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Basic research on batchwise multi-stage extractions using TODGA for Dy/Nd separation

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Abstract

The mutual separation of lanthanides is studied by multi-stage extraction using extractant, DGA (diglycolamide) compounds. \(N,N,N',N'\)-tetraoctyl-DGA (TODGA) has a high extractability to lanthanides and relatively high separation factor (SF) between Dy and Nd (SF: over 20) from HNO\(_3\) media. The complete separation with such SF value can be achieved by multi-stage extraction. Less information on multi-stage extraction compared to batch extraction is presented up to now, thus we conduct the basic study. Confirming the experimental data to be identical to the calculation, the sample solution including both metals is employed for the batchwise multi-stage extraction. Ninety-seven % of Dy with under detection limit of Nd can be recovered into the organic phase from Nd with ten times higher concentration than Dy using the condition, 0.1 M TODGA/\(n\)-dodecane and 0.3 M HNO\(_3\) by multi extraction of 9 x 9 stages for organic and aqueous phases.

Keywords: extraction, DGA, multi-stage extraction, Nd, Dy
Introduction

The separation of lanthanides is important task not only for the atomic energy field but also the high-tech industry. Lanthanide metals are used for high-temperature superconductors, battery, optical devises, and so on. Although there are many general purposes of lanthanides in industry, mutual separation from each other is well-known to be difficult to perform. All lanthanides are situated in the same position in the periodic table, have the same oxidation state and similar ionic radii, so similar chemical behavior can be seen across the series. Thus, mutual separation of lanthanides is one of the important tasks. An example to separate lanthanides for industrial purpose is to recovery Dy from Nd magnet (NdFeB). To maintain the coercivity of Nd-magnets, Dy is introduced into their components. The hydrometallurgical methods to recover valuable Dy from scrapped products have been studied considerably.\textsuperscript{1-4}

Solvent extraction is one of the representative methods for the use in industry. The new extractants concerning lanthanides are developed in the atomic energy field, because of their high concentration in high level radioactive nitric acid waste. One of the useful reagents is diglycolamide (DGA) compounds, the advantages of DGA are (1) strong extractability for lanthanides, (2) relatively high separation factors between lanthanides, and (3) possible gasification after use, thus to reduce the secondary waste. The separation factors (SF) between light and heavy Ln when using DGA are fairly high, exceeding 100 for Lu/La.\textsuperscript{5-9} As is well-known SF values of over 10 should be satisfied for mutual separation, if multi-stage extraction is conducted. Furthermore, multi-stage extraction is generally employed to treat huge volumes of aqueous solutions by mixer-settler equipment, where automatic handling is utilized, thus allowing for mutual separation between aimed two targets.\textsuperscript{10-12} The basic research on the
multi-stage extraction with a few stages has been scarce up to now. In addition, multi-stage extraction work is limited to the research groups having mixer-settler. We have less information on how many SF and extraction stage numbers are necessary to obtain the satisfied results.

The batchwise multi-stage extraction is classically termed as the Craig extraction method.\textsuperscript{13-14} Due to its complicated experimental setup, this method was replaced by chromatography.\textsuperscript{15-17} Mutual separation among Ln elements is commonly performed by using the liquid-solid separation method in conjunction with chromatography.\textsuperscript{18-20} However, the batchwise multi-stage extraction offers some advantages, (1) small volume in each phase is acceptable, (2) not necessary to use mixer-settler and (3) possibly to combine the different stage numbers between organic and aqueous phases.

In the present work, the batchwise multi-stage extraction using DGA compounds is employed for the mutual separation of Ln. Although this extractant has been used for the recovery of Ln from Nd magnet\textsuperscript{21-23}, less information on development as a mutual separation method is present up to now. The optimal numbers of the aqueous and the organic stages can be calculated using their distribution ratios ($D$). Investigating the shaking condition on the experimental data fitting to the calculations, the best conditions for multi-stage extraction to obtain 98\% recovery of Dy with less than 2\% Nd are studied.

**Experimental**

**Reagents**

TODGA ($N,N,N',N'$-tetraoctyl-diglycolamide) is obtained from Wako Pure Chemical Industries. The extractant with $> 98\%$ purity was used for solvent
extraction without further purification. Standard solutions with 1000 mg/L (= ppm) concentration (Wako Pure Chemical Industries) or sample solutions obtained from the dissolution of Nd$_2$O$_3$ and Dy$_2$O$_3$ in nitric acid were used for solvent extraction. Other reagents, for example, $n$-dodecane, nitric acid, Nd$_2$O$_3$, and Dy$_2$O$_3$ were of analytical grade. Their concentration ranges in the experiments are 10 ppm to maximum 14424 (10 mol/dm$^3$ (= M)) ppm.

**Batch extraction method**

The organic and the aqueous phases are pre-equilibrated. The organic phase of TODGA/$n$-dodecane and the aqueous phase of the HNO$_3$ sample solution with and without Nd or Dy were mixed and mechanically shaken at 1500-2000 strokes/min (spm) for 5-20 min at 25 ± 0.1 °C. After centrifugation, the metal concentrations in aliquots taken from the aqueous phases were measured by ICP-OES (SPS3100, Seiko Instruments Inc.) or ICP-MS (SPQ 9000, Seiko-EG&G). The metal concentration in the organic phases was obtained by subtracting the aqueous concentration from the initial concentration. Alternatively, an organic phase was decomposed in HNO$_3$-HClO$_4$, and the residue was dissolved in 0.5 M HNO$_3$ before elemental analysis. The $D$ value was defined as the ratio of [M] in the organic phase to the [M] in the aqueous phase.

**Simulation of metal concentration in each extraction stage through multi-stage extraction**

The excel-based calculations were conducted. Using $D$ values for each metal, the metal concentrations transferred to the organic and the aqueous phases at each extraction stage are calculated using ratios, $D/(1+D)$ and $1/(1+D)$, respectively. This
calculation repeats until times of extraction stages in order to obtain the metal concentration in each organic or aqueous phase. Fitting calculations to experimental data for the metal concentrations in aqueous and organic phases after all extractions is performed by least-square method, which minimizes the residual sum of squares. The entire $D$ value through all extractions can be also calculated using least-square method.

**Batchwise multi-stage solvent extraction**

The schematic diagram of batchwise multi-stage extraction of 3 x 3 for the numbers of organic and aqueous phases is illustrated (Figure 1). Figure 1(a) illustrates the flow of extractions and (b) show that of aqueous and organic phases. An aqueous phase (1’) containing Nd and Dy were mixed with an organic phase (1) and shaken (first stage). After the first extraction stage, the organic phase (1) was removed and introduced into the second aqueous phase (2’) and shaken (2nd stage). The aqueous phase (1’) after the first extraction stage was introduced into the second organic phase (2) and shaken (2nd stage). After 2nd extraction stage, the pairs of organic and aqueous phases at 3rd extraction stage are 1-3’, 2-2’ and 3-1’, 4th ones are 2-3’, 3-2’, and 5th one is 3-3’. The total extraction times for 3 x 3 extraction stages are nine. The Nd and Dy concentrations in all aqueous and organic phases after all extractions were measured by ICP-OES or ICP-MS. In addition, the $D$ values of individual extractions at 1st to 5th stages can be measured, aliquots of aqueous and organic phases are taken and thus obtain $D$ values.

**Results and Discussion**
**Lanthanides extraction by TODGA**

Extraction experiments were performed at 1500 rpm for 20 min shaking using an organic phase of 0.05 and 0.1 M TODGA/\(n\)-dodecane with different HNO\(_3\) concentrations. The results, 0.05 M TODGA and 0.1 M TODGA are shown in Figure 2(a) and (b), respectively. Ln-patterns in Figure 2, which shows a plot of \(D(Ln)\) against the atomic number of Ln, indicate a gradual increase in \(D\) with not only HNO\(_3\) concentration but also the atomic number of Ln. In terms of the condition for Dy/Nd separation, the \(D\) values should be higher or lower than 1 for Dy and Nd. Thus, suitable conditions to separate Dy from Nd, from Figure 2, are 0.05 M TODGA-0.5 M HNO\(_3\) and 0.1 M TODGA-0.3 M HNO\(_3\). The raw data for these conditions are 0.0886 and 2.6 for \(D\)(Nd) and \(D\)(Dy), respectively, at 0.05 M TODGA, and 0.155 and 4.36 for \(D\)(Nd) and \(D\)(Dy), respectively, at 0.1 M TODGA. Both separation factors (SF) of \(D\)(Dy)/\(D\)(Nd) are 28 and 29, so these are enough to separate each other. We choose the condition, 0.1 M TODGA-0.3 M HNO\(_3\) because the set of \(D\) values, 0.155 and 4.36, seems more preferable than 0.0886 and 2.6.

**Basic research of batchwise multi-stage extraction**

The fundamental experiments of batchwise multi-stage extraction are conducted. To obtain the results easily, we choose 3 x 3 of stage numbers of aqueous and organic phases likely shown in Figure 1. We get nine \(D\) values through 1\(^{st}\) to 5\(^{th}\) extraction stages to see the deviation by the small change of extraction condition, although these \(D\) values should be the constant to 0.155 (Nd) and 4.36 (Dy).

We should consider the flow of metal concentrations. Former research has already shown what to expect it\(^{17, 24-26}\) although the previous studies are mainly concerning the chromatography. The metal-flow of the organic and aqueous phases
is described in Figure 1(b). Metal ions are initially present in aq. 1’ (Figure 1(a)). After the 1st stage, the initial metal concentration ([M]) is distributed to org. 1 and aq. 1’ with the proportion of $D$ value. At the 2nd stage, the fresh org. 2 and aq. 2’ phases with no metals are introduced. Metals in org. 1 are distributed to org. 1 and aq. 2’ and that in aq. 1’ is to org. 2 and aq. 1’ after 2nd extraction stage. At the 3rd stage, extraction is done by three types and metal ions are distributed to 6 phases (org. 1-3, aq. 1’-3’). In this stage, fresh phases are used for org. 3 and aq.3’. From upper position of the 3rd extraction stage in Figure 1(b), metals in org. 1 are distributed to org. 1 and aq. 3’, metals in both org. 2 and aq. 2’ are mixed and re-distributed, and [M] in aq. 1’ is distributed to org. 3 and aq. 1’. After the 3rd stage, org. 1 and aq. 1’ are recovered and sampled. At the 4th stage, two type extractions can be seen with no fresh phase. Metals in org 2 and aq. 3’ or that in org. 3 and aq. 2’ are distributed again, and org. 2 and aq. 2’ after extraction are recovered and sampled. At the last stage, metals in org. 3 and aq. 3’ are mixed, distributed to both phases, and sampled. In total, 5 stages and 9 times extractions can be seen in 3 x 3 for extraction stages. Throughout this work, sampling at 9 times extractions was also performed in order to obtain all [M] and $D$ values.

The $D$ values obtained at the nine extractions are compared to each other and [M] in organic and aqueous phases are used to validate the flow of metal in these extraction stages. The results are shown in Table 1 (Nd) and 2 (Dy). Here, the shaking condition, 2000 s pm and 10 min, are employed. The initial Nd and Dy concentrations are 7.634 and 8.163 ppm. In these tables, extraction stages (from 1-1’ to 3-3’ for (org)-(aq)), metal concentrations in these phases, and $D$ values are shown. At the 1st stage, initial Nd concentration (7.634 ppm) is distributed to org. 1 (1.026 ppm) and aq.1’ (6.826 ppm). At the 2nd stage, [Nd] in org. 1 (1.026 ppm) after the 1st stage
is sum of org. 1 (0.104 ppm) and aq. 2’ (0.778 ppm), and that in aq. 1’ (6.826 ppm) is the sum of org. 2 (0.914 ppm) and aq. 1’ (5.8 ppm). At the 3rd stage, [Nd] in org. 1 (0.104 ppm) after the 2nd stage is sum of org. 1 (0 ppm) and aq. 3’ (0.062 ppm), that (0.914 + 0.778 ppm) in org. 2 and aq. 2’ is the sum of org. 2 (0.176 ppm) and aq. 2’ (1.424 ppm), and that (5.8 ppm) in aq. 1’ is the sum of org. 3 (0.746 ppm) and aq. 1’ (4.811 ppm). At the 4th stage, [Nd] (0.176+0.062 ppm) in org. 2 and aq. 3’ after the 3rd stage is the sum of in org. 2 (0 ppm) and aq. 3’ (0.222 ppm), and that (0.746 + 1.424 ppm) in org. 3 and aq. 2’ is the sum of org. 3 (0.247 ppm) and aq. 2’ (1.923 ppm). At the 5th stage, [Nd] (0.247 + 0.222 ppm) in org. 3 and aq. 3’ after the 4th stage is the sum of org. 3 (0.023 ppm) and aq. 3’ (0.448 ppm). These data are consistent approximately, thus flow of metals through experiments is confirmed successfully.

In Table 2, the results for Dy are shown, this table can be seen likely to Table 1, and the metal flow is reasonable from their metal concentration, and the $D$ values are constant at all extractions.

In order to see the suitable condition for batchwise multi-stage extraction, we should change the condition of shaking. Namely, different shaking speed and time are set up and all $D$ values are measured. The results for these extractions are summarized in Table 3(Nd) and 4(Dy). In these tables, conditions 1, 2, 3 and 4 are 1500 spm and 5 min, 2000 spm and 5 min, 1500 spm and 10 min, and 2000 spm and 10 min, respectively. These tables show the average $D$ values and 1 $\sigma$ (standard deviation). Here, data is omitted when [M] in these phases is too low and deviated considerably from other results. From Table 3 and 4, condition 1 shows high deviations, and condition 2-4 show similar deviations. Compared to all raw data, condition 4 show more constant values, thus we determine to use condition 4 for further experiments.
Batchwise multi-stage extraction at the same numbers of organic and aqueous phases

Our goal in this work will be obtaining to the extraction of 98% for Dy with lower than 2% coextraction of Nd. Using the $D$(Nd, Dy) values (0.129 for Nd, 5.01 for Dy in average) at condition 4, the optimum condition of No. of aqueous and organic phases is calculated. The results are listed in Table 5, which shows the extraction (%) at 5 x 5 cross-current extraction stages. Here, the aqueous phases are of two types, one is sample solution including metals (aq+M) and another one is solution for scrubbing (aq/scrub). As shown in Table 5, stage No. of (aq+M) increases, the recoveries of both Nd and Dy increase. Our goal described above can be established by 5-1-4, 5-2-3, and 5-3-2 for numbers of (org)-(aq+M)-(aq/scrub). Thus, we choose the extraction stage No. to be 5-2-3.

The batchwise multi-stage extraction is conducted following the results in Table 5. The experimental and calculation results are shown in Figure 3. Figure 3 show the relationship between extraction stage No. and metal concentration ([M]) in each extraction stage after all extractions, and Figure 3(a) and (b) are the results in aqueous and organic phases. Almost the same behavior of [M] between experiment and calculation at each extraction stage can be seen, which indicates constant $D$ values at all extractions and good accuracy of calculations. This result suggests that the optimum condition of No. of organic phase and aqueous phases can be calculated using our model. The recovery of Dy and Nd in all organic phases by these experiments are 98.9, 0.5 %, respectively. We can also calculate the $D$ values through all extractions using least square method, the results are Dy: 3.32 and Nd: 0.134, which is a lower value for Dy than that obtained the batch experiment (5.01).
phases

The different stage number between organic phases and aqueous ones can be set-up in this batchwise multi stage extractions. This work is done to obtain the optimum numbers of extraction stages. Using $D$ values for multi-stage extraction (Dy: 3.32 and Nd: 0.134), the calculation results of Nd and Dy recoveries after extraction stages are shown in Table 6. Here, we set the same stage No. (5-10) for (org) and (aq+M), with 2-3 stages for (aq/scrub). From Table 6, as the No. of stages in organic phases increase, both recoveries (%) of Nd and Dy increase. The maximal stage No. in Table 6, namely stage No. (org): 10, (aq+M): 10, and (aq/scrub): 3 may show the satisfied result. However, it takes 22 extraction stages, with much effort and complicated work. Thus, we choose, more easily, 6 stages of (org), 6 of (aq+M), and 2 of (aq/scrub), this condition need 13 extraction stages, showing recoveries (%) of Dy and Nd to be 97.6 and 1.3 %.

The results of batchwise multi-stage extraction are shown in Figure 4. Figure 4 shows the relationship between extraction stage No. and [M] in each extraction stage. Figure 4(a) and (b) are the results in aqueous and organic phases. The identical extraction behavior for experiment and calculation can be found in Figure 4. The recoveries of Dy and Nd in all organic phases are 97.7 % and 1.2 %, whose values are almost the same as those in Table 6 (Dy: 97.6 %, Nd: 1.3 %). The $D$ values calculated using the behavior of metals through all extractions are Dy: 2.94 and Nd: 0.13.

Batchwise multi-stage extraction using ten times higher concentration of Nd than Dy

The real sample solution may show higher Nd concentration than Dy due to the initial composition of Nd-magnet,27-29 thus we prepare the sample solution of Nd: 100
mM and Dy 10 mM in 0.3 M HNO₃, where ten times higher concentration of Nd than Dy. Using this condition, our goal is also Dy 98 % recovery with lower than 2 % Nd coextracted. Here, Nd coextracted (%) should be maximal 0.2 % which is based on the standard of Dy concentration. We perform calculation to find the optimal condition for this separation using the $D$ values for Dy: 3.32 and Nd: 0.134, and the results are shown in Table 7. In Table 7, we restrict No. of (aq+M) to be 1 or 2 in order to suppress Nd content in this extraction system, and fix the same stage No. of organic phase as total stages of (aq+M) and (aq/scrub) considering to use the mixer-settler. Table 7 suggest that numbers of extraction stages for (org) increase with the recovery of Dy and decrease of Nd coextracted (%). In addition, when the stage No. of (aq+M) increase, the amount of Nd coextracted increase, when taking at 10 stages of (org). Based on the reference values to be Dy 98 % and Nd 0.2 %, the conditions, 6-1-5 and 10-6-4 for the stages of (org), (aq+M) and (aq/scrub) are omitted, and other conditions show the satisfied values in Table 7. Thus, we choose the condition, 9-1-8 stages in order to run the experiment more easily.

Using the concentration, 0.1 M TODGA/$n$-dodecane, 100 mM Nd and 10 mM Dy in 0.3 M HNO₃ taken for batchwise multi-stage extraction was carried out. The result is shown in Figure 5. Figure 5 shows the relationship between extraction stage No. and [M] in each extraction stage. Figure 5(a) and (b) are the results in aqueous and organic phases. Although behavior of Nd is similar to the expected line, the experimental data of Dy is deviated from calculation, especially early set of four extraction stages in Figure 5(b). Throughout the experiments, the third phase is observed slightly at extraction stage of org. 1-aq. 1‘, although the third phase is disappeared at the 2nd extraction stage. This is one of the reasons to show the different behavior from the calculation. The recovery of Dy in organic phase is 96.9 % and no Nd can be found.
there, so it was successful in separating Dy from ten times higher concentration of Nd. The $D$ values concerning multi-stage extraction are calculated to be Dy: 2.26 and Nd: 0.161, which shows relatively low $D$ values, due to the high concentration of these metals.

We also calculate recoveries at other types of extraction stages, especially many stage numbers of (aq+M). As we already mentioned that large stage numbers of organic and aqueous phases give high recoveries of both metals. In order to reduce amount of Nd co-extracted, stage No. of (aq/scrub) should be increased. Considering to use in mixer-settler, the numbers of organic phases should be the same as that of aqueous phases. If the stage No. of (aq+M) is large, that of (aq/scrub) become small. Effective conditions are difficult to set-up when total extraction stages are small. Large numbers of extraction stages lead flexible conditions to set-up the aqueous and organic phase numbers. The calculation results are summarized in Table 8. In these $D$ values, the minimum stage numbers of (org) and (aq/scrub) are six and five. The extraction sets of (org), (aq+M) and (aq/scrub) to be 6, 1, 5 to 11, 6, 5 give the satisfied results to achieve our goal. In the case (org), (aq+M) and (aq/scrub) is 12-7-5 exceeds 0.2 % of Nd co-extracted, so that set should be modified to 12-6-6.

**Conclusions**

We examine the separation of Dy from Nd using TODGA extractant by batchwise multi-stage extractions. TODGA has relatively high SF(Dy/Nd) to be over 20, thus this extractant can be used to separate the two metal ions from each other. Due to the lack of the fundamental research of multi-stage extraction, we perform the multi-stage extraction using 3 x 3 of cross-current extraction stages at different shaking condition. Ten min shaking and 2000 rpm is important to obtain the constant $D$ values, thus to get
the identical values between experiment and calculation results. Through this experiment, we can set up the optimal condition for numbers of organic and aqueous phases by calculation. From the present work, the extraction stages, 5-2-3 and 6-6-2 of (org)-(aq+M)-(aq/scrub) can be obtained to 98% of Dy with less than 2% of Nd. In order to assume the real solution, concentration of Nd with 10 times higher than that of Dy was also studied. It was successfully obtained that extraction stages, 9-1-8 for (org)-(aq+M)-(aq/scrub) give 96.9% recovery of Dy with negligible small amount of Nd.

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Table 1 Results of all $D$(Nd) values at batchwise multi-stage (3x3) extraction

| Extraction stage No. | org. | aq. | org. | aq. | org. | aq. |
|----------------------|------|-----|------|-----|------|-----|
| Nd concentration (ppm) | 1.026 | 6.826 | 0.104 | 0.778 | 0 | 0.062 |
| $D$ values | 0.15 | 0.134 | 0 |
| Extraction stage No. | 1’ | 1 | 2’ | 2 | 3’ |
| Nd concentration (ppm) | 0.914 | 5.8 | 0.176 | 1.424 | 0 | 0.222 |
| $D$ values | 0.158 | 0.124 | 0 |
| Extraction stage No. | 2 | 1’ | 2 | 2’ | 2 | 3’ |
| Nd concentration (ppm) | 0.746 | 4.811 | 0.247 | 1.923 | 0.023 | 0.448 |
| $D$ values | 0.155 | 0.128 | 0.0513 |

Table 2 Results of $D$(Dy) values at batchwise multi-stage (3x3) extraction

| Extraction stage No. | org. | aq. | org. | aq. | org. | aq. |
|----------------------|------|-----|------|-----|------|-----|
| Dy concentration (ppm) | 6.515 | 1.585 | 5.373 | 1.026 | 4.341 | 0.828 |
| $D$ values | 4.11 | 5.24 | 5.24 |
| Extraction stage No. | 1’ | 1 | 2’ | 2 | 3’ |
| Dy concentration (ppm) | 1.475 | 0.285 | 2.212 | 0.429 | 2.517 | 0.607 |
| $D$ values | 5.18 | 5.16 | 4.15 |
| Extraction stage No. | 2 | 1’ | 2 | 2’ | 2 | 3’ |
| Dy concentration (ppm) | 0.246 | 0.021 | 0.669 | 0.11 | 1.234 | 0.25 |
| $D$ values | 11.7 | 6.08 | 4.94 |
| Extraction stage | org.1-aq.1’ | org.1-aq.2’ | org.1-aq.3’ |
|------------------|-------------|-------------|-------------|
| Condition 1      | 0.0698      | 1.27        | 0.131       |
| Condition 2      | 0.151       | 0.334       | 0.206       |
| Condition 3      | 0.108       | 0.0769      | 0           |
| Condition 4      | 0.15        | 0.134       | 0           |

| Extraction stage | org.2-aq.1’ | org.2-aq.2’ | org.2-aq.3’ |
|------------------|-------------|-------------|-------------|
| Condition 1      | 0.0877      | 0.322       | 0.0796      |
| Condition 2      | 0.149       | 0.17        | 0.159       |
| Condition 3      | 0.127       | 0.132       | 0           |
| Condition 4      | 0.158       | 0.124       | 0           |

| Extraction stage | org.3-aq.1’ | org.3-aq.2’ | org.3-aq.3’ |
|------------------|-------------|-------------|-------------|
| Condition 1      | 0.145       | 0.233       | 0.096       |
| Condition 2      | 0.167       | 0.157       | 0.123       |
| Condition 3      | 0.163       | 0.191       | 0.0618      |
| Condition 4      | 0.155       | 0.128       | 0.0513      |

Average and deviation (1σ) for condition 1: 0.270 ± 0.384

Average and deviation (1σ) for condition 2: 0.18 ± 0.062

Average and deviation (1σ) for condition 3: 0.123 ± 0.045

Average and deviation (1σ) for condition 4: 0.129 ± 0.037
| Extraction stage | org.1-aq.1’ | org.1-aq.2’ | org.1-aq.3   |
|------------------|-------------|-------------|--------------|
| Condition 1      | 1.36        | 9.47        | 5.87         |
| Condition 2      | 3.73        | 8.17        | 5.26         |
| Condition 3      | 2.52        | 4.84        | 7.08         |
| Condition 4      | 4.11        | 5.24        | 5.24         |

| Extraction stage | org.2-aq.1’ | org.2-aq.2’ | org.2-aq     |
|------------------|-------------|-------------|--------------|
| Condition 1      | 1.93        | 5.31        | 5.2          |
| Condition 2      | 3.76        | 5.32        | 5.13         |
| Condition 3      | 3.43        | 5.85        | 4.15         |
| Condition 4      | 5.18        | 5.16        | 4.15         |

| Extraction stage | org.3-aq.1’ | org.3-aq.2’ | org.3-aq.3’ |
|------------------|-------------|-------------|-------------|
| Condition 1      | 4.52        | 5.36        | 4.77        |
| Condition 2      | 6.10        | 5.4         | 5.56        |
| Condition 3      | 4.18        | 7.45        | 5.85        |
| Condition 4      | 11.7        | 6.08        | 4.94        |

Average and deviation (1σ) for condition 1: 4.87 ± 2.34
Average and deviation (1σ) for condition 2: 5.38 ± 1.31
Average and deviation (1σ) for condition 3: 5.04 ± 1.65
Average and deviation (1σ) for condition 4: 5.01 ± 0.64
Table 5 Extraction (%) for Nd and Dy at 5 x 5 for organic and aqueous stages

| Conditions on extraction stage | Nd       | Dy       |
|-------------------------------|----------|----------|
| org.  | aq+M | aq/scrub | co-extracted (%) | extracted (%) |
| 5     | 1     | 4        | 0.2              | 99.1          |
| 5     | 2     | 3        | 0.5              | 99.3          |
| 5     | 3     | 2        | 1.5              | 99.5          |
| 5     | 4     | 1        | 4.7              | 99.6          |
| 5     | 5     | 0        | 12.9             | 99.7          |

Table 6 Extraction (%) for Nd and Dy at different No. of organic and aqueous stages

| Conditions on extraction stage | Nd     | Dy     |
|-------------------------------|--------|--------|
| org.  | aq+M | aq/scrub | co-extracted (%) | extracted (%) |
| 5     | 5     | 2        | 1                | 95.8          |
| 5     | 5     | 3        | 0.2              | 93.5          |
| 6     | 6     | 2        | 1.3              | 97.6          |
| 6     | 6     | 3        | 0.3              | 96.3          |
| 7     | 7     | 2        | 1.6              | 98.6          |
| 7     | 7     | 3        | 0.4              | 97.8          |
| 8     | 8     | 2        | 1.8              | 99.2          |
| 8     | 8     | 3        | 0.5              | 98.7          |
| 9     | 9     | 2        | 2.1              | 99.5          |
| 9     | 9     | 3        | 0.7              | 99.2          |
| 10    | 10    | 2        | 2.4              | 99.7          |
| 10    | 10    | 3        | 0.8              | 99.5          |
Table 7 Extraction (%) in case of low recovery of Nd into organic phase with many stages of organic phases

| Conditions on extraction stage | Nd co-extracted (%) | Dy extracted (%) |
|-------------------------------|--------------------|-----------------|
| org. 1 aq+M aq/scrub          | 0.1                | 97.6            |
| 6 1 5                          | 0.2                | 98.1            |
| 7 1 6                          | 0.03               | 98.6            |
| 7 2 5                          | 0.08               | 98.7            |
| 8 1 7                          | 0.01               | 98.9            |
| 8 2 6                          | 0.03               | 99.2            |
| 9 1 8                          | 0.0045             | 99.3            |
| 9 2 7                          | 0.01               | 99.4            |
| 10 1 9                         | 0.0018             | 99.5            |
| 10 2 8                         | 0.005              | 99.6            |
| 10 3 7                         | 0.015              | 99.7            |
| 10 4 6                         | 0.046              | 99.7            |
| 10 5 5                         | 0.14               | 99.8            |
| 10 6 4                         | 0.42               | 99.8            |
Table 8 Extraction (%) in case of low recovery of Nd into organic phase with many stages of (org)

| Conditions on extraction stage | Nd   | Dy    |
|-------------------------------|------|-------|
| org.                         | aq+M | aq/scrub | co-extracted (%) | extracted (%) |
| 6                            | 1    | 5      | 0.07             | 97.6          |
| 7                            | 2    | 5      | 0.08             | 98.7          |
| 8                            | 3    | 5      | 0.1              | 99.3          |
| 9                            | 4    | 5      | 0.12             | 99.6          |
| 10                           | 5    | 5      | 0.14             | 99.78         |
| 11                           | 6    | 5      | 0.17             | 99.87         |
| 12                           | 6    | 6      | 0.07             | 99.91         |
| 12                           | 7    | 5      | 0.21             | 99.92         |
Figure Captions

Figure 1 Schematic diagram of multi-stage solvent extraction
(a) Flow of multi-stage extractions
(b) Flow of organic and aqueous phases

Figure 2 Ln patterns using condition of 0.05-0.1 M TODGA/n-dodecane and 0.2 – 2 M HNO₃
(a): 0.05 M TODGA, (b): 0.1 M TODGA

Figure 3 Behavior of Nd and Dy concentration at 5 x 5 extraction stages using 0.1 M TODGA-0.3 M HNO₃
(a): aqueous phase, (b): organic phase

Figure 4 Behavior of Nd and Dy concentration at 6 (organic) x 8 (aqueous) extraction stages using 0.1 M TODGA-0.3 M HNO₃
(a): aqueous phase, (b): organic phase

Figure 5 Behavior of Nd and Dy concentration at 9 x 9 extraction stages using 0.1 M TODGA-0.3 M HNO₃ with high concentration of Nd
(a): aqueous phase, (b): organic phase
(a) Flow of multi-stage extractions

(b) Flow of organic and aqueous phases

Fig. 1
Fig. 2

Fig. 3
Fig. 4

Fig. 5
An example of multi-stage extraction for the separation of Nd and Dy (0.1 M TODGA (6 stages)-0.3 M HNO₃ (8 stages))