

J.-G. KIM\*<sup>‡</sup>**PURIFICATION AND SEPARATION OF RARE EARTH ELEMENTS FROM CCFL WITH EXTRACTION CHROMATOGRAPHY****OCZYSZCZANIE I SEPARACJA METALI ZIEM RZADKICH Z LAMP FLUORESCENCYJNYCH Z ZIMNĄ KATODĄ (CCFL) PRZY UŻYCIU CHROMATOGRAFII EKSTRAKCJI**

In this study, Amberite XAD-7HP was used as the solvent-impregnated resin to separate each REE from the standard solution, which was mixed with the REEs (e.g., La, Eu, Tb, Y and Ba). About 100 ppm of each of the REEs was separated from DI water using extraction chromatography. REEs were separated by extraction chromatography using Amberite XAD-7HP resin, the changes in the pH values of the HCl and HClO<sub>4</sub> were between 0.2 N and 5 N, and the extraction rate of the solution was between 0.5 and 3 ml/min. The La solution with the separated REEs was leached. The solid-state REEs were annealed between 1083K. The extraction result was analyzed with ICP-AES and an X-ray diffractometer. Each REE was successfully separated with HCl and HClO<sub>4</sub> with pH values between 0.1 N and 3 N and with extraction rate between 1.0 m/min and 3.0 m/min.

*Keywords:* Extraction Chromatography, CCFL, Rare Earth Elements, Amberite, Recycling

**1. Introduction**

About 60% of rare earth elements (REEs) are consumed by the catalyst, glass, optic and metallurgic industries, and the remaining 40% are used by high-growth industries like the alloy for batteries, ceramics, magnets and other materials, which show 4-10% growth each year [1]. The estimated total global consumption of REEs in 2010 was 129,000 tons, of which the amount of REEs that were actually included in products was 38,800 tons, and about 90,000 tons was generated as scraps. Of the REEs that are included in products, about 65% are sent to landfills, 23% are used in construction materials, 9% are intended for downgraded use and about 3% are stockpiled after their use [2].

China is the world's largest REE producer and consumer. In 2008, the ratio of its REE production to its REE consumption was 1:0.54, and it gradually increased to 1:0.57 in 2009 and to 1:0.64 in 2010. Particularly, its use in magnets is fast increasing so that by 2015, the REE production to consumption ratio is expected to reach to 1:1 [3], which would cause a shortage of REEs. The U.S. is planning to resume its production of REEs in its previously closed Mountain Pass Mine, and Canada is promoting the development of its Mintviel Mine. Similarly, Australia is conducting a feasibility survey on REE mines [4]. Despite such efforts, the fast growth of REE-related industries is expected to cause a shortage of REEs. The growing interest in recent years in REEs that are included in landfill or after-use products has led to recycling efforts, on which many studies have been conducted. In some of these studies, the sol-

vent extraction method and the liquid/solid separation process [5-9] allowed the separation/refining of high-purity REEs due to their excellent selectivity and separation performance. The REE metal recycling and purification processes from after-use REE magnets based on extraction chromatography allowed high purification of REEs from various products by virtue of the compactness, and excellent selectivity of the device.

In this study, Amberite XAD-7HP was used to separate REEs that are difficult to separate or extract due to their similar physical and chemical properties, and extraction chromatography was used to separate the REEs. The concentrations of extractant HCl and HClO<sub>4</sub>, the extraction solutions, and the amount of extraction by element based on the extraction rate were examined. La oxide was recovered from the separated La-ion solution.

**2. Experimental**

CCFL(cold cathode fluorescent lamp) was recycled from the backlight unit of LCD TVs, and the phosphors in it were analyzed with surface morphology and EDAX-based component analysis using FE-SEM (JEOL, JSM-7001F), as shown in Fig. 1. and Fig. 2., to confirm that it contained REEs. Using the REEs in the phosphors substances, the standard solution that was to be used in the experiment was produced.

Using D.I. water, the standard solution was so prepared as to maintain a 100ppm concentration of each of the Ba, La, Eu, Y and Tb elements. The Amberite XAD-7HP bead

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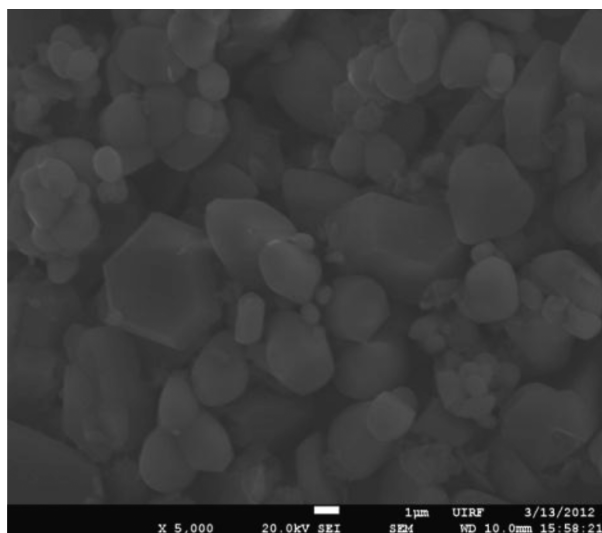


Fig. 1. The shape of phosphors in CCFL

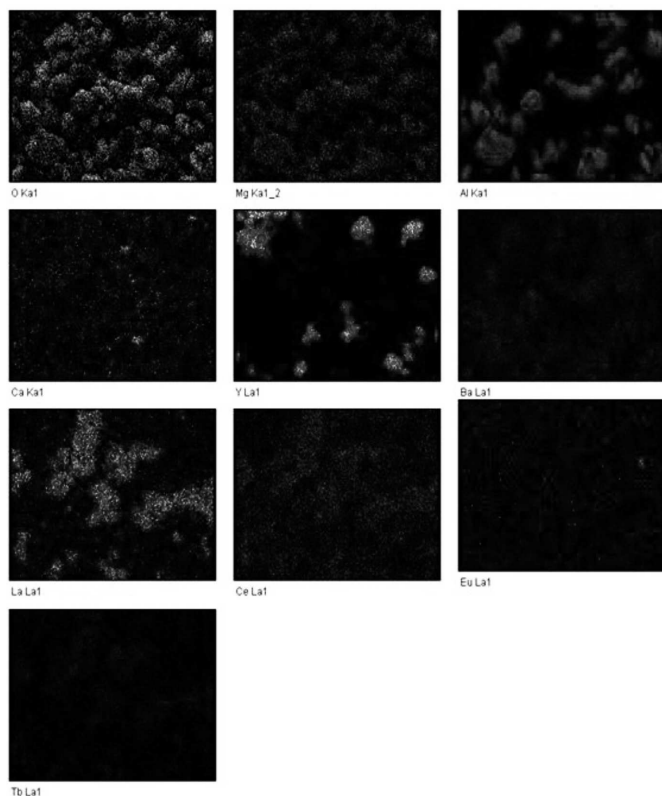


Fig. 2. EDAX analysis of phosphors in CCFL

was used as the polymer support for the solvent-impregnated resins. It was washed with 2M HNO<sub>3</sub> and acetone five times sequentially, and then dried in an oven at 60° for 1 hr. The pre-processed Amberlite XAD-7HP was packed into a column (length: 400 mm, outer diameter: 25.4 mm). The resin-filled column was installed on the Auto-extraction and Carrier system, as shown in Fig. 3., to achieve the accuracy and reproducibility needed for the experiment. Using an automatic supply pump, 10 ml of the standard solution of REEs and the extractant (HCl and HClO<sub>4</sub>) was injected into the column (up to 0.2-3.0 N) at the extraction rate of 1-5 ml/min.

The extraction chromatography was configured with two inputs (a sample stream and a carrier stream that consisted of hydrochloric acid) and two outputs (the drain and the collec-

tion). All the streams were controlled with a six-port valve. 10 mL of the standard solution was loaded into the extraction chromatography column using a peristaltic pump. The loaded standard solution was injected into a 400 mm extraction column through the carrier solution for the adsorption of the REEs on the resin and the removal of the inorganic elements. The extraction solution that passed through the column was analyzed with ICP-OES (PerkinElmer, Optima 7300DV) to determine the amount of REEs in the solution. Among the extracted rare earth ion solutions, the La solution was used to produce La<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> by adding oxalic acid to it while keeping its pH at 1.0. The produced La<sub>2</sub>O<sub>3</sub> was calcinated in a sintering furnace in air and O<sub>2</sub> at 1083K, which was confirmed with an XRD.

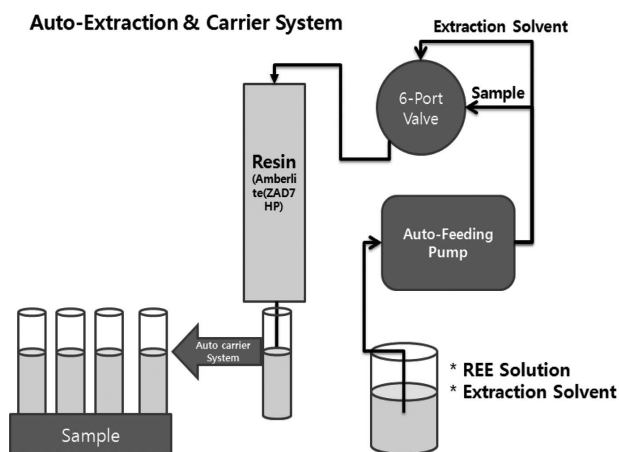


Fig. 3. Auto-extraction and carrier system

### 3. Results and Discussion

Shown in Fig. 2. are the REEs in the CCFL, which was recovered from the LCD (liquid crystal display) backlight unit. The phosphors were polygon-shaped, as shown in Fig. 1., and were composed of Mg, Y, Al and Ca; and the REEs were Ba, La, Eu and Tb.

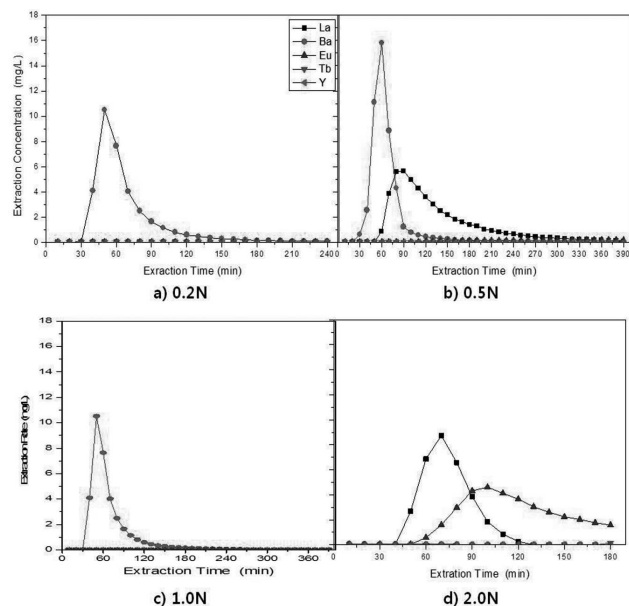


Fig. 4. Extraction elements and concentration by HCl extractant concentration a) 0.2N, b) 0.5N, c) 1.0N, d) 2.0N at 2 ml/min

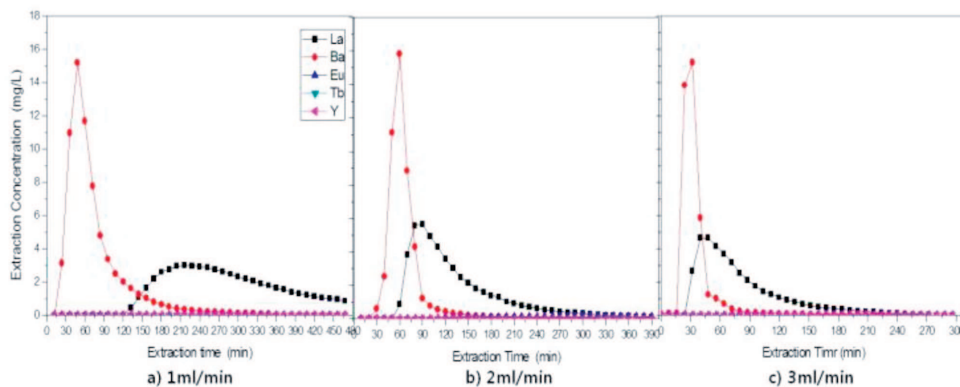


Fig. 5. Extraction rate a) 1 ml/min, b) 2 ml/min, c) 3 ml/min) Change at 0.5N, HCl

Shown in Fig. 4. are the changes based on the concentration of the extractant HCl at extraction rate 2 ml/min. At 0.2N HCl, only pure Ba was extracted from 30 min to 240 min. At 20 min after the Ba extraction start point, the Ba extraction concentration was about 11 mg/L. The extraction concentration of Ba rose and the extraction start point became faster until the extractant concentration 0.5N. However, after the extractant concentration 1.0N, the extraction start point was 40min; and after 2.0N, no more extraction appeared.

For Ba, the extraction was started at extractant concentration 0.2N, the extraction concentration was 15.8 mg/L at 0.5N HCl, 10.5 mg/L at 1.0N HCl and 9 mg/L at 2.0N HCl. The point of extraction start increasing with extractant HCl concentration became constant at 30min; However, There were no extraction start point for Ba at 2.0N. For La, the extraction was started to show from the extractant concentration at 0.5N; and at 2.0N, the extraction concentrations was 9 mg/L. As the extractant concentration rose, the extraction start point became delayed by about 45 min at 0.5N. And at 2.0N, the extraction start point was at 40 min. For Eu, the extraction was started to show from the extractant concentration at 2.0N. The Eu extraction start point was 50 min at 2.0N. The extraction concentrations of Eu was 4 mg/L at 2.0N. During the extraction using the extractant HCl, Ba was extracted at the low extractant concentrations of 0.2N, 0.5N and 1.0N, whereas La was extracted at 0.5 N and 2.0N, and Eu, at 2.0 N.

Shown in Fig. 5. are the changes in the extraction properties of the REEs at the extraction rate 1, 2 and 3 ml/min. At the extractant HCl concentration 0.5N, at which Ba started to be extracted at around 15 min regardless of the extraction rate. However, La started to be extracted from 120 min at 1 ml/min, 50 min at 2 ml/min and 20 min at 3 ml/min. The concentration of the extracted La was kept at around 16 mg/L, although the extraction start point became earlier due to the change in the extraction rate.

While Ba, La and Eu were extracted from the extraction chromatography using HCl, only Ba showed accurate resolving power. In the separation investigation using extractant HCl, it was difficult to acquire the resolving power of La, Tb, Eu and Y. Therefore, it was investigated if these elements have resolving power using extractant HClO<sub>4</sub>, which has strong oxidizing power. Shown in Fig. 6. is the change in the extractant HClO<sub>4</sub> concentration from 0.2N to 1.0 N at the extraction rate 2 ml/min. In the case of the extractant HClO<sub>4</sub> with strong

oxidizing power, only Ba was extracted and its concentration was 3 mg/L. At 0.5N HClO<sub>4</sub>, La started to be extracted at 40 min; and at 90 min, its concentration was 2.3 mg/L and it continued to be extracted, although its concentration gradually declined. At 1.0N HClO<sub>4</sub>, Ba started to be extracted 20 min from the extraction start point, and its concentration was 17 mg/L at 40 min. The extraction was continued until 180 min. However, La started to be extracted about 70 min until the 240 min, and its maximum extraction concentration was 12 mg/L about 100 min after the start of the extraction. Eu started to be extracted from 250 min, but its extraction concentration was low at 2 ml/L. It was confirmed that the resolving power of La was at 1.0 N HClO<sub>4</sub>, at which the extraction concentration was 12 mg/L.

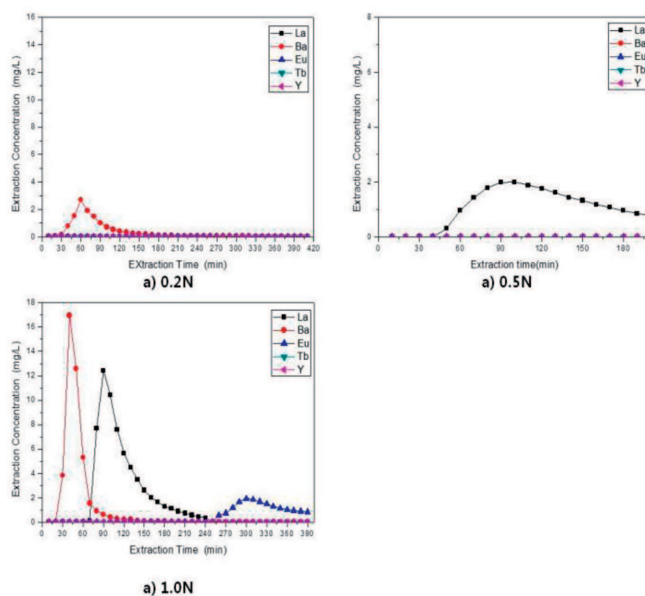


Fig. 6. Extraction elements and concentration by extractant HClO<sub>4</sub> concentration a) 0.2N, b) 0.5N, c) 1.0N at 2ml/min

Shown in Fig. 7. are the extraction properties based on the change in the elution speed when the concentration of the elution solution HClO<sub>4</sub> was 0.5N. In the case of HClO<sub>4</sub>, the elution speed of Ba increased; and at 1 ml/min, it started to be eluted after 10 min; at 3 ml/min, after 30 min; and at 5 ml/min, after 25 min. The extraction concentration increased as the speed increased; and at 5 ml/min, it was about 17 mg/L. As for La, its extraction time shortened with the increase in

its extraction rate. Its extraction started after 120 min at 1 ml/min, 100 min at 3 ml/min, and 80 min at 5 ml/min, and its extraction concentration hardly differed at 3-4 mg/L.

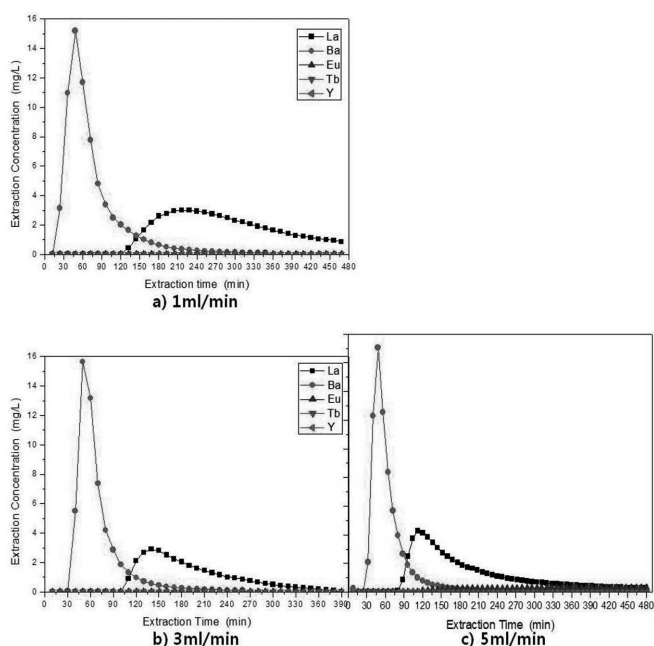


Fig. 7. Extraction rate (a) 1 ml/min, b) 3 ml/min, c) 5 ml/min) change at 0.5N, HCl

It can be confirmed from Fig. 8. that Ba, La, Eu, Tb and Y were separated and extracted in sequence from the standard solution using HCl and HClO<sub>4</sub>, in which 100 ppm of each component was included. Ba can be separated at the extraction rate 2 ml/min using 0.2N HCl. Here, Ba was extracted 35 min until 240 min. After 50 min has passed extraction start point, the extraction concentration was 10.2 mg/L. La started to be extracted 70 min after the extraction using 0.1N HClO<sub>4</sub> at the extraction rate 2 ml/min and until 250 min. About 110 min after the start of the extraction, the La extraction concentration was 12.2 mg/L. At the same condition, Eu started to be extracted 250 min after the extraction start point, but its concentration was very low at 2 mg/L. And at 2.0N HClO<sub>4</sub>, Eu started to be extracted 40 min and was extracted until 320 min at the extraction rate 3 ml/min. At 60 min from the extraction start point, the extraction concentration was 8.8 mg/L.

It was confirmed that Tb was extracted at the extraction rate 2.3 ml/L using 3.0N HCl. It started to be extracted 20 min after the start of the extraction until 190 min. Due to the high HCl concentration, the concentration of the extracted Tb was also high, and about 45 min after the extraction start point, the extraction concentration was 37 mg/L.

It was confirmed that Y was extracted at the extraction rate 3.0 ml/L using 3.0N HCl and at the extraction rate 3.0 ml/L using 3.5N HClO<sub>4</sub>. For Y, the extraction concentration using the extractant HCl was 3.5 mg/L at extraction rate 3 ml/min. If extraction time was extended, separation of Y is possible. Under this condition, REEs could be separated from CCFL phosphors that are used in LCD backlight units.

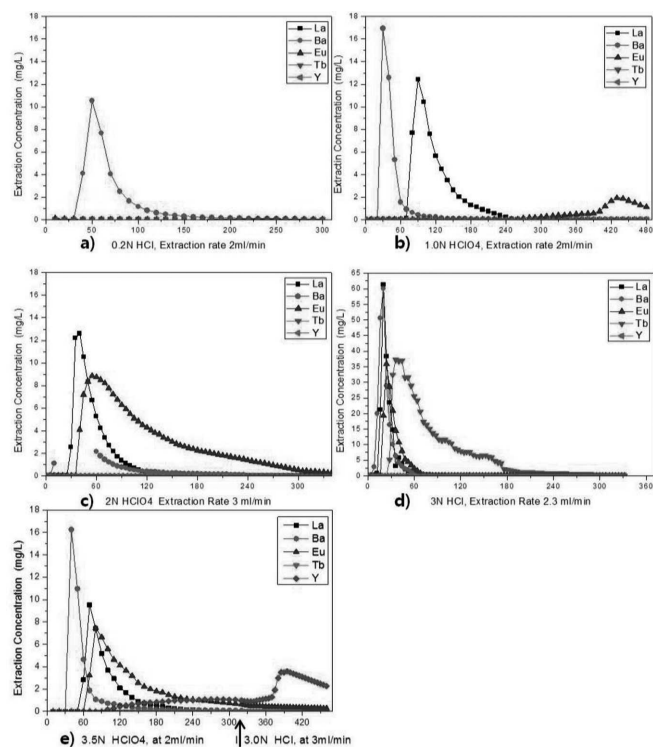


Fig. 8. Sequential separation of REEs from the standard solution

In this study, the La<sup>3+</sup> solution, among the separated rare earth ion solutions, was stirred by adding oxalic acid to it while maintaining its pH at 1.0. The precipitation that resulted from the response to the oxalic acid was separated by washing the solution with DI water. The separated precipitation was dried in the sintering furnace to recycle the La oxide in atmosphere air and O<sub>2</sub>. The XRD analysis results are shown in Fig. 9. The recycled La<sub>2</sub>O<sub>3</sub> were confirmed by the XRD analysis results. It's thought that La(OH)<sub>3</sub> was formed by moisture in air.

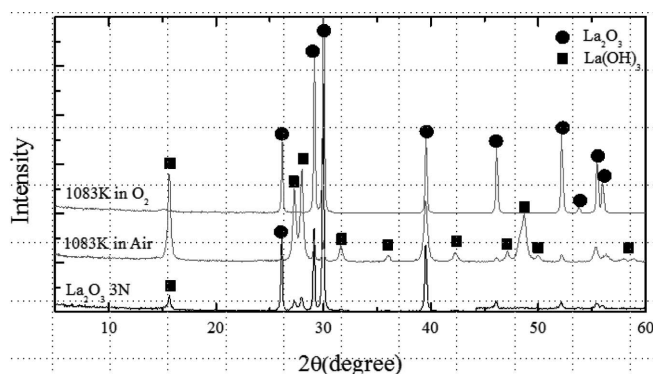


Fig. 9. XRD of La<sub>2</sub>O<sub>3</sub> precipitation as atmosphere

#### 4. Conclusions

The elements in CCFL, which is used in LCD TV backlight units, are Ba, La, Tb and Eu, as well as Mg, Al, Ca and Y. Among these elements, the REEs, Y, La, Ba, Tb and Eu, could be sequentially separated from the standard solution with 100 ppm of each element through extraction chromatography using the Amberlite XAD-7HP resin. Ba started to be separated from HCl 0.2N, 30 min after the start of the extraction until 240 min at the extraction rate 2 ml/min, and La

started to be separated from  $\text{HClO}_4$  1.0N, 70 min after the start of the extraction until 250 min at the extraction rate 2 ml/min. Eu was extracted, but its extraction concentration was very low, at 2 mg/L. However, in  $\text{HClO}_4$  2.0N, Eu started to be extracted 35 min from the start of the extraction until 330 min. Tb started to be extracted 25 min from the start of the extraction until 210 min at the extraction rate 2.3 ml/min, and its maximum extraction concentration was 36 mg/L. Finally, Y was extracted at the extraction rate 3.0 ml/L using 3.0N HCl. La oxide was produced by precipitating the La ion from the separated La solution.

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