A review of chromatographic analysis for rare-earth elements with focus on Ln resin

Jihye Kim[1, ★] and Kihwan Choi[2, ★]

[1]*Nuclear Chemistry Technology Division, Korea Atomic Energy Research Institute, Daejeon 34057, Korea*
[2]*Organic Metrology Group, Division of Chemical and Biological Metrology, Korea Research Institute of Standards and Science, Daejeon 34113, Korea*
[3]*Graduate School of Analytical Science and Technology, Chungnam National University, Daejeon 34134, Korea*

Abstract: The demand for rare-earth elements (REEs) is increasing owing to their significance as prominent materials in electronics, high-tech industries, geological research, nuclear forensics, and environmental monitoring. In general, the utilization of REEs in various applications requires the use of chromatographic techniques to separate individual elements. However, REEs have similar physicochemical properties, which makes them difficult to separate. Recently, several studies have examined the separation of REEs using LN resin as the stationary phase and aqueous nitric acid and hydrochloric acid solutions as eluents. Using this method, light REEs have been separated using dilute acid solutions as the eluent, whereas heavy REEs are separated using solutions with high acid concentrations. To increase the separation resolution between different REEs, either the column length or resin size is changed. In addition, the suggested methods are implemented to decrease the analysis time. This review presents technical information on the chromatographic separation of REEs using the LN resin and discusses the optimal experimental conditions.

Key words: rare-earth elements, analysis, chromatographic separation, column chromatography, LN resin, separation resolution

1. Introduction

Rare-earth elements (REEs) are necessary components of more than 200 products used in various applications, especially high-tech consumer products that function as technology-critical elements, including cellular telephones, electric and hybrid vehicles, as well as flat-screen monitors and televisions.[1,2] The applications of REEs vary greatly, depending on the characteristics of each element. For example, elements such as lanthanum (La), cerium (Ce), praseodymium (Pr), and gadolinium (Gd) can be used in the production of glasses, whereas neodymium (Nd) and samarium (Sm) have applications in permanent magnets. Promethium (Pm), europium (Eu), terbium (Tb), dysprosium (Dy), and yttrium (Y) are utilized in fluorescent substances, while Sm, holmium (Ho), and erbium (Er) are used in the nuclear power industry. Therefore,

---

★ Corresponding author
Fax: +82-(0)42-868-8148; +82-(0)42-868-5800
E-mail : jihyekim21@kaeri.re.kr; kihwan.choi@kriss.re.kr

it becomes crucial to separate each element individually in order to enhance the utilization of REEs.[3] Typically, chromatographic techniques have been used to separate individual REEs from an REE mixture for the REE industry.[4] The separated or purified REE can be further analyzed using secondary analysis equipment, such as a mass spectrometer, or used in devices such as Ni-MH batteries, permanent NdFeB magnets, and liquid crystal display backlights.[5] Ion-exchange chromatographic methods are commonly used to separate REEs.[4] In the late 1950s, the separation of lanthanum and thorium was accomplished using an anion exchange resin (Dowex 1-X8).[6] Further, a study on the properties of the anion exchange resin revealed that the distribution coefficients of REEs varied significantly according to the resin type (Dowex 1-X2, Dowex 1-X4, Dowex 1-X8, Dowex 1-X10, or Dowex 1-X16).[7] Ever since, active studies have been focused on increasing the resolution of REE separation by evaluating the distribution coefficient and changing the composition of eluents.[7-9] In 1975, Horwitz developed a method that used di-2-ethylhexylphosphoric acid (HDEHP) as a coating for the stationary phase of a column and measured the distribution coefficients of various REEs.[10] The resulting resin was then commercialized as an LN resin for REE separation by Eichrom Technologies (USA, IL, Lisle). Recently, HDEHP-based LN resins have been utilized in many other studies, such as in the analysis of $^{143}Nd/^{144}Nd$ in geological samples,[11,12] the separation of lanthanide isotopes from mixed fission product samples,[13] and individual separation of REEs.[14,15] This review article focuses on the chromatographic analysis of REEs using the LN resin. As the LN resin has high selectivity, it increases the REE separation resolution, allowing for a fast and easy separation of REEs via a simple selection of an appropriate solvent for elution. This review presents the classification and physical properties of REEs and summarizes the recent studies on analyzing REEs using the LN resin to help improve analytical methods based on chromatography for REE separation.

2. Definition and Physical Properties of REEs

The International Union of Pure and Applied Chemistry (IUPAC) defines REEs as the 17 elements in period VI of the periodic table. The REEs include the fifteen lanthanides (atomic numbers 57 to 71) as well as scandium (Sc) and Y. The REEs can be divided into two main categories, with scandium being unclassified[16]: (i) light REEs (LREEs), which include La, Ce, Pr, Nd, Pm, Sm, and Eu with atomic numbers ranging from 57 to 63, and (ii) heavy REEs (HREEs), which include Gd, Tb, Dy, Ho, Er, thulium (Tm), ytterbium (Yb), and lutetium (Lu) with atomic numbers ranging from 64 to 71.[17] Pm with an atomic number of 61 is a radioactive element with a half-life of 2.62 years that is rarely found in the natural environment.[18] Additionally, the REEs can be classified into three groups: first, LREEs with atomic numbers of 57 to 60, from La to Nd. Second, the group of middle REEs (MREEs) with atomic numbers of 61 to 64, from Pm to Gd. Finally, HREEs, including Tb to Lu and Y, with atomic numbers of 65 to 71; Sc is not included in any of these categories because of its chemical

Table 1. Atomic numbers and electron configuration of REEs[32]

Name	Symbol	Atom number	Electron Configuration
Lanthanum	La	57	$[Xe]4f^05d^16s^2$
Cerium	Ce	58	$[Xe]4f^15d^16s^2$
Praseodymium	Pr	59	$[Xe]4f^36s^2$
Neodymium	Nd	60	$[Xe]4f^46s^2$
Promethium	Pm	61	$[Xe]4f^56s^2$
Samarium	Sm	62	$[Xe]4f^66s^2$
Europium	Eu	63	$[Xe]4f^76s^2$
Gadolinium	Gd	64	$[Xe]4f^75d^16s^2$
Terbium	Tb	65	$[Xe]4f^96s^2$
Dysprosium	Dy	66	$[Xe]4f^{10}6s^2$
Holmium	Ho	67	$[Xe]4f^{11}6s^2$
Erbium	Er	68	$[Xe]4f^{12}6s^2$
Thulium	Tm	69	$[Xe]4f^{13}6s^2$
Ytterbium	Tb	70	$[Xe]4f^{14}6s^2$
Lutetium	Lu	71	$[Xe]4f^{14}5d^16s^2$
Scandium	Sc	21	$[Ar]3d^14s^2$
Yttrium	Y	39	$[Kr]4d^15s^2$

difference from the other REEs.[19,20]

The ground-state electronic configuration of lanthanides commonly has at least one electron in the 4f electronic orbital and is represented as [Xe] $4f^{0-14} 5d^{0-1} 6s^2$, with the exception of Sc ($3d^1 4s^2$) and Y ($4d^1 5s^2$). The electron configurations and atomic numbers of REEs are listed in *Table* 1, with the 4f orbital being filled progressively with increasing atomic number. The presence of seven 4f orbitals can result in up to seven unpaired electrons, because of which lanthanides have large magnetic moments. Most lanthanides lose one electron pair from the 6s orbital and one electron from the 4f orbital, resulting in the formation of a trivalent cation (M^{3+} or Ln^{3+}) with highly similar chemical properties. In addition, as electrons fill the 4f orbital, the ion size decreases and contracts with increasing atomic number. For example, the ion size of La is 103 pm, and it decreases along the lanthanide series to 86.1 pm for Lu.[18] In general, the atomic and ion radii decrease as the atomic number increases along the same period in the periodic table (from left to right). Because the number of electron shells remains constant, whereas the number of protons increases with increasing atomic number along the period, a larger effective nuclear charge attracts more electrons and contracts the atom. Therefore, the ionic radius decreases along the period. According to this principle, the ionic radius of lanthanides becomes much smaller than expected, a phenomenon commonly referred to

as "lanthanide contraction".[18] The reason for this phenomenon is the electron configuration of the REEs with a 4f orbital, which does not facilitate effective shielding of the valence electrons from the nuclear charge. Relativistic effects account for approximately 10 % of the lanthanide contraction, mainly because the 6s orbital electrons are closer to the nucleus than the 4f electrons. This can be explained by the fact that the ionization energy increases with increasing number of protons and decreasing atomic radius, because a more positively charged nucleus attracts more electrons, resulting in an increase in the effective nuclear charge. An effective nuclear charge is created for a nucleus having a higher positive charge compared to the negative charge of the electrons. Density, melting point, and hardness increase with increasing atomic number of the lanthanide.[21] Additionally, hydration enthalpy also increases as the atomic number of the lanthanide increases. Owing to their strong Lewis acid properties, trivalent cationic lanthanides (M^{3+}) easily bind to highly basic compounds. For example, they form a strong ionic bond with carboxylates. Additionally, the large entropy effect produced by multidentate ligands results in binding stabilization.[21]

3. Recent Chromatographic Separation of REEs using LN Resin

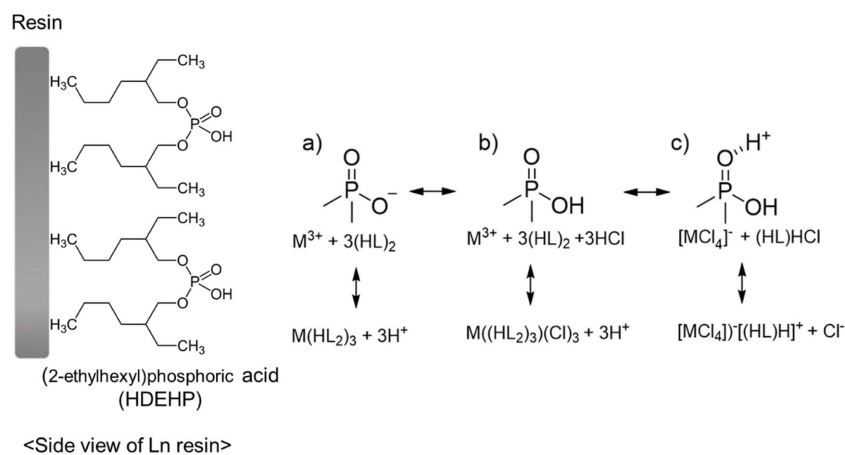In 1975, Horwitz utilized an undiluted HDEHP-

Fig. 1. Side view of LN resin and interaction mechanism of REEs on LN resin

Celite resin in a column to determine the distribution coefficients (K_d) of lanthanides.[10] The separation mechanism involves the interaction between the negative phosphate group of HDEHP and the positive trivalent lanthanide, which then interacts with the stationary phase. *Fig.* 1 shows a side view of the LN resin and the expected binding of the trivalent lanthanide cation (M^{3+}) to HDEHP (ligand, L).[22] Possible binding structures of the lanthanide and HDEHP have been reported to be binary and ternary complexes.[23]

The LN resin is primarily utilized for separating an LREE. *Table* 2 summarized the experimental conditions of previously reported chromatographic methods using LN resin. For example, a dating study was conducted to determine the geological age of a silicate rock sample by analyzing the LREE using an LN resin, and 50 % reduction in the analysis time

was achieved compared with that of conventional column chromatography.[24] This study used a narrow column with a length of 8 cm and an inner diameter (ID) of 4 mm packed with 50–100 mm LN resin particles. Further, by eluting the column with a 0.25 M HCl solution, 98 % of La was recovered in the initial 0.75 mL fraction, followed by the recovery of 99 % Ce and 15 % Pr using 1.25 mL aliquots of the solution. Subsequently, Nd was retrieved from the column with a recovery of 25 % using an additional 2.5 mL of solvent while Sm was separated by employing 0.75 M HCl. In this study, Nd and Sm, which were initially challenging to separate, were isolated and subsequently analyzed using isotope dilution thermal ionization mass spectrometry (ID-TIMS). In addition, the study found that the difference between the measured $^{143}Nd/^{144}Nd$ ratio and the

Table 2. Summary of experimental conditions previously reported chromatographic methods using LN resin

Analyte	Column size	Ln resin size	Elution solvent	Flow rate	Remarks	Reference
$^{143}Nd/^{144}Nd$, Sm, Nd	8 cm length 4 mm ID	50-100 μm (300 mg)	0.25 M HCl: La, Ce, Pr, Nd 0.75 M HCl: Sm, Eu	-	Fe^{3+} ions (impurities) were removed by cation exchange chromatography	[24]
$^{143}Nd/^{144}Nd$	5.5 cm length 4 mm ID	50-100 μm (0.3 mL)	0.25 M HCl: Nd	-	Remove the Ce by converting Ce^{3+} to Ce^{4+} using $KBrO_3$	[11]
$^{143}Nd/^{144}Nd$	6 cm length 4 mm ID	50-100 μm (300 mg)	0.25 M HCl: La, Ce, Pr 0.25 M HCl: Nd 0.75 M HCl: Sm	45 μL/min	Multi-column (Sr resin, TRU resin, Ln resin)	[26]
Ac, La, Ce	-	-	Ln resin: 0.1-0.5 M HNO_3 TRU resin: 1-5 M HNO_3	0.2 mL/min	Capacity factors of Ac, La, Ce using LN resin, DGA resin, TRU resin	[27]
$^{146}Sm/^{142}Nd$, $^{147}Sm/^{143}Nd$	-	50-100 μm	0.1 M HNO_3: Nd, Sm 10 M HNO_3: Nd, Sm	-	Multi-column, Remove the Ce using $KBrO_3$, Column recovery: Nd; 92%, Sm; 93%	[28]
Er, Yb	3 mm ID	20-50 μm	1.5 M HCl: Dy 2.5 M HCl: Er 3.5 M HCl: Yb 6.4 M HCl: Lu	0.1~0.2 mL/min (flow by pressure)	Column recoveries of Er, Yb: ~100%, Analysis time: 4.5~6 h	[30]
Nd isotopes	4.8 cm length 4 mm ID	100-150 μm	2.5 M HCl: Nd	0.3~0.4 mL/min (gravity flow)	Multi-column (DGA resin, Ln resin)	[12]
La, Ce, Nd	25 cm length 0.03" ID (0.8 mm)	50-100 μm 100-150 μm	0.25 M HCl: La, Ce, Nd	67.5 μL/min (flow by pressure)	Gas pressurized extraction chromatography system	[22]
La, Ce, Pr, Nd, Sm, Eu, Tb, Y	-	50-100 μm (0.78 g)	0.1-0.3 M HNO_3: La, Ce, Pr, Nd 0.4-0.5 M HNO_3: Sm, Eu 0.5-0.75 M HNO_3: Eu 1.5-2.5 M HNO_3: Tb 2.5-8 M HNO_3: Y	-		[13]
Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	15-45 cm length 10 mm ID	100-150 μm	0.1-0.25 M HNO_3 0.15-8 M HNO_3	-	Separation resolution ~ 1 for some pairs, Separation recovery > 91% for all	[15]
Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	20 cm length 0.7 mm ID	50-100 μm (0.78g) 100-150 μm (0.78g)	0.25-8 M HNO_3	5~7 mL/min	Analysis time: 9-12 h for 50-100 μm LN resin, Analysis time: 2 h for 100-150 μm LN resin	[14]
Pb, Sr, Nd	4.3 cm length 3 mm ID	-	0.2 M HNO_3: Nd, La	-	Remove the Ce using $NaBrO_3$ Multi-column (AG50W-X8 resin, Sr resin, Ln resin) Analysis time for Nd fraction: ~7 h	[25]

reference values from the literature fell within the range of analytical uncertainty. In a similar study that analyzed $^{143}Nd/^{144}Nd$ using an LN resin, Ce could not be effectively separated using aqueous HCl as the eluent. Therefore, Ce was initially separated using $KBrO_3$ as the oxidizing agent, followed by the separation of La, Pr, and Nd using a dilute HCl solution. In this study, inductively coupled plasma quadrupole mass spectrometry (ICP-qMS) was used to confirm the recovery of the sample, and ID-TIMS was used for dating the specimen. In another study, Dey et al. initially oxidized REE samples from silicates using 5 mM $NaBrO_3$. After oxidation, they removed Ce and then separated pure Nd using an LN resin. It is noted to quickly degrade the $NaBrO_3$ solution and apply it within 2–3 d.[25] Further, Pin et al. separated Ba, Sr, Pb, and LREEs using an LN resin for geological age dating.[26] In the age dating process, La, Ce, and Pr were first separated, followed by the separation of Nd and Sm through column chromatography. Initially, a 0.25 M HCl solution was used as the eluent, which was then changed to a 0.75 M HCl solution for separating Nd and Sm. The flow rate of the column was 45 μL/min, and a total eluent volume of approximately 8 mL was used for REE separation; considering the flow rate and elution volume, the REE separation process lasted approximately 3 h.[26] In particular, in this study, to prevent the adsorption of Fe^{3+} to the Ln resin, Fe^{3+} was separated from the LREE by reducing it to Fe^{2+} using ascorbic acid. Tazoe et al. analyzed Nd isotopes in a large sample volume, i.e., 3 L of seawater to investigate marine Nd.[12] After performing Fe hydroxide co-precipitation to remove excess Fe in seawater, only the REEs were extracted through column chromatography using a DGA resin. Subsequently, Nd was separated using an Ln resin and 0.25 M HCl as the eluent. The recovered sample was then quantitatively analyzed using multicollector ICP-MS.

Ostapenko et al. separated REEs using a nitric acid solution instead of hydrochloric acid solution as the eluent.[27] In this study, the capacity factors of TRU-spec resin and Ln-spec resin were compared for the analysis of Ac, La, and Ce. The capacity factors of Ln-spec resin for La and Ce were found to be much larger than those of the TRU-spec resin. When separating La and Ce from an Ln resin, the highest capacity factor can be achieved using nitric acid concentrations ranging from 0.1 to 0.5 M. On the other hand, the largest capacity factor for TRU-spec resin can be obtained using 1 to 5 M HNO_3. However, the lack of a substantial difference in the capacity factors of different REEs results in poor separation resolution. A study on column chromatography with an Ln resin has been reported, in which a higher concentration of nitric acid was used for elution.[28] To separate REEs from other elements such as Ba, Cs, and Fe. The column was rapidly eluted with 10 M HNO_3 without the need for individual separation of REEs. Although Nd and Sm were not separated from each other after column chromatography, both species could be successfully analyzed using ID-ICP-MS.[28] Arrigo et al. used a nitric acid gradient to separate Ln from a radioactive fission product, aiming to facilitate nuclear forensics and nuclear data production. For separating La, Ce, Pr, Nd, Sm, Eu, Tb, and Y, gradient elution was performed by varying the HNO_3 concentration in the eluent from 0.01 to 8 M. As a result, the radiometric purity of the Sm and Eu fractions increased significantly, and the limit of detection could be lowered.[14] In this case, column chromatographic recoveries of Ce, Sm, Eu, and Tb were evaluated using gamma spectroscopy, ICP-MS, and ICP-optical emission spectroscopy (OES), and the recovery of these REEs ranged from 56.5 to 94.1 %.

LREE separation using the Ln resin can be considered significantly faster compared to traditional column chromatography. In the analysis of Sm and Nd, Pin et al. reported that it took 3 h to separate them using an Ln resin, whereas, despite differences in column sizes in the two cases, it took 16 h to separate them using an anion exchange resin with a 1000 mL elution volume at a flow rate of 1 mL/min.[26,29] Kim et al. developed a column chromatography, known as a gas-pressurized extraction chromatography system (GPEC), for analyzing LREEs. A small fraction volume of 270 mL was applied using this device, and La, Ce, and Nd were separated with a total elution volume of 3 mL. The whole analysis time

was 45 min at a flow rate of 67.5 μL/min.[22] They reduced the entire analysis time within 1h. Upon decreasing the size of the LN resin particles from 100-150 to 50-100 μm, the separation resolution of Nd and La increased from 0.2 to 0.8 using a GPEC system.

Column chromatography has also been used to analyze HREEs such as Er and Yb and their isotopes.[30] LN resin particles of 20-50 μm size were used to elute Dy using 1.5 M HCl, Er using 2.5 M HCl, Yb using 3.5 M HCl, and Lu using 6.4 M HCl. Then, the separation process was repeated using a secondary column to obtain high-purity Er and Yb. The first and second column chromatography took 4.5-6 h each, with the recovery being 100 % for both elements.[30]

Ward *et al.* reported a study in which a total of 15 REEs were separated from a mixture of 14 lanthanides and Y, excluding Pm. The longer the column was, the greater the separation resolution was. However, an optimal separation condition was achieved with a column having an ID of 21.5 cm × 10 mm to avoid an excessively long elution time associated with a long column. Additionally, the isocratic method was used to separate REEs using 0.15 to 8 M HNO$_3$ for each section. The separation resolution was greater than 1 for five pairs: La/Ce, Sm/Eu, Gd/Tb, Tb/Dy, and Tm/Y.[15] Argio *et al.* also compared the separation resolution in the analysis of 14 lanthanides, excluding Pm, based on the size of LN resin particles. Isocratic elution with 0.25 to 8 M HNO$_3$ was used for each separated section. When resin particles of 100-150 and 50-100 μm sizes were used, the smaller-sized resin provided a greater separation resolution for MREEs. However, the chromatographic analysis using smaller resin particles (50-100 μm, weight: 0.78 g) took a significantly longer time of 9-12 compared with that of 100-150 μm resin particles (weight: 0.78 g), which took a total of 2 h. According to the theory of column chromatography, the result can be explained using the van Deemter equation for plate height.[31] In Eq. (1), A represents the multiple path length, B/u_x corresponds to longitudinal diffusion, and C u_x denotes the equilibration time. As the particle size decreases, the A and C terms decrease, leading to an increase in the separation efficiency and thus separation resolution.

$$H \approx A + \frac{B}{u_x} + Cu_x \qquad (1)$$

In addition, pressure can be applied to the column to decrease the elution time, as shown in Eq. (2). Column pressure (P) is determined by the flow rate (u_x), solvent viscosity(η), column length (L), column radius (r), particle diameter (d_p), and specific permeability (*f*). Because the column pressure is inversely proportional to the square of the particle diameter, the separation of REEs using smaller resin particles requires a higher pressure. If the elution is performed under gravity, the analysis time can be longer.

$$P = f \frac{u_x \eta L}{\pi r^2 d_p^2} \qquad (2)$$

4. Conclusions

REEs refer to 15 elements with atomic numbers ranging from 57 to 71, namely lanthanum to lutetium, and are classified as the lanthanide series in the periodic table. The lanthanide series also includes scandium and yttrium. Most of the elements in this group form trivalent cations with similar chemical properties, and the small size difference of the ionized lanthanides owing to lanthanide contraction makes the separation of these elements highly challenging. The 1950s witnessed earnest research on analyzing lanthanides using column chromatography, a traditional technique that has been widely used to pretreat samples or separate inorganic and organic mixtures. Various separation methods have been studied to determine parameters that affect the separation of REEs, such as the column length, flow rate, stationary phase type, and mobile phase type. Although traditional column chromatography offers excellent precision and accuracy, it is a time-consuming analytical process. Recent developments in resins have led to the development of methods that can reduce the amount of chemicals used and shorten the analysis time. Recently, the LN resin, a newly developed material, has been shown to facilitate faster and easier separation

of REEs. Various pretreatment methods have been developed for REE analysis based on the sample matrix for analyzing REEs. Furthermore, an increasing number of studies have focused on the separation of REEs, which are typically challenging to separate. LREEs are primarily separated using the LN resin and dilute hydrochloric acid or nitric acid solutions with acid concentrations ranging from 0.1 to 0.5 M or less for elution. Moreover, as the atomic number of the REE increases, a higher acid concentration of up to 8 M is required to elute the REE from the LN resin. When analyzing the entire range of the REEs, it is generally challenging to achieve a separation resolution higher than 1 for each element in the order of their atomic number; however, in certain cases, it exceeds 1. To enhance the separation resolution, small resin particles of size ranging from 50 to 100 μm are used. However, the drawback of using small resin particles is that a high column pressure is required for elution and the analysis time is longer. Although increasing the column length improves the separation resolution, the analysis time increases in this case as well.

The development of analytical methods for REE separation enables more efficient, faster, and reliable analyses. Furthermore, it can serve as a foundation for industries related to electronics, geology, and nuclear power.

Acknowledgements

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. C. E. D. Cardoso, J. C. Almeida, C. B. Lopes, T. Trindade, C. Vale, and E. Pereira, *Nanomaterials,* **9**(6), 814 (2019). https://doi.org/10.3390/nano9060814

2. G. Xie, Q. Guan, F. Zhou, W. Yu, Z. Yin, H. Tang, Z. Zhang, and R. Chi, *Molecules,* **28**(17), 6284 (2023). https://doi.org/10.3390/molecules28176284

3. D. Yan, S. Ro, O. Sunam, and S. Kim, *IOP Conf. Ser. Earth Environ. Sci.,* **508**, 012084 (2020). https://doi.org/10.1088/1755-1315/508/1/012084

4. B. Chen, M. He, H. Zhang, Z. Jiang, and B. Hu, *Phys. Sci. Rev.,* **2**(4), 1-35 (2017). https://doi.org/10.1515/psr-2016-0057

5. Y. El Ouardi, S. Virolainen, E. S. Massima Mouele, M. Laatikainen, E. Repo, and K. Laatikainen, *Hydrometallurgy,* **218**, 106047 (2023). https://doi.org/10.1016/j.hydromet.2023.106047

6. T. Sekine and N. Satio, *Nature,* **181**, 1464-1465 (1958). https://doi.org/10.1038/1811464a0

7. R. Dybczyński, *J. Chromatogr. A,* **50**, 487-503 (1970). https://doi.org/10.1016/S0021-9673(00)97977-9

8. I. Roelandts, G. Duyckaerts, and A. O. Brunfelt, *Anal. Chim. Acta,* **73**(1), 141-148 (1974). https://doi.org/10.1016/S0003-2670(01)82815-4

9. A. O. Brunfelt, I. Roelandts, and E. Steinnes, *Analyst,* **99**(1178), 277-284 (1974). https://doi.org/10.1039/AN9749900277

10. E. P. Horwitz and C. A. A. Bloomquist, *J. Inorg. Nucl. Chem.,* **37**(2), 425-434 (1975). https://doi.org/10.1016/0022-1902(75)80350-2

11. Y. Hirahara, Q. Chang, T. Miyazaki, T. Takahashi, and J.-I. Kimura, *JAMSTEC Report of Research and Development,* **15**, 27-33 (2012). https://doi.org/10.5918/jamstecr.15.27

12. H. Tazoe, H. Amakawa, K. Suzuki, J. Nishioka, T. Hara, and H. Obata, *Talanta,* **232**, 122435 (2021). https://doi.org/10.1016/j.talanta.2021.122435

13. L. M. Arrigo, J. Jiang, Z. S. Finch, J. M. Bowen, S. M. Herman, L. R. Greenwood, J. I. Friese, and B. N. Seiner, *Separations,* **8**(7), 104 (2021). https://doi.org/10.3390/separations8070104

14. L. M. Arrigo, J. Jiang, Z. S. Finch, J. M. Bowen, C. L. Beck, J. I. Friese, L. R. Greenwood, and B. N. Seiner, *J. Radioanal. Nucl. Chem.,* **327**(1), 457-463 (2021). https://

doi.org/10.1007/s10967-020-07488-9

15. J. Ward, B. Bucher, K. Carney, and M. Snow, *J. Radioanal. Nucl. Chem.,* **327**(1), 307-316 (2021). https://doi.org/10.1007/s10967-020-07491-0

16. P. Henderson, In "Rare Earth Minerals: Chemistry, Origin and Ore Deposits", pp. 1-19, Chapman and Hall, New York, 1996.

17. G. A. Moldoveanu and V. G. Papangelakis, *Hydrometallurgy,* **117-118**, 71-78 (2012). https://doi.org/10.1016/j.hydromet.2012.02.007

18. M. T. Aide and C. Aide, *Int. Sch. Res. Notices,* **2012**, 783876 (2012). https://doi.org/10.5402/2012/783876

19. D. Qi, In "Hydrometallurgy of Rare Earths", pp. 1-185, D. Qi, Ed., Elsevier, Amsterdam, 2018.

20. J. A. Galhardi, K. Luko-Sulato, L. N. M. Yabuki, L. M. Santos, Y. J. A. B. da Silva, and Y. J. A. B. da Silva, In "Emerging Freshwater Pollutants", pp. 309-329, T. Dalu and N. T. Tavengwa, Eds., Elsevier, Amsterdam, 2022.

21. J.-C. G. Bünzli, *J. Coord. Chem.,* **67**(23-24), 3706-3733 (2014). https://doi.org/10.1080/00958972.2014.957201

22. N. Kim, J. Park, W. Um, and J. Kim, *Mass Spectrom. Lett.,* **12**(4), 186-191 (2021). https://doi.org/10.5478/MSL.2021.12.4.186

23. C. Marie, B. Hiscox, and K. L. Nash, *Dalton Trans.,* **41**(3), 1054-1064 (2012). https://doi.org/10.1039/C1DT11534K

24. C. Pin and J. S. Zalduegui, *Anal. Chim. Acta,* **339**(1), 79-89 (1997). https://doi.org/10.1016/S0003-2670(96)00499-0

25. B. Dey, T. Shibata, and M. Yoshikawa, *Geochem. J.,* **57**(2), 73-84 (2023). https://doi.org/10.2343/geochemj.GJ23006

26. C. Pin, A. Gannoun, and A. Dupont, *J. Anal. At. Spectrom.,* **29**(10), 1858-1870 (2014). https://doi.org/10.1039/C4JA00169A

27. V. Ostapenko, A. Vasiliev, E. Lapshina, S. Ermolaev, R. Aliev, Y. Totskiy, B. Zhuikov, and S. Kalmykov, *J. Radioanal. Nucl. Chem.,* **306**(3), 707-711 (2015). https://doi.org/10.1007/s10967-015-4331-y

28. S. Kagami and T. Yokoyama, *Anal. Chim. Acta,* **937**, 151-159 (2016). https://doi.org/10.1016/j.aca.2016.07.004

29. F. W. E. Strelow, *Anal. Chem.,* **52**, 2420-2422 (1980). https://doi.org/10.1021/ac50064a043

30. T. Yokoyama, R. Fukai, and M. Nakahara, *Geostandard. Geoanal. Res.,* **44**(2), 265-285 (2020). https://doi.org/10.1111/ggr.12317

31. D. C. Harris, In "Quantitative Chemical Analysis", pp. 517-558, W. H. Freeman, New York, 2007.

32. E. Butter, *Cryst. Res. Technol.,* **20**(5), 662-662 (1985). https://doi.org/10.1002/crat.2170200510

Authors' Positions

Jihye Kim   : Senior Research Scientist
Kihwan Choi   : Principal Research Scientist