

Separation of Lanthanoids by SiO₂-P Adsorbent Impregnated with Extractants – 13103

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ABSTRACT

The adsorption and separation properties of lanthanoids (Ln) were investigated for the mutual separation of trivalent minor actinoids (MA) by using different adsorbents of hydrophobic extractant/SiO₂-P in solutions of hydrophilic extractant/HNO₃. The synergistic effect by use of the hydrophobic and hydrophilic extractants was evaluated by batch and column experiments. The results of batch experiments showed the synergistic effect which lowered the K_d values of Ln. In column experiments, effective mutual separation between Nd and Sm was demonstrated. These results suggest that the mutual separation between Am and Cm is possible because the K_d values of Am and Cm are probably similar to those of Nd and Sm.

INTRODUCTION

The separation of trivalent minor actinoids (MA: Am and Cm) from lanthanoids (Ln) is an important issue for the efficient processing of high-level radioactive liquid waste (HLLW) and the reduction of radioactive wastes. Novel extractants have been widely developed for use in the reprocessing of spent nuclear fuel and the partitioning for HLLW. For example, it is well-known that octylphenyl-*N,N*-diisobutyl-carbamoylmethylphosphine oxide (CMPO) and dimethyldibutyl-tetradecylmalonamide (DMDBTDMA) show high distribution ratio for actinoids (An) [1].

Recently, tridentate ligands were developed, which are expected to have both high extractability and selectivity. For instance, *N,N,N',N'*-tetraoctyl-1,3-oxapentane-1,5-diamide (TODGA), having three hard oxygen donors in the central frame, has been known as a strong extractant [2, 3]. Such diglycolamide (DGA) also have extractability for several fission products (FP). Therefore, masking agents are required to suppress the FP extraction.

In 2009, the new tetradentate extractant, *N,N,N',N'*-tetraoctyl-3,6-dioxaoctanediamide (DOODA), was reported and has been studied for metal ion extraction [4]. The DOODA has four oxygen atoms in the central frame as electron donors. Two types of DOODA, *N,N,N',N'*-tetraoctyl-3,6-dioxaoctane-1,8-diamide (DOODA(C8)) and *N,N,N',N'*-tetradodecyl-3,6-dioxaoctane-1,8-diamide (DOODA(C12)), have so far been synthesized. It was reported that the extractability trend of Ln(III) of DOODA was DGA >> DOODA > malonamide [4]. Moreover, the hydrophobic and hydrophilic properties of DGA and DOODA are changed by the attachment of a different alkyl group to the N-atoms. *N,N,N',N'*-tetraethyl-3-diglycolamide (TEDGA), which have short alkyl chain shows strong complexing ability with middle and heavy Ln in the aqueous phase [5, 6]. *N,N,N',N'*-tetraethyl-3,6-dioxaoctanediamide (DOODA(C2)), which have short alkyl chain shows strong complexing ability with

light Ln in the aqueous phase [6, 7]. Such hydrophilic ligand is often used as masking agent or water-soluble ligand to back extractant in solvent extractions [5]. Thus, it has been known that DGA has a high complexing ability with middle and heavy Ln, while DOODA has high complexing ability for light Ln. Therefore the synergistic effect on mutual separation of all Ln are expected by the use of both hydrophobic and hydrophilic extractants. In solvent extraction system, the combination of the extractants has been reported [5, 6, 7].

The purpose of this study is to mutually separate Ln using column chromatography. Compared to solvent extraction which is the main method in reprocessing and partitioning processes, the column chromatography which uses solid adsorbent has many attractive advantages, such as very limited organic solvent, compact equipment and less waste accumulation, so that it has a great potential in the application for the partitioning of MA and rare earths (RE). This work deals with to synthesize available adsorbents by impregnating TODGA and DOODA(C8) as extractants into SiO₂-polymer composite and to evaluate the adsorption properties of RE onto these adsorbents in HNO₃ in the presence of hydrophilic extractants such as TEDGA or DOODA(C2). SiO₂-polymer has been used as a matrix effective for selective separation of the elements in the world [12]. The column chromatography using the DGA and DOODA type extractants are worth applying to the partitioning process. Hence, the evaluation of adsorption properties of RE onto the novel adsorbents and the comparison with other adsorbents are very important for advancing the column chromatography of MA in HLLW. Figure 1 shows chemical structures of four represent types.

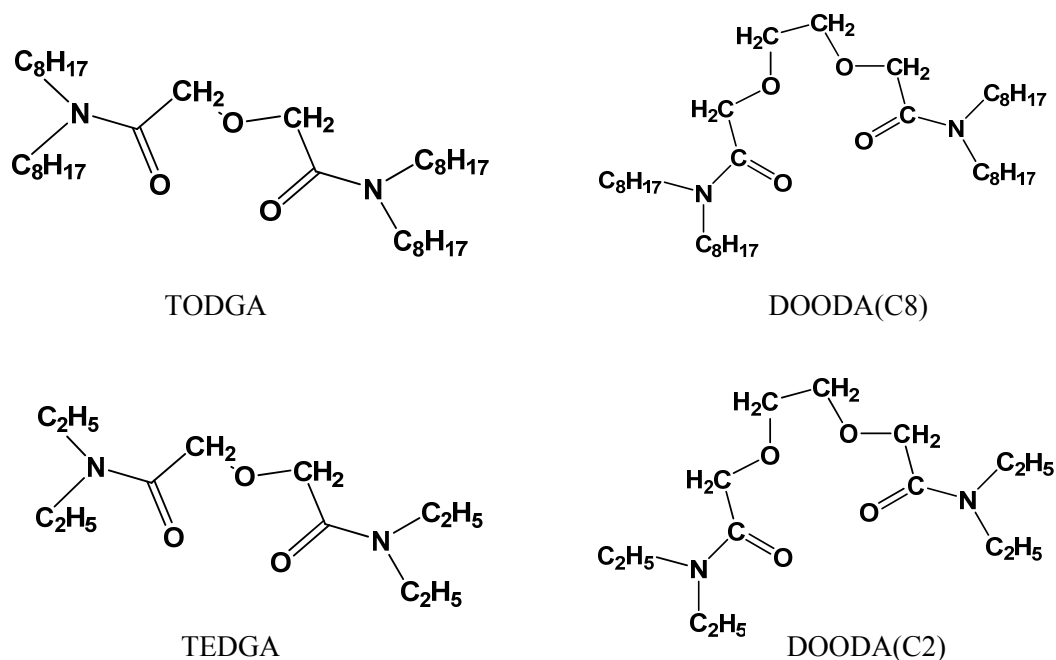


Fig.1. Chemical structures of four represent types.

EXPERIMENTAL

Chemical

The macroporous SiO₂-polymer particles, which were silica-based composites synthesized by immobilizing styrene-divinylbenzene copolymer inside SiO₂ matrices through a polymerization reaction, were produced by Unique and Innovative Sciences Inc. All metal ions for the extraction experiments were supplied from standard solutions (Wako Pure Chemical Industries Ltd.). The extractants used as examples of DGA and DOODA types were as follows; TODGA, TEDGA, DOODA(C8) and DOODA(C2). These extractants were prepared at JAEA (Japan Atomic Energy Agency).

Synthesis of silica-based adsorbents

Figure 1 shows a schematic diagram for silica-based adsorbent preparation [8, 9, 10, 11]. The SiO₂-polymer particles (3.2 g) were dried in a vacuum oven (Yamato Scientific Co. Ltd) at about 313 K for 12 h. Two kinds of hydrophobic extractants (TODGA or DOODA(C8)) dissolved in dichloromethane were mixed with the SiO₂-polymer particles in a flask, and the resultant mixture was then subsequently evaporated on a rotary evaporator (Yamato Scientific Co. Ltd) for about 4.5 h at 298-323 K using a water bath (Yamato Scientific Co. Ltd) to impregnate extractant molecules into the pores of SiO₂-polymer. After drying in a vacuum oven at about 313 K for 12 h, the synthesized macroporous silica-based polymeric adsorbents were ready for use.

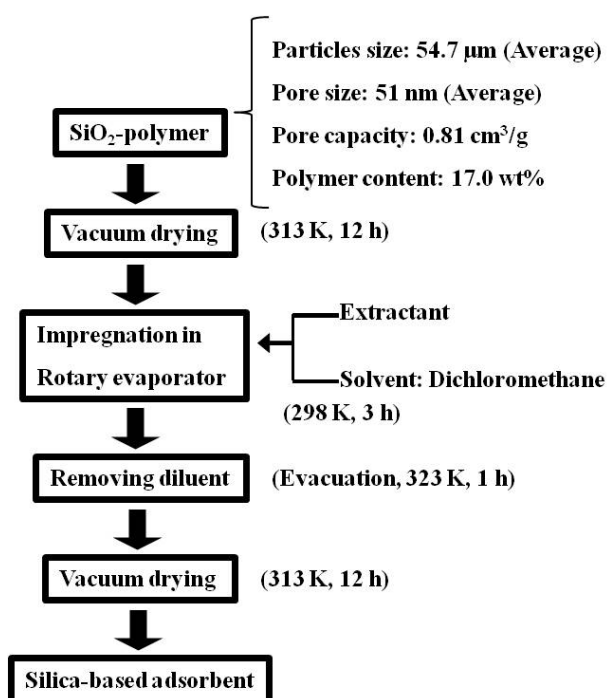


Fig.2. Schematic diagram of silica-based adsorbent synthesis.

Batch adsorption experiments

In all batch adsorption experiments, the temperature was maintained at 298 K. The adsorption behavior of RE was investigated under the following conditions: different HNO₃ concentrations from 0.1 M to 5 M, and different hydrophilic extractant concentrations from 0.05 M to 0.5 M for DOODA(C2) and from 0.003 M to 0.03 M for TEDGA. The adsorbent (0.05 g) was mixed with RE solution (5 ml) and shaken at 60 rpm for 3 h in a centrifugal tube. Each RE concentration was adjusted to 10 ppm. The combination of hydrophilic and hydrophobic extractants was as follow: DOODA(C2) vs. TODGA and TEDGA vs. DOODA(C8). After phase separation through filtration, the concentration of metal ions in the liquid phase was determined by ICP-AES (Seiko Instruments Inc. SPS7800). The distribution coefficient (K_d) [cm³/g] in batch experiments was calculated by the following equation:

$$K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{m} \quad (\text{Eq. 1})$$

where C_i : initial concentration of RE, C_f : concentration of RE after experiment.

Column separation experiments

The separation behavior of metal ions with adsorbent was evaluated by column experiment for chromatographic separation. About 3.8 g of a dry adsorbent were packed into a glass column. The condition of column experiments were decided as follows; column: ϕ 5 mm \times h 300 mm, flow rate: 0.18-0.23 ml/min, feed solution: [Ln³⁺] = 50 ppm/3 M HNO₃, washing solution: 3 M HNO₃, and elution solution: 0.05 M DOODA(C2)/0.1 M HNO₃ for TODGA/SiO₂-P and 0.003-0.03 M TEDGA/3 M HNO₃ for DOODA(C2)/SiO₂-P. The K_d value in the column experiments and recovery yield (R) [%] of Ln were obtained by the following equations:

$$K_d = \frac{V_R - V_0}{m} \quad (\text{Eq. 2})$$

$$R = \frac{q_i - q_f}{q_i} \times 100 \quad (\text{Eq. 3})$$

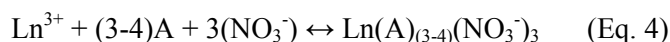
where V_R : retention volume [ml] of each Ln, V_0 : dead volume (8.4 ml), m : mass of adsorbents in column (3.76 g), q_i : initial quantity of Ln, q_f : recovered quantity of Ln.

RESULTS AND DISCUSSION

Adsorption behavior of batch experiments

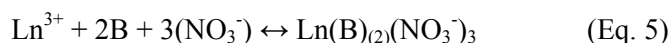
As for batch adsorption, the uptake of Ln for TODGA/SiO₂-P markedly increased with HNO₃ concentration from 0.1 to 3 M, and the distribution coefficient (K_d) of Ln increased with the size of ionic

radius. The increase in K_d corresponds to the Ln extraction formula. Main extraction formula is expressed by the following equation:



where A is DGA type extractant. Equation 4 indicates that the higher the HNO_3 concentration, the higher the ion pair extraction of cation and NO_3^- .

On the other hand, the uptake of Ln for DOODA(C8)/ SiO_2 -P gradually increased with increasing HNO_3 concentration, while the K_d value of Ln decreased with the size of ionic radius. These changes seemed to be associated with their extraction reaction, so main reaction was described by the following equation:



where B is DOODA type extractant. Equation 5 indicates that the DOODA type extractant behaved in the same way as the DGA extractant for the adsorption of RE elements.

Figures 2 and 3 show the respective results of TODGA and DOODA type batch adsorption. From these results, when the condition of $[\text{DOODA}(\text{C}2)] = 0.05 \text{ M}/[\text{HNO}_3] = 0.1 \text{ M}$, the K_d values of Ln (Nd, Sm, Eu, Gd and Tb) for TODGA/ SiO_2 -P were lowered to $1\sim 10^2 \text{ cm}^3/\text{g}$, and the separation factor (SF) between Nd and Sm was 3.4. When the condition of $[\text{TEDGA}] = 0.005\text{-}0.03 \text{ M}/[\text{HNO}_3] = 3\text{-}5 \text{ M}$, the K_d values of Ln (Nd, Sm, Eu, Gd and Tb) for DOODA(C8)/ SiO_2 -P were lowered to $1\sim 10^2 \text{ cm}^3/\text{g}$, and the SF between Nd and Sm was 1.9~3.6. Compared to the condition of hydrophilic extractants free, the synergistic effect was confirmed by existing the hydrophilic extractants. These conditions were considered to be appropriate for column chromatographic separation because the K_d values were reasonably low and the SF values were around 2-4. The previous report suggests that the K_d values of Am and Cm are similar to those of Nd and Sm [6]. Therefore evaluating of these element's K_d and SF values is very important for mutual separation of MA.

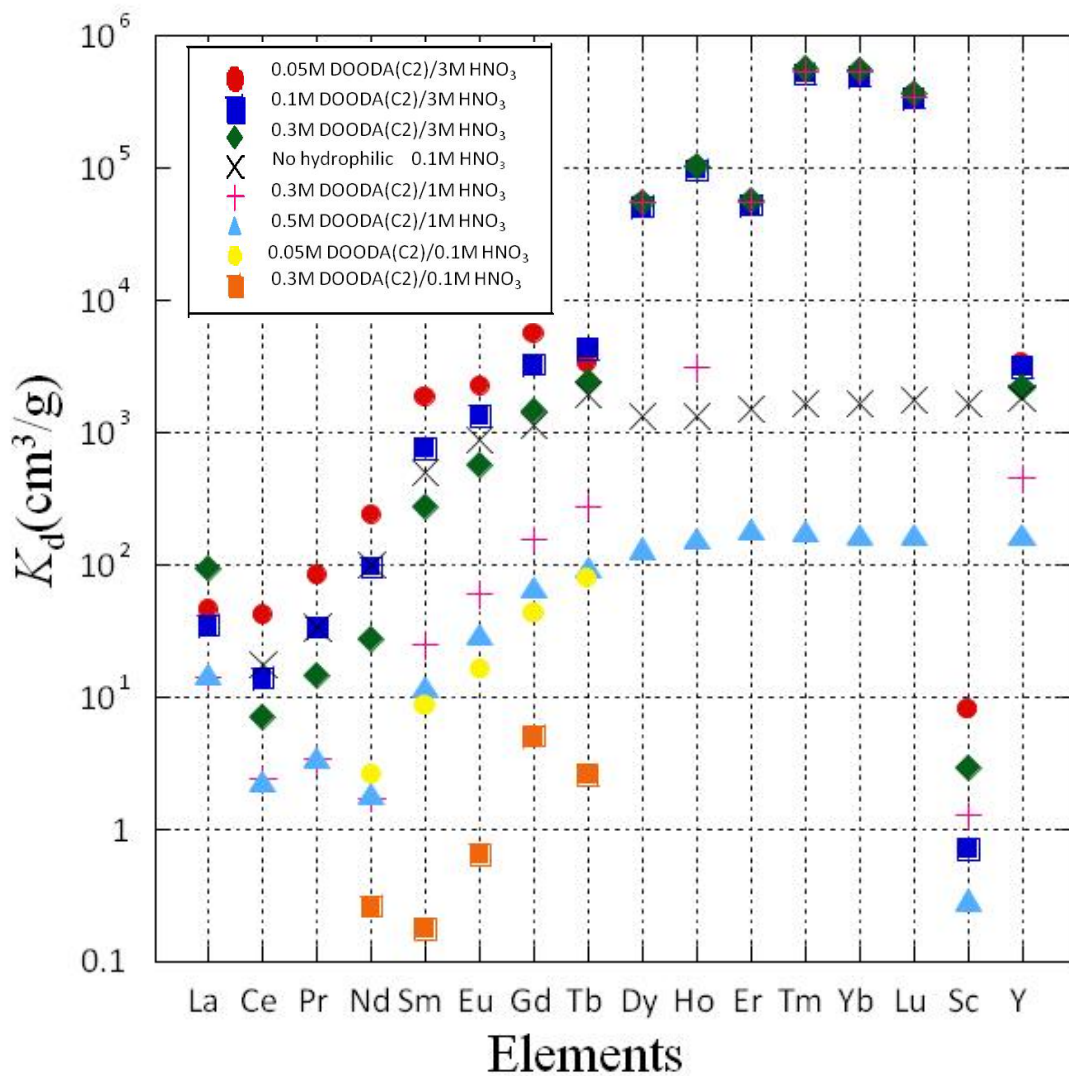


Fig. 3. K_d values of RE for TODGA/SiO₂-P in 0-0.5M DOODA(C2)/0.1-3 M HNO_3 , $[\text{RE}^{3+}] = 10$ ppm.

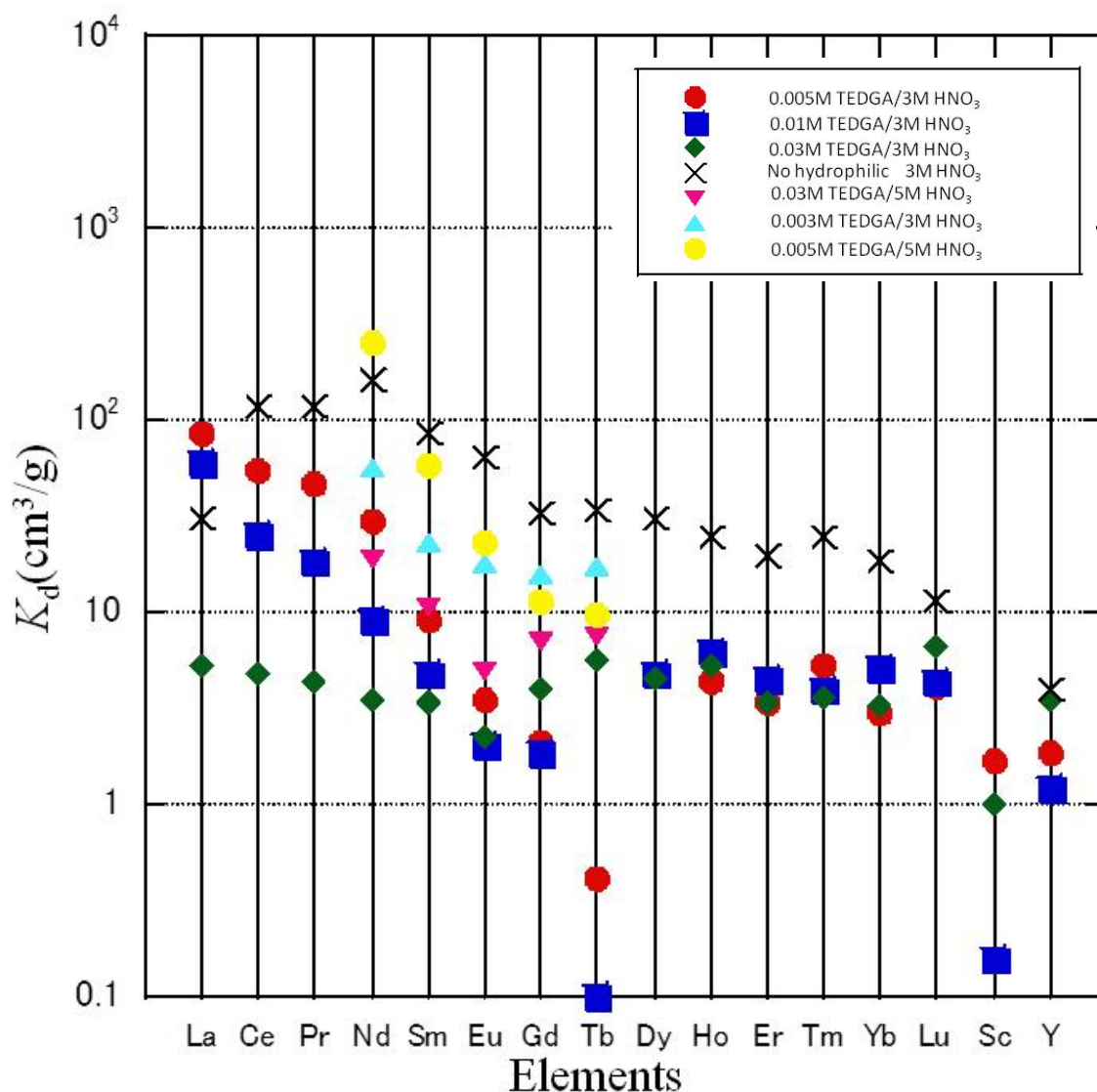


Fig. 4. K_d values of RE for DOODA(C8)/SiO₂-P in 0-0.03M TEDGA/3-5 M HNO₃, $[RE^{3+}] = 10$ ppm.

Separation behavior of column experiments

From the results of batch experiments, the condition of column experiments was decided for the separation of Nd, Sm, Eu, Gd and Tb. As for TODGA type column experiments, 0.05 M DOODA(C2)/0.1 M HNO₃ was selected as elution solution. Figure 4 shows the result of the TODGA type column experiment. C/C_0 means the ratio of the initial concentration of Ln to the Ln concentration of each fraction. While Nd, Sm, Eu and Gd were clearly separated, a part of Gd and Tb was still retained in the column. Because of the synergistic effect, the Ln elements were chromatographically eluted with an adequate amount of solution. The elution order of Ln was Nd-Sm-Eu-Gd. TABLE I shows the retention volume (V_R), recovery yield (R), K_d and relative SF to Nd in TODGA type column experiment condition. The SF between Nd and Sm was 13 and mutual separation between Am and Cm will be also possible.

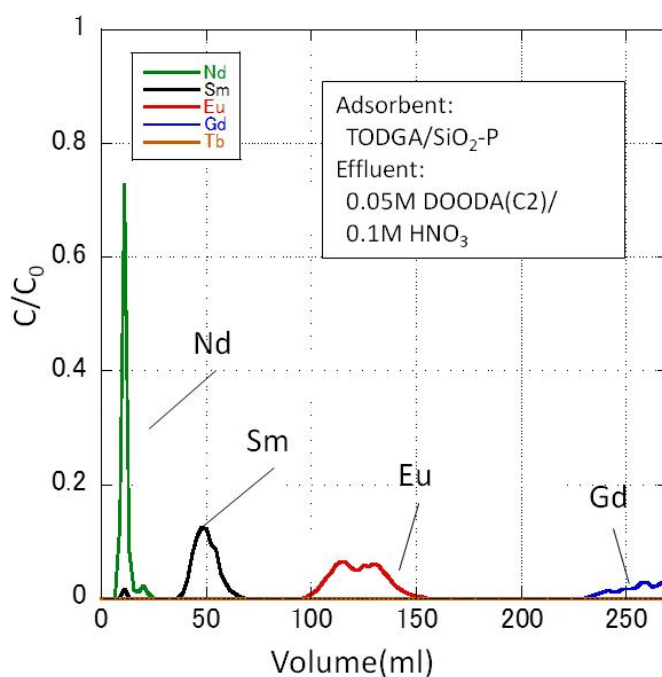


Fig. 5. The result of TODGA type column experiment (flow rate: 0.19 ml/min, feed solution: $[\text{Ln}^{3+}] = 50$ ppm/3 M HNO_3 , washing solution: 3 M HNO_3 , and elution solution: 0.05 M DOODA(C2)/0.1 M HNO_3).

TABLE I. V_R , R , K_d and SF in the TODGA type column experiment (see Fig. 4)

	Nd	Sm	Eu	Gd	Tb
V_R (ml)	11	48	114	260	-
R (%)	99	77	88	26	-
K_d (cm^3/g)	0.8	11	28	67	-
SF (Ln/Nd)	1	13	35	84	-

As for DOODA column experiments, 0.005-0.03 M TEDGA/3-5 M HNO_3 was selected as elution solution. Figures 5-7 show the results of the DOODA type column experiments. The V_R , R , K_d and SF in the column experiments are shown in TABLE II-IV. The order of Ln elution was from middle to light Ln: Tb-Gd-Eu-Sm-Nd. In Fig. 5, where 0.005 M TEDGA/3 M HNO_3 was used as elution solution, effective separation between Nd and Sm was observed. The SF of Sm/Nd was 3.3 (see TABLE II) and mutual separation between Am and Cm will be probably done. Although all elements were quantitatively recovered ($R \geq 94\%$), the mutual separation among Sm, Eu, Gd and Tb was not effective.

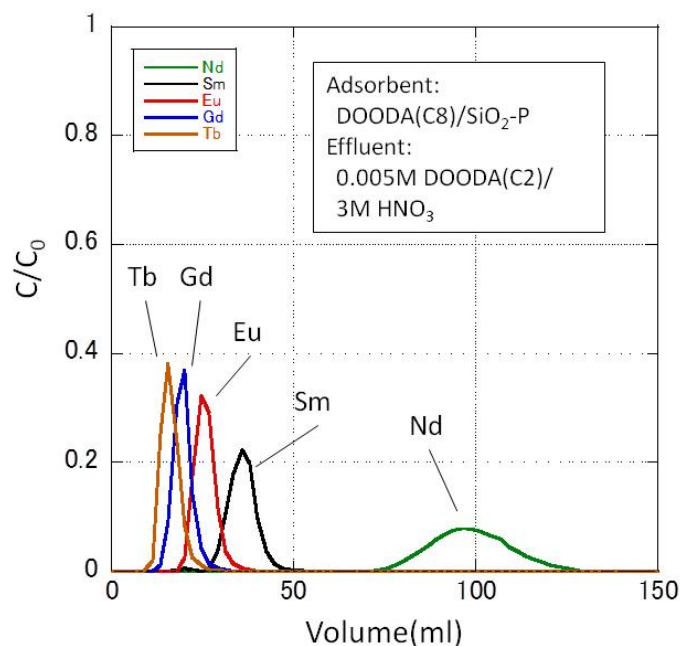


Fig. 6. The result of DOODA type column experiment-I (flow rate: 0.20 ml/min, feed solution: $[Ln^{3+}] = 50$ ppm/3 M HNO_3 , washing solution: 3 M HNO_3 and elution solution: 0.005 M TEDGA/3 M HNO_3).

TABLE II. V_R , R , K_d and SF in the DOODA type column experiment-I (see Fig. 5)

	Nd	Sm	Eu	Gd	Tb
V_R (ml)	98	36	25	20	16
R (%)	95	94	99	99	99
K_d (cm ³ /g)	24	7.3	4.3	3.1	1.9
SF (Nd/Ln)	1	3.3	5.6	7.7	13

In Fig. 6, where concentration of the hydrophilic extractant was a little low (0.003 M TEDGA/3 M HNO_3) compared with Fig. 5 (0.005 M TEDGA/3 M HNO_3), the values of V_R and K_d became approximately twice. Effective separation between Nd and Sm was also achieved and the SF of Nd/Sm was 3.1 (see TABLE III). Therefore mutual separation between Am and Cm will be successfully performed. However, the R of Nd and Sm was not necessarily good only in this column experiment and the mutual separation among Sm, Eu, Gd and Tb also was not effective.

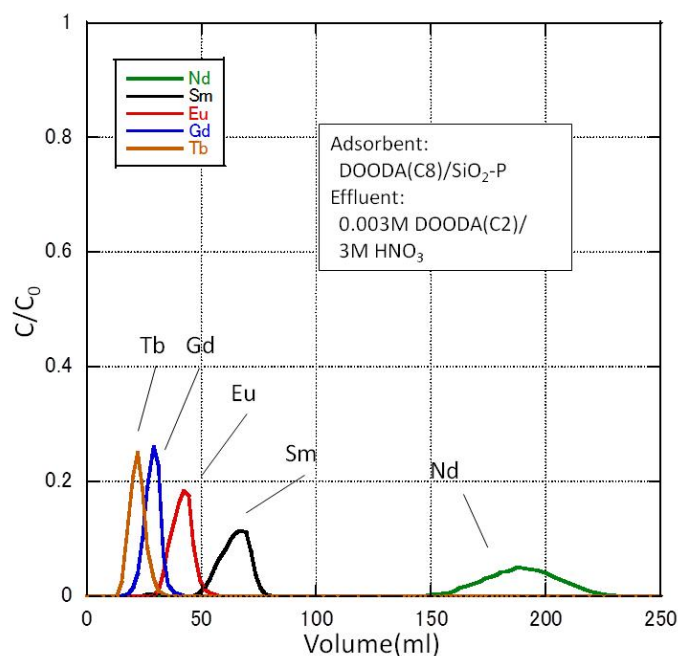


Fig. 7. The result of DOODA type column experiment-II (flow rate: 0.18 ml/min, feed solution: $[Ln^{3+}] = 50$ ppm/3 M HNO_3 , washing solution: 3 M HNO_3 and elution solution: 0.003 M TEDGA/3 M HNO_3).

TABLE III. V_R , R , K_d and SF in the DOODA type column experiment-II (see Fig. 6)

	Nd	Sm	Eu	Gd	Tb
V_R (ml)	187	67	42	29	22
R (%)	60	81	93	94	92
K_d (cm^3/g)	48	16	9.0	5.5	3.7
SF (Nd/Ln)	1	3.1	5.3	8.7	13

In Fig. 7, where concentrations of hydrophilic extractant and HNO_3 was higher (0.03 M TEDGA/5 M HNO_3) compared with Figs. 5 and 6, the values of V_R and K_d became too small. While the mutual separation among Sm, Eu, Gd and Tb seemed to be ineffective, the SF of Nd/Sm (4.1) was obtained rather high value (see TABLE IV).

From the results of these column experiments, the conditions in Figs. 5 and 6 (adsorbent: DOODA(C8)/SiO₂-P, elution solution: 0.003-0.005 M TEDGA/3 M HNO_3) are considered to be the optimum for not only separation between non-radioactive Nd and Sm but also likely separation between Am and Cm that actual waste species.

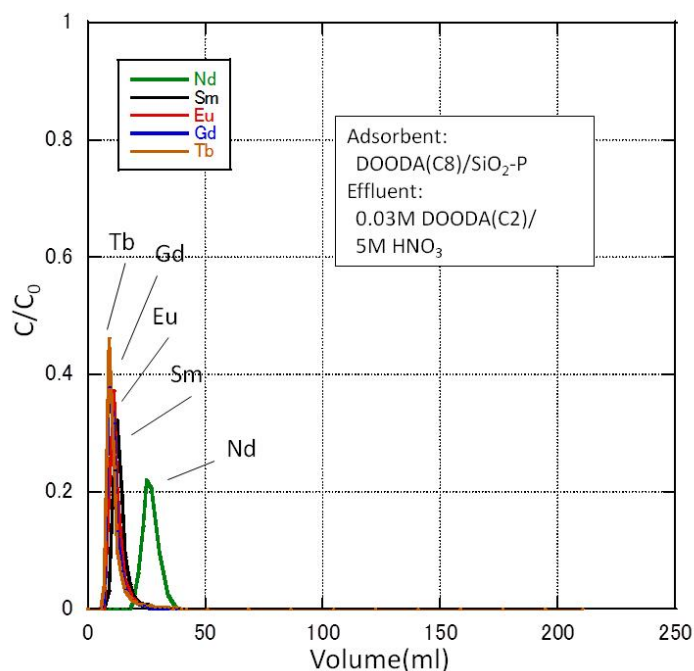


Fig. 8. The result of DOODA type column experiment-III (flow rate: 0.22 ml/min, feed solution: $[Ln^{3+}] = 50 \text{ ppm}/3 \text{ M HNO}_3$, washing solution: 3 M HNO_3 and elution solution: $0.03 \text{ M TEDGA}/5 \text{ M HNO}_3$).

TABLE IV. V_R , R , K_d and SF in the DOODA type column experiment-III

	Nd	Sm	Eu	Gd	Tb
V_R (ml)	25	13	11	9	9
R (%)	99	98	98	99	100
K_d (cm^3/g)	4.5	1.1	0.6	0.2	0.2
SF (Nd/Ln)	1	4.1	7.5	23	23

CONCLUSION

The results of batch experiments showed the synergistic effect which lowered the K_d values of RE and the possibility of mutual separation. In column experiments, effective mutual separation between Nd and Sm was demonstrated. The mutual separation between Am and Cm will be achieved because behavior of Am and Cm is similar to those of Nd and Sm. In near future, the authors will adopt these condition to the column experiment of trivalent MA (Am and Cm) for their mutual separation.

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