

Separation of Light Rare-Earth Elements Using Gas-Pressurized Extraction Chromatography

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Abstract : A new method for chemical separation of light rare-earth elements (LREEs) using gas-pressurized extraction chromatography (GPEC) is described. GPEC is a microscale column chromatography system that features a constant flow of solvents, which is created by pressurized nitrogen gas. The separation column with a Teflon tubing was packed with LN resin. The proposed GPEC method facilitates production of lesser chemical wastes and faster separation owing to the use of low solvent volume compared to traditional column chromatography. We evaluated the separation of Ba, La, Ce, and Nd using various elution solvents. The column reproducibility of the proposed GPEC system ranged from 2.4% to 4.9% with RSDs of recoveries, and the column-to-column reproducibility ranged from 3.1% to 6.3% with RSDs of recoveries. The proposed technique is robust, and it can be useful for the fast separation of LREEs.

Keywords : light rare-earth elements, gas-pressurized extraction chromatography, column chromatography, separation

Introduction

Rare-earth elements (REEs) are a series of chemical elements in period 6 of the periodic table, and they are known as lanthanides; they also include scandium and yttrium. The outer electrons in lanthanide REEs have common electron configuration of $4f^{0-14}5d^{0,1}6s^2$ except Sc ($3d^14s^2$) and Y ($4d^15s^2$) and they are generally trivalent, M^{3+} . These elements are characterized by the successive addition of an electron to the seven 4f orbitals, meaning that they all have similar electron configurations, atomic radii, and chemical properties, which makes their separation very challenging.¹ This study focused on light

REEs (LREEs) and barium, because of their increasing needs in various industries, such as age dating for geology, nuclear safeguards, and burnup measurement of nuclear fuel.²⁻⁶ LREEs include lanthanum, cerium, praseodymium, neodymium, promethium, and samarium with atomic numbers from 57 to 62.⁷ The analysis of LREEs of fission products in spent nuclear fuel is challenging due to isobaric interferences prior to mass spectrometry (e.g., ^{138}La versus ^{138}Ce , ^{142}Nd versus ^{142}Ce , and ^{150}Nd versus ^{150}Sm),⁸⁻¹⁰ and thus, chemical separation processes are necessary for isolating individual LREEs and achieving good quantitative results.

Typically, chromatographic techniques have been applied to separate LREEs.¹¹ Ion exchange chromatographic method has been commonly applied to analyze REEs.¹¹ In the late 1950s, separation of lanthanum and thorium using anion exchange resin was published.¹² Many other studies using anion exchange or cationic exchange resin have been performed, such as separation resolution studies using various concentrations of cross-linking agents in 1970s¹³ and distribution coefficients using various concentrations of different eluents.¹⁴ Based on the results until 1980s, samarium and neodymium were completely separated, but considering the flow rate (1.0 mL/min) and the amount of elute (~1 L) for whole separation, one cycle required at least 16 h.¹⁵ Thus, though the ion exchange chromatographic method provides high separation resolution, it requires

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extremely long analysis time and wastes large amounts of eluents.

After the 1990s, research on LREE separation has been more focused on reducing analysis time and increasing resolution. Based on the study of chemical separation using 2-ethylhexylphosphoric acid (HDEHP) by Horwitz in 1975,¹⁶ the resin for separation of LREE was commercialized as LN resin by Eichrom Technologies. Recently, this HDEHP-based LN resin has been utilized in many other studies, such as the separation of ¹⁷⁷Lu from neutron irradiated ¹⁷⁶Yb,¹⁷ the analysis of ¹⁴³Nd/¹⁴⁴Nd in geological samples,¹⁸ and sequential separation of LREE in silicate rocks,¹⁹ which allows minimized experimental labor and analysis time. The analysis time of LREE using column chromatography method has decreased considerably from ~16 h¹⁵ (calculated with the volume of eluents and the flow rate) to 1.5 h.²⁰ In particular, for analyses of radioactive samples, reducing the volume of liquid radioactive waste and total analysis time are essential for protecting the environment from hazardous radioactive waste and radiation dose to which researchers are exposed.²¹

LREEs as fission products from irradiated nuclear fuels are used for burnup determination.²² Burnup of irradiated nuclear fuels is defined as the energy produced per total mass of fuel, and it is determined by measuring the content of burnup monitor atoms and the fractional fission yield.²³ Commonly, lanthanum, cerium, and neodymium have been utilized as burnup monitor atoms among LREEs.²⁴ Thus, the chemical analyses of lanthanum, cerium, and neodymium are essential for spent fuel burnup determination.²⁴

In this study, we evaluate the separation of LREEs using gas-pressurized extraction chromatography (GPEC). This technique is advantageous as it helps reduce the total volume of eluents for decreasing chemical or radioactive waste and the analysis time for efficient analysis. The GPEC system also provides a constant flow rate because of use of pressurized-nitrogen gas via the column.²⁵⁻²⁷ It ensures good reproducibility of the results compared to the traditional column chromatographic method that uses gravity. Herein, we investigate the effect of eluent type, acid concentration of eluent, and resin size to identify the optimal separation conditions for barium, lanthanum, cerium, and neodymium using the GPEC system. We also measure column reproducibility and column-to-column reproducibility with the recoveries from the four elements. The proposed GPEC system used as a separation technique prior to ICP-MS can overcome isobaric interferences. When mass spectrometry is used alone, it is very difficult to analyze various LREE radioactive isotopes, such as nuclear fission products including ¹³⁹La-¹⁴⁰La, ¹⁴⁰Ba, ¹⁴⁰Ce-¹⁴⁴Ce, and ¹⁴³Nd-¹⁵⁰Nd, among different LREEs.²⁸ To develop a GPEC method, we applied the natural isotopes of LREEs (¹³⁹La, ¹⁴⁰Ce, and ¹⁴⁴Nd) and barium (¹³⁸Ba) instead of radioactive isotopes for the preliminary test; as a result, unnecessary radioactive waste was reduced.

Experimental

Reagents and materials

Barium (ICP-04N-1), lanthanum (ICP-28N-1), cerium (ICP-11N-1), and neodymium (ICP-36N-1) were purchased from AccuStandard (1000 µg/mL each, New Haven, CT, USA). Ultrapure nitric acid was obtained from Merck (Suprapur 65%, St. Louis, MO, USA). Ultrapure-grade of hydrochloric acid was from Seastar chemicals (Sidney, BC, Canada). Deionized water (18 MΩ) was produced using a Milli-Q water system (Millipore, Burlington, MA, USA).

GPEC system and operation

All tubing used for the GPEC system was made of transparent Teflon to help easily observe the movement of the colorless chemical stream during the experiment. Teflon tubing (1/16" OD × 0.03" ID, VICI, Houston, TX, USA) was used for the analytical column (25 cm length). Two LN resins (Eichrom Technologies, Darien, IL, USA) with different resin particle sizes (50-100 µm (LN-B50-S) and 100-150 µm (LN-B50-A)) were used for the analytical column. The column was packed by a syringe using 0.2 mg resin and 1 mL of water. A peristaltic pump was used to inject the washing solvent, sample, and eluent by sucking from the sample vial to the sample loop, as shown in Figure 1. First, with a sample loop of defined volume (270 µL), the washing solvent was filled into the sample loop and excess was discarded. After injecting the washing solvent, nitrogen gas was supplied by a valve at a flow rate of 67.5 µL/min. Thereafter, the washing solvent was eluted out through the analytical column. Using the same procedure, the column was preconditioned by rinsing three times with water and once with 0.05 M HCl. Between analyses, the column was rinsed with 0.75 M HCl, water, and 0.05 M HCl, sequentially. Thereafter, sample injection (one time) and eluent injections (repeat ten times) were successively collected (270 µL-fractionations). Sample mixtures of the three LREEs (La, Ce, and Nd) and barium

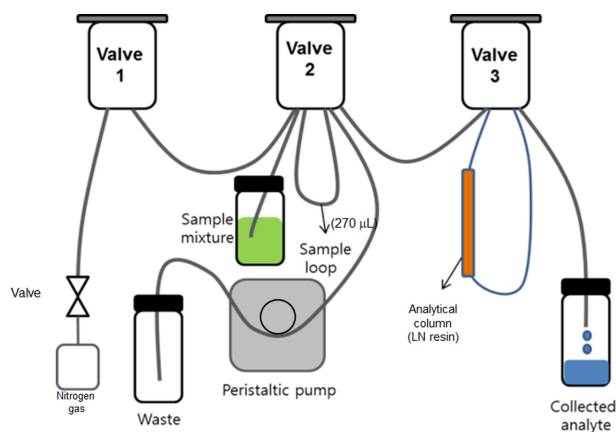


Figure 1. GPEC system.

at 10 $\mu\text{g/mL}$ were dissolved in 0.05 M HCl. Eluents were evaluated with 0.1–0.3 M HCl and 0.5–1.0 M HNO_3 with 100–150 μm sized resins. Elution solvent of 0.25 M HCl was applied with 50–100 μm sized resins to measure column reproducibility and column-to-column reproducibility with the recoveries. Figure 1 illustrates the GPEC system.

Precision experiment

Column reproducibility were the RSDs of the recoveries of LREEs and barium (five consecutive runs). Column-to-column reproducibility were the RSDs of the recoveries of LREEs and barium (five consecutive runs on each column) made on two columns packed with the same packing material. Sample mixtures of the three LREEs (La, Ce, and Nd) and barium at 10 $\mu\text{g/mL}$ were dissolved in 0.05 M HCl. Gradient elution was applied using 0.25 M HCl and water as the eluent with a 50–100 μm -sized resin as Figure 4.

Inductively coupled plasma-mass spectrometry (ICP-MS)

The performance of GPEC with collected fractions was measured using ICP-MS (SPECTRO MS, Kleve, Germany) equipped with a cyclonic spray chamber (Labkings, Hilversum, Netherlands) and a seaspray U-series nebulizer (Labkings, Hilversum, Netherlands). The samples were prepared by dilution to 5 mL with 1% nitric acid. Calibration solutions were prepared with 1000 $\mu\text{g/mL}$ single element standards and were in the range 1–20 ng/mL. The operating conditions for ICP-MS are listed in Table 1.

Results and Discussion

LN resin contains acidic alkylphosphorus-based extractants, such as (2-ethylhexyl)phosphoric acid (HDEHP), on an inert polymeric support. Trivalent cations of LREEs (M^{3+}) form binary or ternary complexes with HEDHP, as shown in Figure 2. As the pH of solution decreases, the equilibrium in Figure 2 shifts from (a) to (b) and from (b) to (c) under acidic aqueous conditions. Binding of LREEs on the column from low-acidity aqueous phases proceeds

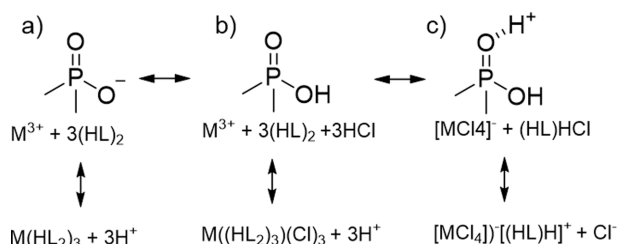


Figure 2. Interaction mechanism of LREEs by LN resin.

primarily through the cation exchange mechanism presented in Figure 2 (a).²⁹

As the P-OH groups become protonated at higher acid concentrations, less LREEs are retained on the column. At the highest acidities, LREEs become eluted. Based on this mechanism, 0.05 M HCl was used as a sample matrix and the elution solvent was applied at a higher concentration (0.1–0.3 M HCl) than the sample matrix.

Separation of LREEs by GPEC depending on eluents

Different types and concentrations of eluents were investigated for the separation of three LREEs and barium by isocratic elution. First, three eluents, namely, nitric acid, hydrochloric acid dissolved in water, and hydrochloric acid dissolved in methanol were evaluated with 100–150 μm sized resins. When nitric acid was used as the eluent with concentrations between 0.5 and 1 M, four elements were co-eluted within 3 fraction volumes ($3 \times 270 \mu\text{L}$). According to Ostapenko et al., 0.1 M–0.5 M HNO_3 was the optimal condition for the separation of REEs using LN resin.²⁹ Therefore, low concentration of nitric acid is effective for the separation of LREEs. When hydrochloric acid-methanol mixtures (10% and 30% methanol (0.2 M HCl/MeOH, v/v)) were applied to separate the three LREEs and barium, the four elements were not detected within 20-fraction volumes ($< 5.4 \text{ mL}$). We examined the 20-collected fractions obtained from the hydrochloric acid-methanol mixtures using ICP-MS. Once methanol was loaded into the column, there was no eluate of LREEs. Hence, it can be considered that methanol ruined the LN resin. Hydrochloric acid dissolved in water is known to be effective for the separation of LREEs using LN resin.¹⁹ Figure 3 shows isocratic separations using hydrochloric acid dissolved in water (concentrations ranging from 0.1 to 0.3 M) and 100–150 μm sized resins. First, barium was not distributed on the column and eluted immediately. This result was consistent with the report by Hortwitz, wherein K_d of barium was zero when 0.01 M HNO_3 was used with the LN resin. Then, La, Ce, and Nd sequentially were eluted depending on their relative orders of partitioning. Below 0.15 M HCl, the recoveries of three LREEs were very low. As the concentration of HCl was increased (above 0.2 M HCl), the recoveries of three LREEs

Table 1. Operating conditions for ICP-MS.

Plasma power	1400 W
Peristaltic pump speed	15 rpm
Coolant Ar gas flow rate	12 L/min
Auxiliary Ar gas flow rate	1.0 L/min
Nebulizer Ar gas flow rate	0.9 L/min
Skimmer cone	Ni
Sample cone	Ni
Base interval/Integration time	20 ms/30 s
Measure elements	^{138}Ba , ^{139}La , ^{140}Ce , ^{144}Nd
Software	Mass Analyzer Vision

and peak efficiencies increased, but the resolution decreased. Based on the above conditions, the optimum condition of eluent was 0.25 M HCl.

Separation of LREEs depending on the particle size of resin

Typically, resin particle size affects the resolution. Smaller particles provide higher resolution. Figure 4 shows the separation of three LREEs and barium with a 50-100 μm -sized resin. In the case of larger particle sized resins using 0.25 M HCl (Figure 3), the resolution between La and Nd was 0.2. For the same eluent, the resolution increased to 0.8 with a 50-100 μm -sized resin.

Further, to separate barium and lanthanum, gradient elution was developed using water as the elution solvent during initial 3 fraction volumes by GPEC (as shown in Figure 4). Based on the report that K_d of barium was ~ 500

with 0.008 M HNO_3 and LN resin, barium was easily eluted out of the column with water. Compared to the isocratic elution using 0.25 M HCl (Figure 3), Ba and La were completely resolved via gradient elution (Figure 4). The recoveries and peak efficiencies also increased with smaller sized resins. Therefore, we suggest that the final optimal condition for GPEC method was as shown in Figure 4, with a 50-100 μm -sized resin using 0.25 M HCl and water as the eluent.

Recovery and reproducibility of GPEC system

GPEC is a robust method, and it has great application potential for separation because of constant flow rate owing to the use of pressurized nitrogen gas. To evaluate the column reproducibility of this application, each column was tested for five consecutive runs, and the recoveries and RSDs of the recoveries of LREEs and barium were measured. Experimental conditions were the same as those used in Figure 4. Table 2 shows that $>90\%$ recoveries, except for Nd, were accomplished by GPEC for LREEs and barium, and the RSDs of recoveries were in the range 2.4%-4.9%. We performed the experiment with a new column and same procedures for investigating column-to-column reproducibility as those shown in Table 3. Thus, it was demonstrated that GPEC provides very high precision (3.1%-6.3%) for column-to-column reproducibility, and very high overall recoveries and reproducibility, as shown

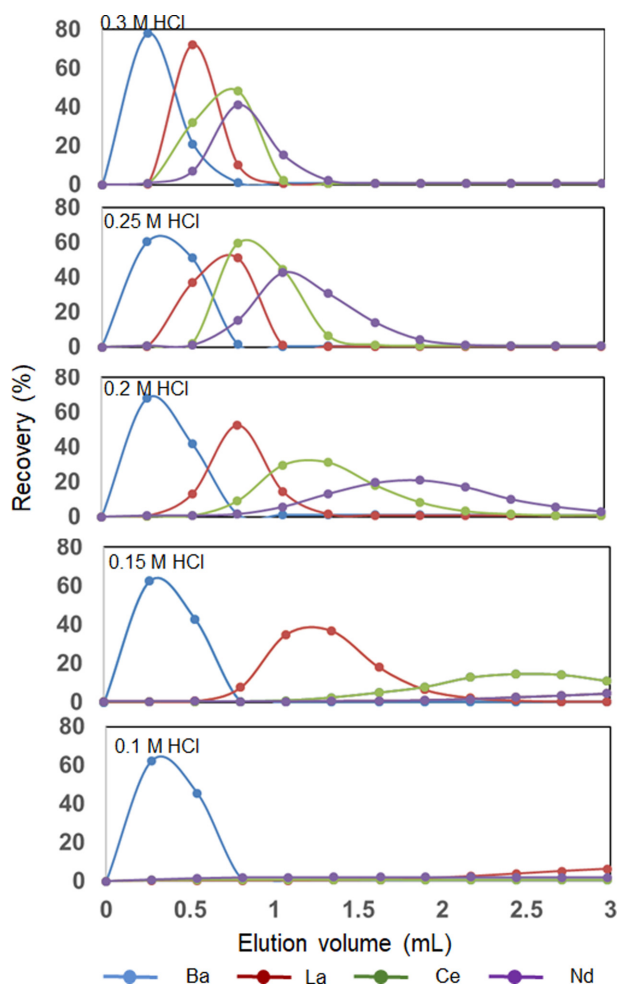


Figure 3. Separation of LREEs and barium by GPEC depending on the concentrations of hydrochloric acid (0.1 M, 0.15 M, 0.2 M, 0.25 M, and 0.3 M, 25 cm column length, 100-150 μm -sized LN resin) Other conditions as experimental section.

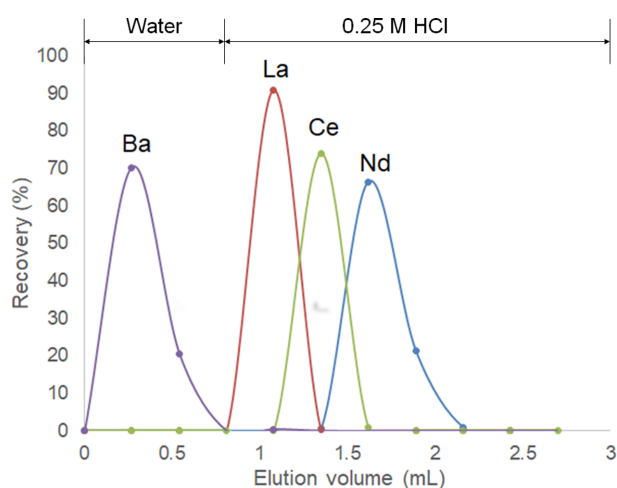


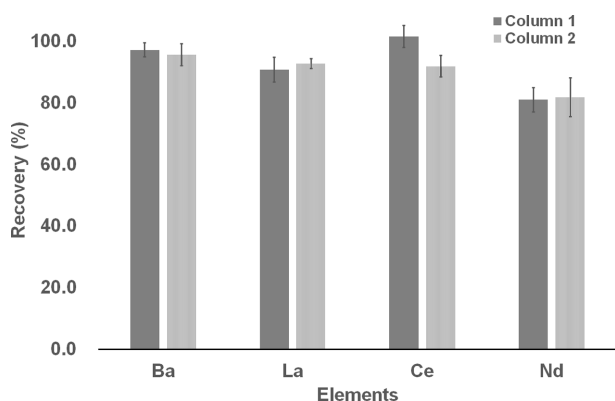
Figure 4. Separation of LREEs and barium by GPEC with a 50-100 μm sized resin and using 0.25 M HCl and water as eluent. Other conditions are presented in the experimental section.

Table 2. Column reproducibility and recovery by GPEC.

	Ba	La	Ce	Nd
Average of recovery ($n = 5$, %)	97.3	90.9	101.6	81.1
RSD (%) of recovery	2.4	4.4	3.5	4.9

Table 3. Column-to-column reproducibility and recovery by GPEC.

	Ba	La	Ce	Nd
Average of recovery (<i>n</i> = 10, %)	96.5	91.9	96.8	81.5
RSD (%) of recovery	3.1	3.3	6.3	6.1

**Figure 5.** Comparisons of recovery and reproducibility between column-to-column obtained by GPEC.

in Figure 5, showing that GPEC is suitable for separation of LREEs.

Conclusions

A new method for chemical separation of LREEs using GPEC is proposed. To overcome the isobaric interference in mass spectrometry, GPEC is a robust separation method as it is a microscaled chromatographic method. The optimal elution type, acid concentration, total volume of eluent, resin particle size, and amount of time needed for separation of Ba, La, Ce, and Nd were verified. Optimal conditions determined were 0.25 M HCl as elute with 50–100 μm sized LN resin as they provided high recoveries of the three LREEs considered in this study. For barium elution, a gradient method was developed with water as the solvent. Owing to the constant flow of nitrogen, the column reproducibility of recoveries by GPEC were in the range 2.4%–4.9%. The column-to-column reproducibility was in the range 3.1%–6.3%. These results show that GPEC gives high precision and good recovery for separation of LREEs and barium. Thus, this method may have considerable potential for analysis of LREEs from fission products using radioactive materials and less exposure of researchers.

Total analysis time required for a batch experiment was approximately 40 min using an elution volume of 270 μL and flow rate of 67.5 $\mu\text{L}/\text{min}$. Flow rate can be easily changed with a valve. Sample loading volume and elution volume can be changed by modifying the sample loop

length. In future studies, analysis time can be further reduced by adjusting the flow rate and the elution volume for different elements.

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References

- Gergoric, M.; Ekberg, C.; Steenari, B.-M.; Retegan, T. *J. Sustain. Metall.* **2017**, *3*, 601, DOI: 10.1007/s40831-017-0117-5.
- Kim, J. S.; Jeon, Y. S.; Park, S. D.; Han, S. H.; Kim, J. G. *J. Nucl. Sci. Technol.* **2007**, *44*, 1015, DOI: 10.1080/18811248.2007.9711341.
- Dry, D. E.; Bauer, E.; Petersen, L. A. *J. Radioanal. Nucl. Chem.* **2005**, *263*, 19, DOI: 10.1007/s10967-005-0005-5.
- Navarro, J.; Zhao, F. *Front. Energy Res.* **2014**, *2*, 45, DOI: 10.3389/fenrg.2014.00045.
- McCulloch, M. T.; Wasserburg, G. J. *Science* **1978**, *200*, 1003, DOI: 10.1126/science.200.4345.1003.
- Charalampides, G.; Vatalis, K. I.; Apostoplos, B.; Ploutarch-Nikolas, B. *Procedia Eco. Financ.* **2015**, *24*, 126, DOI: 10.1016/S2212-5671(15)00630-9.
- Omodara, L.; Pitkäaho, S.; Turpeinen, E.-M.; Saavalainen, P.; Oravisjärvi, K.; Keiski, R.L. *J. Clean. Prod.* **2019**, *236*, 117573, DOI: 10.1016/j.jclepro.2019.07.048.
- Hirata, T. *J. Mass Spectrom. Soc. Jpn.* **2004**, *52*, 171, DOI: 10.5702/masspec.52.171.
- Bradley, V.; Manard, B.; Roach, B.; Metzger, S.; Rogers, K.; Ticknor, B.; Wysor, S.; Brockman, J.; Hexel, C. *Minerals* **2020**, *10*, 55, DOI: 10.3390/min10010055.
- Laycock, A.; Coles, B.; Kreissig, K.; Rehkämper, M. *J. Anal. At. Spectrom.* **2016**, *31*, 297, DOI: 10.1039/C5JA00098J.
- Chen, B.; He, M.; Zhang, H.; Jiang, Z.; Hu, B. *Phys. Sci. Rev.* **2017**, *2*, DOI: 10.1515/psr-2016-0057.
- Sekine, T.; Satio, N. *Nature* **1958**, *181*, 1464, DOI: 10.1038/1811464a0.
- Dybczyński, R. *J. Chromatogr. A* **1970**, *50*, 487, DOI: 10.1016/S0021-9673(00)97977-9.
- Roelandts, I.; Duyckaerts, G.; Brunfelt, A. O. *Anal. Chim. Acta* **1974**, *73*, 141, DOI: 10.1016/S0003-2670(01)82815-4.
- Strelow, F. W. E. *Anal. Chem.* **1980**, *52*, 2420, DOI: 10.1021/ac50064a043.
- Horwitz, E. P.; Bloomquist, C. A. A. *J. Inorg. Nucl. Chem.* **1975**, *37*, 425, DOI: 10.1016/0022-1902(75)80350-2.

17. Horwitz, E. P.; McAlister, D. R.; Bond, A. H.; Barrans, R. E.; Williamson, J. M. *Appl. Radiat. Isot.* **2005**, 63, 23, DOI: 10.1016/j.apradiso.2005.02.005.
18. Hirahara, Y.; Chang, Q.; Miyazaki, T.; Takahashi, T.; Kimura, J.-I. *JAMSTEC Rep. Res. Dev.* **2012**, 15, 27, DOI: 10.5918/jamstecr.15.27.
19. Pin, C.; Zalduogui, J. S. *Anal. Chim. Acta* **1997**, 339, 79, DOI: 10.1016/S0003-2670(96)00499-0.
20. Payne, R.; Schulte, S.; Douglas, M.; Friese, J.; Farmer, O.; Finn, E. *J. Radioanal. Nucl. Chem.* **2011**, 287, 863, DOI: 10.1007/s10967-010-0838-4.
21. Rahman, R. O. A.; Ibrahim, H. A.; Hung, Y.-T. *Water* **2011**, 3, 551, DOI: 10.3390/w3020551.
22. de Regge, P.; Boden, R. J. *Radioanal. Nucl. Chem.* **1977**, 35, 173, DOI: 10.1007/BF02518224.
23. Kim, J. S.; Jeon, Y. S.; Park, S. D.; Ha, Y.-K.; Song, K. *Nucl. Eng. Technol.* **2015**, 47, 924, DOI: 10.1016/j.net.2015.08.002.
24. Bera, S.; Sujatha, K.; Sivaraman, N.; Narasimhan, T. S. L. *Radiochim. Acta* **2019**, 107, 685, DOI: 10.1515/ract-2018-3017.
25. Steeb, J.; Mertz, C.; Sandi, G.; Bass, D.; Graczyk, D.; Goldberg, M. *J. Radioanal. Nucl. Chem.* **2012**, 292, 757, DOI: 10.1007/s10967-011-1492-1.
26. Sommers, J.; Cummings, D.; Giglio, J.; Carney, K. *J. Radioanal. Nucl. Chem.* **2009**, 282, 591, DOI: 10.1007/s10967-009-0210-8.
27. Mertz, C. J.; Kaminski, M. D.; Shkrob, I. A.; Kalensky, M.; Sullivan, V. S.; Tsai, Y. *J. Radioanal. Nucl. Chem.* **2015**, 305, 199, DOI: 10.1007/s10967-015-4123-4.
28. Marie, C.; Hiscox, B.; Nash, K. L. *Dalton Trans.* **2012**, 41, 1054, DOI: 10.1039/C1DT11534K.
29. Ostapenko, V.; Vasiliev, A.; Lapshina, E.; Ermolaev, S.; Aliev, R.; Totksiy, Y.; Zhuikov, B.; Kalmykov, S. *J. Radioanal. Nucl. Chem.* **2015**, 306, 707, DOI: 10.1007/s10967-015-4331-y.