SCX resin-packed column

A model solution including Na, Mg, K, Ca, Sr, Mo, Ba (20 μg), fourteen rare earth elements (2 μg of each), and U (2 μg) was prepared to obtain the elution behavior of the cation-exchange chromatography. The same SCX resin used for preparing the REE-adsorbed particles was packed into a polyethylene column with an inner diameter of 4 mm. The bed volume of the column was adjusted to 1.2 mL in wet state. The resin-packed column was conditioned immediately before use by passing 5 mL of 68%(v/v), 40%(v/v), 12%(v/v) and 1%(v/v) HNO_3 through the column to remove impurities. Prior to loading the column, the diluted synthetic standard solution were added in a PTFE beakers and dried at 80 °C. Then the residue was dissolved with 0.2 mL of 1%(v/v) HNO_3. The concentrations of each component in the loading solution were confirmed with ICP-MS. The separation procedure is shown in Fig. 2. The effluent from the column was continuously collected in a PTFE beaker and heated to dryness. The resultant residue was dissolved with 10 mL of 1%(v/v) HNO_3 and used as a final solution.

To evaluate the recoveries of the REE, the same model solution was passed through the column and the REE retained in the column were eluted with 6 mL of 40%(v/v) HNO_3.

2.5. Determination of REE in U-bearing sample

Due to the absence of certified reference material for REE in U-bearing sample, commercially available U standard solution (10 mg-U/mL) was used for the validation of the proposed method instead. Since there was no information on the impurities, the concentrations of REE were determined by PN-ICP-MS after the column chromatographic separation according to the procedure described in 2.4. To determine other coexisting elements, the non-separated solution with the dilution factor of 100 was also measured with ICP-MS.

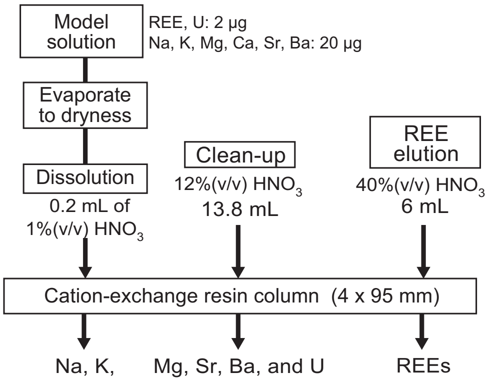


Fig. 2. Separation procedure of the REE using cation-exchange.

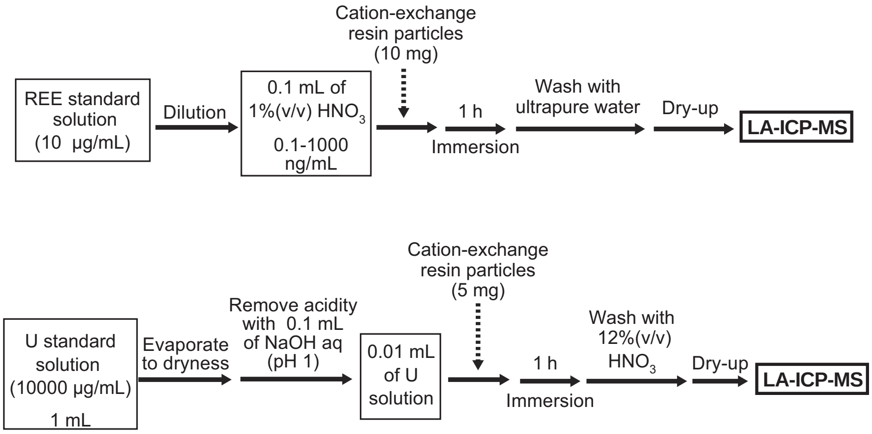


Fig. 1. Sample treatment procedures for LA-ICP-MS.

3. Results and discussion

3.1. LA-ICP-MS signals of REE in REE-adsorbed particles

About 10 mg of SCX particles were immersed in 0.1 mL of an REE solution at the concentration of 1 μg/mL. After removing the REE containing particles from the solution, the resultant particles were dried and measured via LA-ICP-MS according to the procedure described before. Fig. 3 presents a microscopic image of a crater created by 30 seconds ablation and the derived time-resolved signals for ^{140}Ce, ^{151}Eu, ^{167}Er, and ^{171}Yb. The signals of the REE were stable during the laser pulse ablation, suggesting that REE are homogeneously adsorbed in the radial direction of the resin particle. When performing experiments with much shorter reaction times derived LA-ICP-MS signals decreased towards the center of the resin particles, indicating that insufficient contact time causes heterogeneous REE adsorption. The signal intensities of REE increased with increasing the laser output energy and the laser spot size. The intensities at the spot size of 110 μm were 10 times higher than those at 25 μm. When the laser output energy was set to more than 35%, the particle structure was broken immediately after the ablation started. This indicates that the maximum output energy that provides high and stable signal was 35%. Considering the stability of the signals and the particle structure, a laser spot ranging in size between 80 and 110 μm is suitable. However, the laser spot size should be at least 30 μm smaller than the particle diameter to avoid complete destruction of the particles.

Integrated counts of REE are shown in Fig. 4 along with the sensitivities of REE measured with PN-ICP-MS. Both the immersion solution used for preparing the REE-adsorbed particles and the measured solution for PN-ICP-MS included 14 REE at the same concentration. Integrated counts were obtained by integrating time regions with stable signals. The gas-blank signals were subtracted from each integrated count. As shown in Fig. 4, the integrated counts of the REE increase in ascending order of the atomic number, which agrees with the sensitivity (cps/ ng mL^{-1}) trend observed in PN-ICP-MS. The similarity of the trend suggests that there are no additional interferences or elemental fractionation arising from LA-ICP-MS and the increase in the sensitivity is mainly caused by the detection efficiency. Consequently, raw signals need to be normalized appropriately. This was done via in-house prepared "standard reference particles" which were spiked known amounts of REE. The relationship between measured REE signal ratio and initial concentration ratio in immersion solution was evaluated by measuring SCX resin particles prepared using three different solutions. Each solution had different concentration ratios of La, Nd, and Eu as shown in Fig. 5. Here, the raw signal was corrected using standard reference particles which were prepared by immersing the SCX particles into the REE standard solution with all the REE concentrations of 10 ng /mL. The raw signals were corrected by dividing them by a relative sensitivity R_S which is obtained from the following equation:

$$R_S = [(\text{raw signal of interest isotope})/A_S]/[(\text{raw signal of standard isotope})/A_R] \quad (1)$$

where A_S and A_R are abundances of an isotope of interest and standard isotope, respectively. The integrated count ratios completely agreed with the initial relative concentration ratios. These results show that the REE concentration pattern in a sample solution can be reflected in LA signal ratios.

3.2. Minimum measurable amounts of REE

To find the minimum measurable amounts of REE, the relationship between the signal intensity (integrated count) and the amount of the REE in the immersion solution was investigated. Integrated counts are roughly proportional to the amount of REE in immersion solution varying from 0.1 to 1000 ng. RSD of the counts decreased when increasing the amounts of the REE in the immersion solution. Particles prepared with the solution containing more

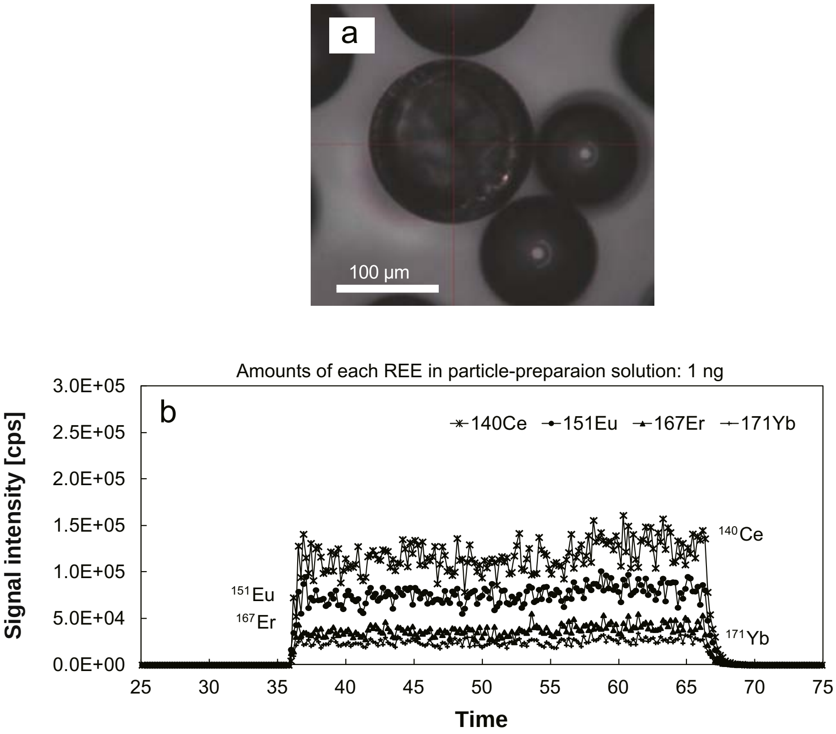


Fig. 3. Elution behaviors of (a) various elements and (b) REE oncation-exchange column chromatography.

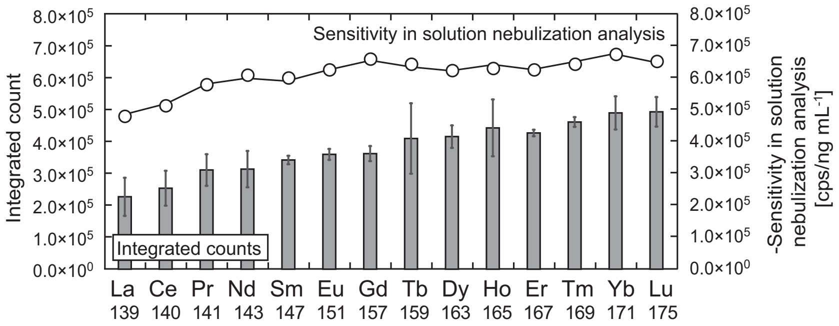


Fig. 4. Integrated counts of REE for LA-ICP-MS and the sensitivities measured with PN-ICP-MS. Error bars represent the standard deviation derived from measurement of 5 REE-containing particles. Amounts of each REE in the particle-preparation solution was 1 ng.

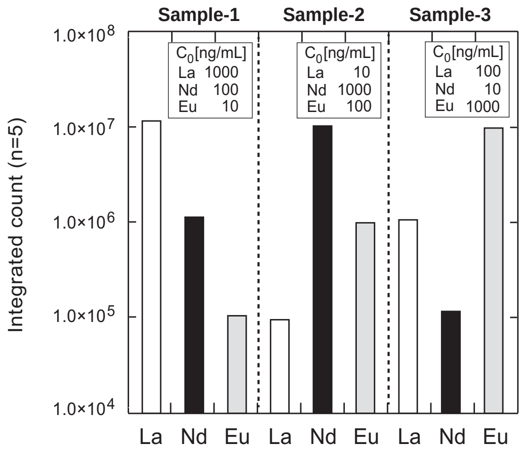


Fig. 5. Relationship between relative signal ratio and concentration ratio of immersion solution.

than 1 ng of the REE provide stable signals with the RSD around and below 5%. For the particles prepared with 0.1 ng of REE-containing solution, the average integrated counts were around 20,000 with the RSD ranging from 7–15%. This suggests that 0.1 ng of REE is the minimum measurable amount under the LA-ICP-MS conditions summarized in Table 1.

3.3. *Interferences in REE measurement with LA-ICP-MS*

Major interferences in REE measurement are oxides and hydroxides of the light REE and Ba. Additionally, argides of Sr, Zr, and Mo may interfere with the REE signals when a sample contains excessive amounts of such elements. The light REE with high dissociation energy to oxygen, such as La and Eu [9], easily form oxides in PN-ICP-MS, causing various interferences in spectra of the heavy REE. Such oxide formation is expected to be attenuated in LA owing to the solvent-free sample introduction. The comparison of MH^+/M, MO^+/M and MOH^+/M of the light REE (La, Nd, and Eu) and Ba between PN-ICP-MS and LA-ICP-MS is shown in Table 2. The MH^+/M, MO^+/M and MOH^+/M for LA were obtained by measuring the particles prepared with the mono-element standard solution (1 μg/mL in 1%(v/v) HNO_3). In LA-ICP-MS, the formation of the oxides of the light REE and Ba were suppressed by 80%–99%. In particular, the formation of LaO^+ was effectively reduced to a formation rate of 0.0001. Consequently, the interferences caused by oxides and hydroxides of the light REE in the heavy REE measurement are almost negligible. For argides, sufficiently low formation of polyatomic ions including Sr, Zr, and Mo (less than 10^{-6}) were observed, which was comparable to those observed in PN-ICP-MS. This demonstrates that there are generally no significant interferences unless sample includes unusually high contents of the light REE and Ba.

Other than the interference originating from the light REE and Ba, the components of the particles and some noble gases which exist as an impurity of Ar gas, also have the potential to contribute to the interferences in the REE measurements. Integrated counts obtained by measuring non-adsorbed particles, which were only prewashed with concentrated nitric acid to remove impurities but not treated with REE standard, indicate the formation of various polyatomic species in the REE mass range. Most of the integrated signals were below 500 counts and their signals were unstable. These signals originating from noble gases (gas blank signals) and signals observed in the measurement of the non-adsorbed particles were consistent. This demonstrates that there were no major interferences specific to the resin particles. To obtain reliable REE concentration ratios, a particle that gives more than 100,000 counts of each REE corresponding to the particles prepared with 1 ng of the REE-containing solution is required.

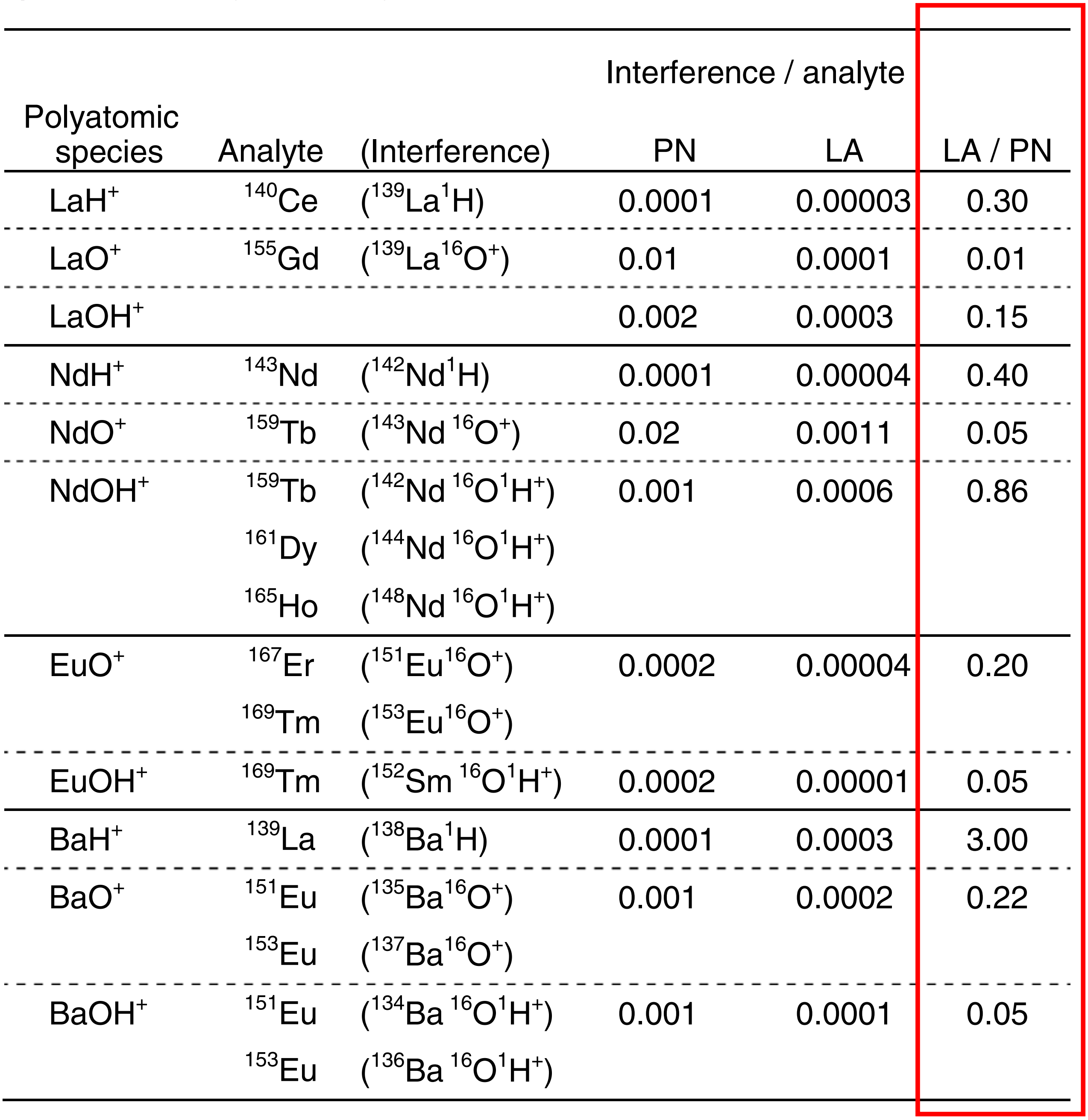
3.4. *Influence of U on the retention of REE on SCX-particles*

In a UOC sample, the concentration of U is expected to be more than seven orders of magnitude higher than those of REE. To investigate the effect of increasing U concentrations on the recoveries of REE, adsorption experiments with 10 ng analyte in the presence of varying amounts of U (10 ng to 1000 μg) were performed. The integrated counts of REE as a function of concentration ratio REE/U are shown in Fig. 6. No major change along with the increase in REE/U was found in the REE signals, demonstrating that the amounts of REE in SCX-particles are constant regardless of the U content. Additionally, the signals of REE are nearly free from the major interferences and U matrix when the REE/U is less than 10^{-5}. The RSDs were gradually decreased with increasing REE/U. This indicates that high concentration of U affects the signal stability of REE. Nevertheless, even for the lowest REE/U ratio, the RSD below 10% were achieved, which is sufficient for the intended determination of REE patterns in UOC samples.

3.5. *Determination of REE in U standard solution*

To evaluate the applicability of the LA-ICP-MS method using REE-adsorbed particle to REE plot analysis, verification with U-bearing sample is desirable. Although there are some U_3O_8 certified reference materials (CRM) with certified values of several REE [8], none of them cover all REE. Therefore, a commercially available U standard solution (SPEX CertiPrep, Inc.) was used for the evaluation. This solution is expected to include REE as impurities in comparable contents as produced from typical U_3O_8 sources. Before comparison, it is necessary to determine

Table 2
Comparison of formation rate for hydrides, oxides and hydroxides between PN- and LA-ICP-MS



Polyatomic species	Analyte	(Interference)	Interference / analyte PN	LA	LA / PN
LaH^+	^{140}Ce	$(^{139}La^1H)$	0.0001	0.00003	0.30
LaO^+	^{155}Gd	$(^{139}La^{16}O^+)$	0.01	0.0001	0.01
$LaOH^+$			0.002	0.0003	0.15
NdH^+	^{143}Nd	$(^{142}Nd^1H)$	0.0001	0.00004	0.40
NdO^+	^{159}Tb	$(^{143}Nd\,^{16}O^+)$	0.02	0.0011	0.05
$NdOH^+$	^{159}Tb	$(^{142}Nd\,^{16}O^1H^+)$	0.001	0.0006	0.86
	^{161}Dy	$(^{144}Nd\,^{16}O^1H^+)$			
	^{165}Ho	$(^{148}Nd\,^{16}O^1H^+)$			
EuO^+	^{167}Er	$(^{151}Eu^{16}O^+)$	0.0002	0.00004	0.20
	^{169}Tm	$(^{153}Eu^{16}O^+)$			
$EuOH^+$	^{169}Tm	$(^{152}Sm\,^{16}O^1H^+)$	0.0002	0.00001	0.05
BaH^+	^{139}La	$(^{138}Ba^1H)$	0.0001	0.0003	3.00
BaO^+	^{151}Eu	$(^{135}Ba^{16}O^+)$	0.001	0.0002	0.22
	^{153}Eu	$(^{137}Ba^{16}O^+)$			
$BaOH^+$	^{151}Eu	$(^{134}Ba\,^{16}O^1H^+)$	0.001	0.0001	0.05
	^{153}Eu	$(^{136}Ba\,^{16}O^1H^+)$			

the concentrations of REE in U standard solution with a conventional approach using a reliable separation procedure for REE.

As discussed in the introduction section, REE ions has a strong affinity to cation-exchange group (sulfonic acid group) in dilute HNO_3 [16], while the other cations, UO_2^{2+} and the possible impurities, *e.g.*, Na^+, Mg^{2+}, K^+, Ca^{2+}, Sr^{2+}, and Ba^{2+} have lower distribution coefficients enough to achieve the removal by cation-exchange chromatography. The elution behavior of cations in model solution is shown in Fig. 7. The separation was carried out following the procedure shown in Fig. 2. The monovalent and divalent cations were eluted in the ascending order of the affinity to the cation-exchange group, while REE were not eluted. After passing 14 mL of 12%(v/v) HNO_3 through the column, some of REE started to elute. The recovery percentages of REE were found to range between 94 ± 4 (La) and 99 ± 4 (Nd), demonstrating that almost all of the REE were adsorbed and readily recovered from the column. None of the monovalent and divalent cations were found in the REE fraction (REE-separated solution).

The separation procedure presented above was applied to U standard solution. In order to check contamination, the blank signal was monitored. The concentrations of REE in the REE-separated solution and the amounts of blank are summarized in Table 3. The co-elution of coexisting components in the REE-separated solution was negligibly low. The amount of U co-eluted was 0.004%, showing that the matrix effect based on U is very low. The REE concentrations in the U standard solution before separation were well agreed with those after separation with the exception of Ce, which was affected by the isobaric interference caused by $^{40}Ar^{238}U^{++}$. The blank signals

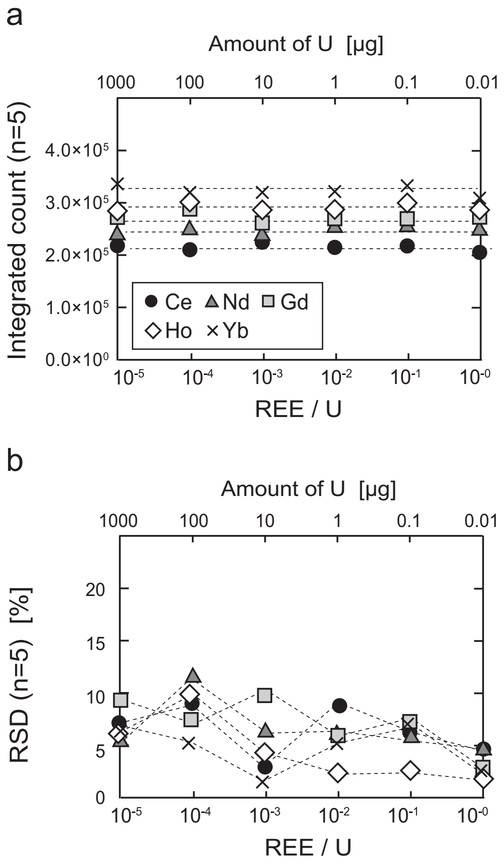


Fig. 6. Effect of U matrix on REE signals. (a) integrated counts and (b) RSD as a function of abundance ratio REE/U.

were much smaller than those in the REE-separated solution, which demonstrates that method blank contributes little to the sample measurement. These facts suggest that the measured concentration values of the REE-separated solution are reliable.

3.6. *Chondrite-normalized REE plots*

The same U standard solution used for cation-exchange chromatography was used for REEs adsorption on the SCX particles prior to their analysis using LA-ICP-MS.

The integrated signals of REE obtained by measuring the REE-adsorbed particles with LA-ICP-MS are shown in Fig. 8(a) along with the measured concentrations of REE in the REE-separated solution in PN-ICP-MS. The sensitivities in the raw signals of REE were corrected using standard reference particles prepared by immersing the SCX particles into the REE standard solution with all the REE concentrations of 10 ng/g. The intensities of all REE were high enough to identify the presence of each REE in U standard solution. The REE signal trend is similar to that of the concentrations obtained through PN-ICP-MS. This indicates that the signal trends of LA-ICP-MS give close agreement with the original REE concentration ratios in U standard solution.

Only for La, the signal intensity at m/z 139 was about 4 times higher than the expected signal intensity, indicating that a doubly charged ion ^{40}A^{r238}U^{2+} mainly contributes to the interference in the ^{139}La measurement. The interference associated with ^{238}U molecular ion was corrected using the formation rate of ^{40}Ar^{238}U^{2+}. The formation rate R_{139} was calculated as follows:

$$C_{N238} = \frac{C_{N234}A_{238}}{A_{234}} \qquad (2)$$

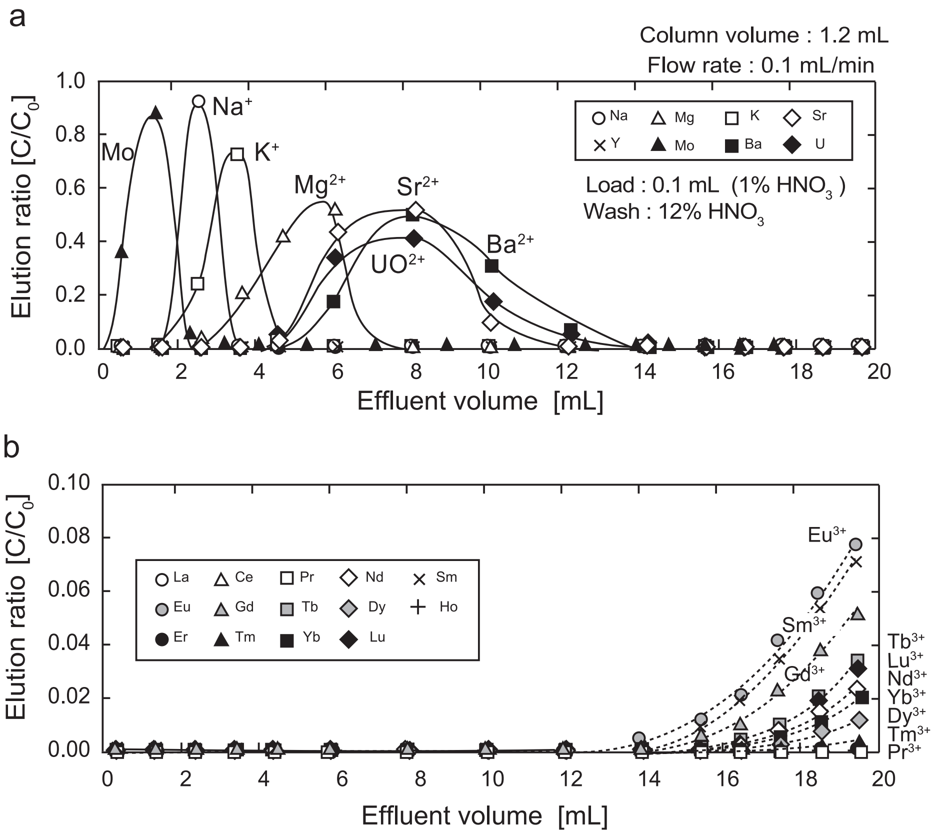


Fig. 7. Elution behavior of (a) various elements and (b) REEs oncation-exchange column chromatography.

Table 3
Measured concentrations of REE in U standard solution along with amounts of REE in method blank

Element	Measured concentration [μg/L]	Concentration in uranium [ng/mg-U]	Blank [pg]
La	0.48 ± 0.11	0.10 ± 0.02	1.3
Ce	1.32 ± 0.14	0.27 ± 0.03	9.0
Pr	0.20 ± 0.02	0.040 ± 0.003	0.6
Nd	1.46 ± 0.13	0.29 ± 0.03	3.4
Sm	1.17 ± 0.21	0.23 ± 0.04	2.3
Eu	0.57 ± 0.06	0.11 ± 0.01	0.9
Gd	2.04 ± 0.25	0.41 ± 0.05	1.8
Tb	0.67 ± 0.05	0.13 ± 0.01	0.2
Dy	5.42 ± 0.38	1.08 ± 0.08	1.3
Ho	1.25 ± 0.08	0.25 ± 0.02	0.4
Er	4.12 ± 0.33	0.82 ± 0.07	1.1
Tm	0.70 ± 0.05	0.14 ± 0.01	0.3
Tb	5.71 ± 0.31	1.14 ± 0.06	1.2
Lu	0.71 ± 0.05	0.14 ± 0.01	0.2

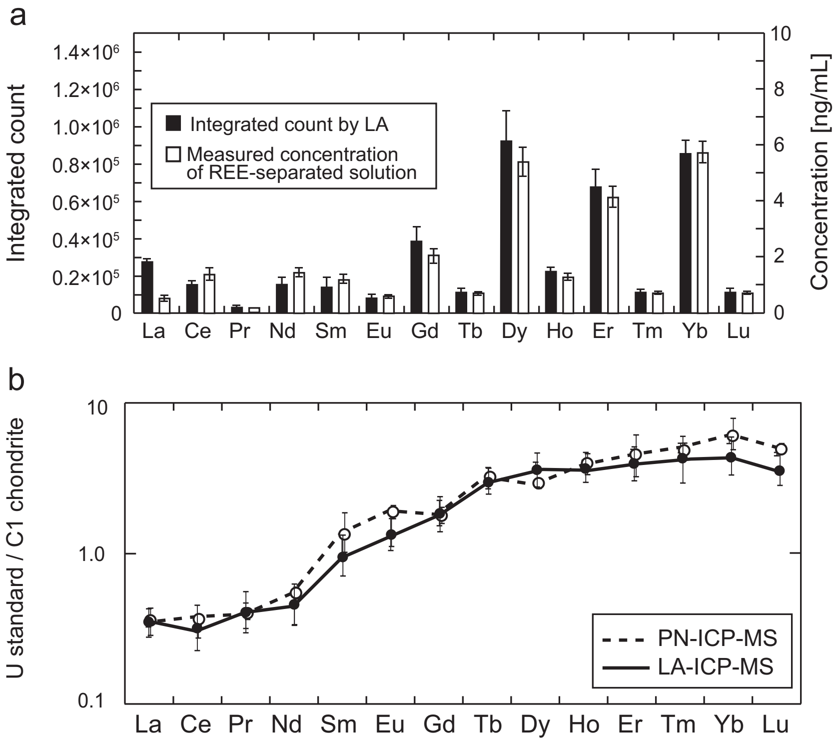


Fig. 8. Comparison of the LA-ICP-MS with PN-ICP-MS, (a) LA signals and measured concentrations, and (b) chondrite-normalized REE plots of U standard.

$$R_{139} = \frac{(C_{N139} - C_{S139})}{C_{N238}} \tag{3}$$

where C_{N238} and C_{N234} are the net cps at m/z 238 and 234 in the non-separated solution with the dilution factor of 100, respectively. A_{238} and A_{234} are the natural abundances of ^{238}U and ^{234}U. C_{N139} and C_{S139} are the net cps at m/z 139 in the non-separated solution and the cps at m/z 139 in the REE-separated solution, respectively. For C_{S139}, the net cps was converted to adjust the U concentration of the initial sample solution to that of the non-separated solution. The resultant R_{139} was 1.5×10^{-7}.

The signal at m/z 139 was decreased by subtracting the interference originating from $^{40}\mathrm{A}^{r238}\mathrm{U}^{2+}$ after the correction using R_{139}, resulting in the close fit to the concentration pattern of the REE-separated solution. The chondrite-normalized REE plots [17] obtained through PN-ICP-MS and LA-ICP-MS are shown in Fig. 8 (b). The Both REE plots were consistent within the uncertainty. This demonstrates that LA-ICP-MS using the REE-adsorbed resin particles can be applicable to REE abundance analysis.

4. Conclusion

A new analytical method for chondrite-normalized REE plot has been developed in this study. Strong acid SCX particles were used as a substrate to retain REE for LA-ICP-MS analysis. The effective adsorption of REE in solid phase allows sufficiently high and stable signals of REE during laser ablation. Compared with the conventional approach comprised of chemical separation and PN-ICP-MS, the proposed method enables much simpler preparation, shortening the processing time prior to measurement. In addition, effective suppression of the formation of oxides and hydroxides of the light REE has been achieved, which was unachievable with conventional approach. The U standard solution employed in this study for checking the accuracy contains Sr, Zr, Mo, and Ba at low concentrations, resulting in the interference-free measurement of REE with LA-ICP-MS. Even if a sample contains a significant level of such elements, they may be removed by an additional washing step of the resin particles with appropriate solution prior to LA-ICP-MS analysis. The most important finding in this study is that the signal trend of REE in LA analysis is in consistency to the amount ratios of REE adsorbed in the resin particles and the initial concentration ratios in the immersion solution. This demonstrates that the REE signals are practically free from elemental fractionations and major interferences caused by resin matrix.

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