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A Study on Photochemical Separation of Rare Earths: The Separation of Europium from an Industrial Concentrate Material of Samarium, Europium, and Gadolinium

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Abstract

Eu can be separated by photoreduction from the Sm, Eu, and Gd concentrate in a mixed alcohol (ethanol and isopropanol) system by using a high-pressure mercury lamp as the light source. The influencing factors, such as the concentration of EtOH–isopropanol, irradiation time, and the lamp power, on the photoreduction were investigated in detail in this research, and the optimum technological conditions were determined. The separation coefficients were $\beta_{Gd/Eu} > \beta_{Sm/Eu} = 960$, and the yield of Eu(II) is 95%. The purity of Eu obtained is 92%.

I. INTRODUCTION

Rare earths have been widely used in the fields of chemical engineering, metallurgy, atomic energy, agriculture, and magnetic and luminescence materials (*1*).

There are several processes employed to produce the individual rare-earth elements to meet a required specification by using a concentrate of rare earths as the raw material. Generally, the mixture of rare-earth elements is first separated into groups by extraction in a HCl medium by using the extractant P-204 [di(2-ethyl hexyl phosphoric acid)] to obtain concentrates of light rare earths (La, Ce, Pr, Nd, etc.), middle rare earths (Sm, Eu, Gd, etc.), and heavy rare earths (Tb, Dy, Ho, Er, Tm, Yb, Lu, Y). The individual rare-earth elements are then separated and purified by solvent extraction or by chromatography. Currently in China, the speci-

fications of the mixed concentrate of Sm, Eu, and Gd are $Eu_2O_3 \geq 8\%$, $Sm_2O_3 \geq 30\%$, and $Gd_2O_3 \approx 30\%$, with the remainder being other rare-earth oxides.

The reduction extraction process is mainly used for the separation of Eu from the concentrated liquid of Sm, Eu, and Gd. The process is based on the fact that the distribution coefficient of Eu(II) is much less than that of other trivalent rare-earth elements. As for the reduction of Eu, there are several methods available; for example, mercury cathode electrolysis, reduction with Zn powder, and carbon electrode electrolysis. Mercury cathode electrolysis is already obsolete because of mercury contamination, and Zn powder reduction is seldom used because Zn powder easily coagulates and causes inconvenience in operating the extraction. Carbon electrode electrolysis is still in the process of scientific research (*1*).

Besides the above, there is another method—photoreduction of Eu. Some literature is available that covers the photoredox reaction of Eu (*2–8*). Donohue (*8*) proposed the possibility of separating some elements of the lanthanide and the actinide by photoredox reaction. By using a laser or a low-pressure mercury lamp as the light source to irradiate an Eu(III) solution containing water, ethanol, and isopropanol, Eu can be precipitated by photoreduction. In 1985, Kang et al. (*9*) investigated the separation of Eu from a two-component system by photoreduction. Liu et al. (*10*) investigated the photooxidation of Ce(III) with IO_3^- which resulted in the precipitation of insoluble $Ce(IO_3)_4$, and Ce and Eu were thus separated from each other. The photochemical method for separating Eu with a laser as the light source increases the cost, and the method employing a low-pressure mercury lamp has the problem of inadequate power, so that both are seldom used in industry. Furthermore, in an aqueous system, Eu(II) reduces H^+ and forms H_2. This side reaction causes a low yield of Eu. Our aim was to investigate the possibility of separating Eu by photoreduction with a high-pressure mercury lamp as the light source from a solution in which a mixture of ethanol and isopropanol is used as the solvent and saturated with a concentrate of Sm, Eu, and Gd.

II. PRINCIPLE

In order to link up the P-204 extraction process in industry, a Sm, Eu, and Gd chloride solution was prepared from an industrial concentrate of Sm, Eu, and Gd. Because the solubility of $RECl_3 \cdot nH_2O$ in ethanol is larger than in isopropanol and the reduction ability of the hydrogen linked with the secondary carbon atom in isopropanol is stronger than that in ethanol, a mixture of these two alcohols was used as the solvent in which a saturated solution of Sm, Eu, and Gd was used as the initial solution for

photoirradiation. Under irradiation with a high-pressure mercury lamp, $EuCl_2$ was produced by photoreduction and, owing to its low solubility, precipitated from the alcoholic solution (*8*). The steps of the photoprocess are as follows:

Step 1. Dissolving and complexing:

$$\underset{(s)}{(Sm,Eu,Gd,...)Cl_3\cdot nH_2O} + \underset{(l)}{3EtOH} \rightarrow \underset{(l)}{(Sm,Eu,Gd,...)Cl_3\cdot 3EtOH} + \underset{(l)}{nH_2O}$$

$$\underset{(s)}{(Sm,Eu,Gd,...)Cl_3\cdot nH_2O} + \underset{(l)}{3isopropanol} \rightarrow \underset{(l)}{(Sm,Eu,Gd,...)Cl_3\cdot 3isopropanol} + \underset{(l)}{nH_2O}$$

Step 2. Photoexcitation:

$$(Sm,Eu,Gd,...)Cl_3\cdot 3EtOH \xrightarrow{h\nu} (Sm,Eu,Gd,...)^*Cl_3\cdot 3EtOH$$

$$(Sm,Eu,Gd,...)Cl_3\cdot 3isopropanol \xrightarrow{h\nu} (Sm,Eu,Gd,...)^*Cl_3\cdot 3isopropanol$$

Step 3. Electron transition:

$$Eu^*Cl_3\cdot 3EtOH \rightarrow EuCl_2 + 2EtOH + \text{organic oxidation products}$$

$$Eu^*Cl_3\cdot 3isopropanol \rightarrow EuCl_2 + 2isopropanol + \text{organic oxidation products}$$

Although Sm(III) and Gd(III) can be excited as well, their reduction potential is more negative than that of Eu(III)/Eu(II), and the reductive ability in this system is insufficient. As a result, only the reductive reaction of Eu(III)–Eu(II) occurs.

Step 4. As the solubility of $EuCl_2$ in an EtOH–isopropanol mixture is low, $EuCl_2$ precipitated and was separated from other RE(III) elements. If the

water content in this alcoholic mixture was increased, $EuCl_2$ would not precipitate because it easily dissolves in water.

III. EXPERIMENT

1. Raw Material and Pretreatment

Eu_2O_3, 99.95%
Sm_2O_3, 99.5%
Gd_2O_3, 99.99%
Industrial concentrate of Sm, Eu, and Gd
The composition analysis of the concentrate is as follows:

RE_2O_3	Y_2O_3	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3
Wt%	0.79	25.75	0.46	0.86	2.62	30.80	8.01
Gd_2O_3	Tb_4O_7	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3
29.00	0.55	0.66	<0.30	<0.30	<0.30	<0.30	<0.30

Hydrochloric acid, c.p.
Ethanol (EtOH), c.p. > 99.5%
Isopropanol, c.p. > 99.5%
Hydrogen peroxide, c.p.
Preparation of the initial irradiation solution (IS).

The procedure for Pretreatment Process I is as follows: Weighing a certain amount of RE_2O_3 → dissolving with HCl acid → filtering → evaporating and concentrating → drying (<100°C) (*11*) → dissolving with absolute EtOH → drying (<100°C) → saturated solution of RE in EtOH–isopropanol mixture.

The procedure of the Pretreatment Process II is the same as Process I except for dissolving with absolute EtOH and drying.

2. Apparatus and Operations

Operations

A certain amount of IS was measured and its acidity was determined. It was then poured into the quartz tube, and the rotational mercury lamp was turned on. When the lamp's luminosity remained unchanged, the tube was quickly put into the reaction tube shelves and the timing was started. When the predetermined time was reached, the tube was taken off the shelves. The precipitate was separated by a centrifuge and was first washed with the mixture of alcohols and then with isopropanol. Finally, the samples were prepared for measurements, such as IS, remnant solution, and the precipitate.

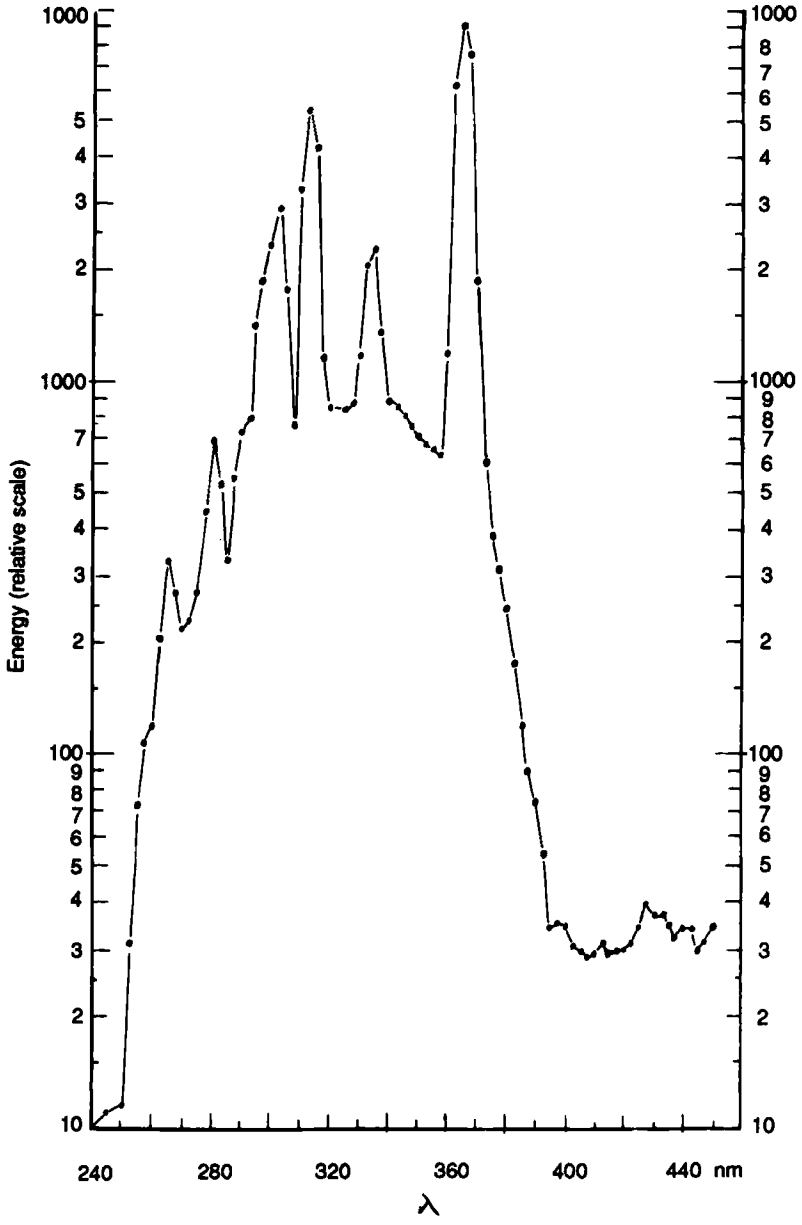

FIG. 1. The emission spectra of the high-pressure mercury lamp (quartz) and the energy distribution.

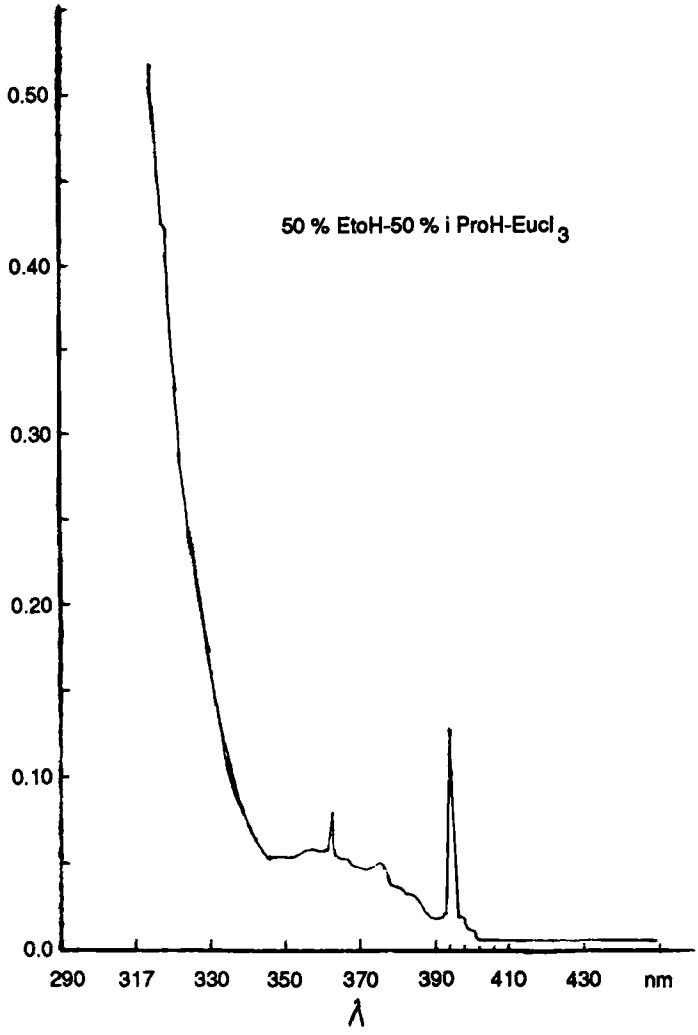

FIG. 2. The absorption curve of the $EuCl_3$–EtOH–isopropanol system.

3. Measurement

The absorption spectra of Eu^{3+}, Sm^{3+}, and Gd^{3+} in 1 mol/L HCl were measured by using a 751 spectrometer. The acidity of the solution was analyzed by titration. The purity of the photoreductive products was determined by x-ray fluorimetry, and the H_2 content generated during the reaction was measured by gas chromatography.

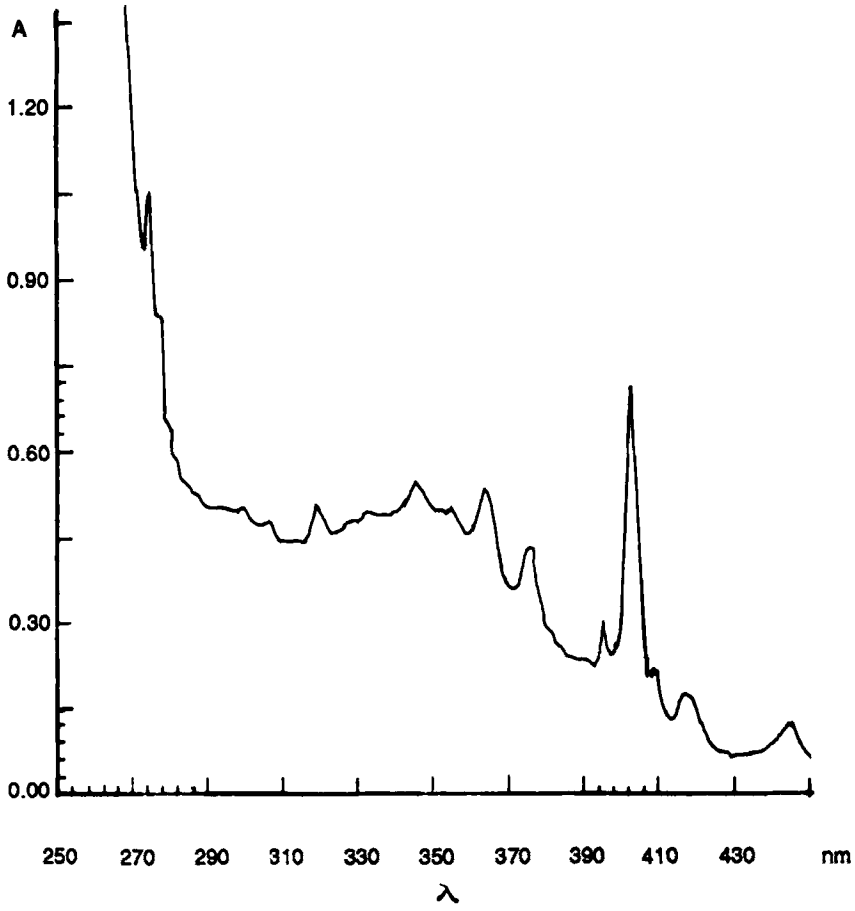

FIG. 3. The absorption curve of the (Sm, Eu, Gd, ...)Cl_3–EtOH–isopropanol system.

4. Data Management

The separation coefficient of Sm from Eu is

$$\beta_{Sm/Eu} = \frac{(\text{total amount of Sm/total amount of Eu})_{IS}}{(\text{total amount of Sm/total amount of Eu})_{ppt}}$$

$\beta_{Sm/Eu}$ can also be expressed as

$$\beta_{Sm/Eu} = \left(\frac{A\ Sm}{A\ Eu}\right)_{IS}\left(\frac{A\ Eu}{A\ Sm}\right)_{ppt}$$

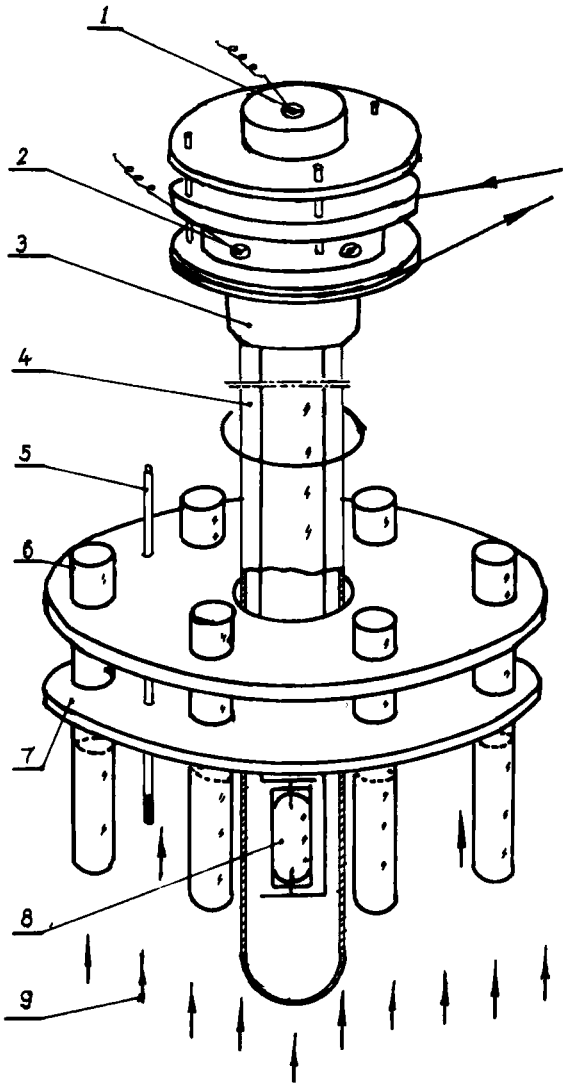

FIG. 4. Photoreaction apparatus: (1, 2) mains, (3) lamp holder, (4) quartz outer casing of lamp, (5) thermometer, (6) quartz tube, (7) tube shelf, (8) luminary, (9) air cooling.

Similarly:

$$\beta_{Gd/Eu} = \left(\frac{A\ Gd}{A\ Eu}\right)_{IS}\left(\frac{A\ Eu}{A\ Gd}\right)_{ppt}$$

$$\text{Yield of Eu(II)\%} = \frac{(\text{Eu total amount})_{ppt}}{(\text{Eu total amount})_{IS}}$$

The deviation of the experimental data was less than ±0.5%.

IV. RESULTS AND DISCUSSION

1. The Solubility of $RECl_3 \cdot nH_2O$ in EtOH–Isopropanol Solvent

Figure 5 shows that the solubility of $RECl_3$ increases with an increase in the concentration of EtOH.

2. The Results of Photoreduction of $SmCl_3$, $EuCl_3$, and $GdCl_3$ Individually in EtOH–Isopropanol (see Table 1)

The precipitant obtained was immediately dissolved with 1 mol/L HCl, and then the absorption spectra were measured as shown in Fig. 6. This solution was then oxidized by a small amount of H_2O_2. When the excessive H_2O_2 was completely decomposed, the absorption spectra were measured as shown in Fig. 7.

From Fig. 6 it can be seen clearly that the spectra are similar to that of Eu^{2+} [12], but the absorption peak at $\lambda = 393.5$ nm of Eu^{3+} is not observed. On the contrary, in Fig. 7 only the absorption peak of Eu^{3+} exists, and the white precipitate is no doubt Eu(II). From Table 1 it can also be seen that bubbles occur when the photoreaction is going on. Analysis shows that they are composed of H_2, probably due to the side reaction, i.e., the reduction of H_2O by Eu(II). Table 2 shows the positive results of the two-component system in which Sm and Eu are well separated, and the experiments indicate that Gd and Eu can be even better separated.

In order to imitate the content proportions of Sm, Eu, and Gd in the industrial concentrate, the IS of the three components were prepared with proportions of $Sm_2O_3:Eu_2O_3:Gd_2O_3 = 30:8:30$. The influences of the initial acidity of IS, the initial water content in the IS, and the initial EtOH concentration in the photoreduction system were studied.

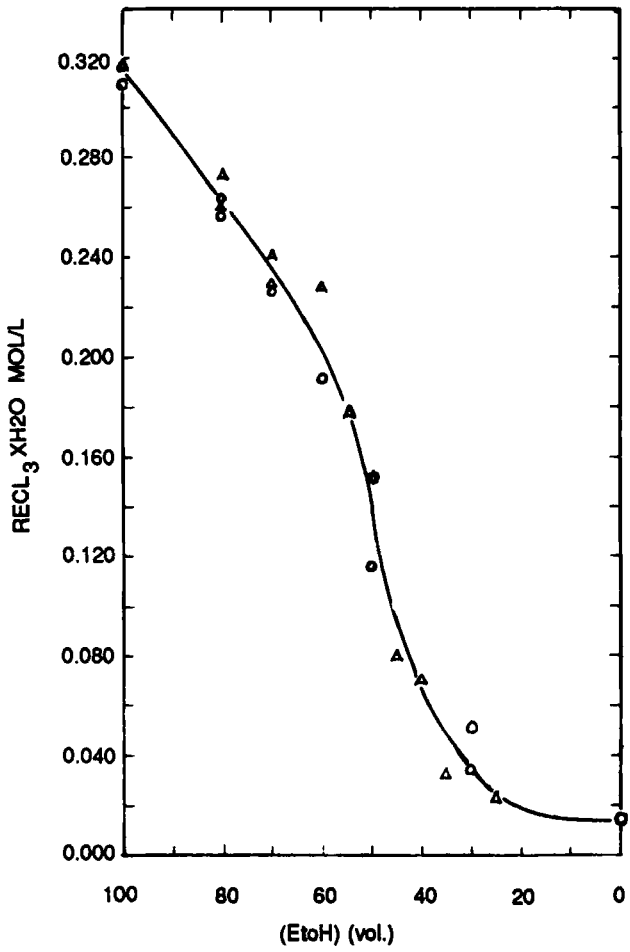

FIG. 5. The solubility of $RECl_3 \cdot nH_2$) in EtOH–isopropanol: (○) pretreatment Process I, (△) pretreatment Process II.

Influence of the Initial Acidity of IS

The results obtained are shown in Table 3 and Fig. 8.

As $\beta_{Gd/Eu}$ is always greater than $\beta_{Sm/Eu}$, the data of $\beta_{Gd/Eu}$ are not shown in Table 3. It is obvious that the influence of IS acidity on $\beta_{Sm/Eu}$ is greater than the yields (%), and the preferred result is at $[HCl]_0 = 0.125$ mol/L. The acidity of the remnant solution analyzed is greater than that of IS, which indicates that the acid is formed while the reaction is taking place.

TABLE 1[a]

Test	$RECl_3$	Volume of IS (mL)	Concentration of $RECl_3$ (mol/L)	Observed phenomenon
II-02-1	$EuCl_3$	6	0.1016	Bubbles, white precipitate
II-02-1	$SmCl_3$	6	0.0995	No bubbles, no precipitate
II-02-3	$GdCl_3$	12	0.0536	No bubbles, no precipitate

[a]The IS was prepared according to pretreatment Process I. Irradiation time: 60 min. High-pressure mercury lamp: 125 W. $[EtOH]_0$ = 30% (by volume).

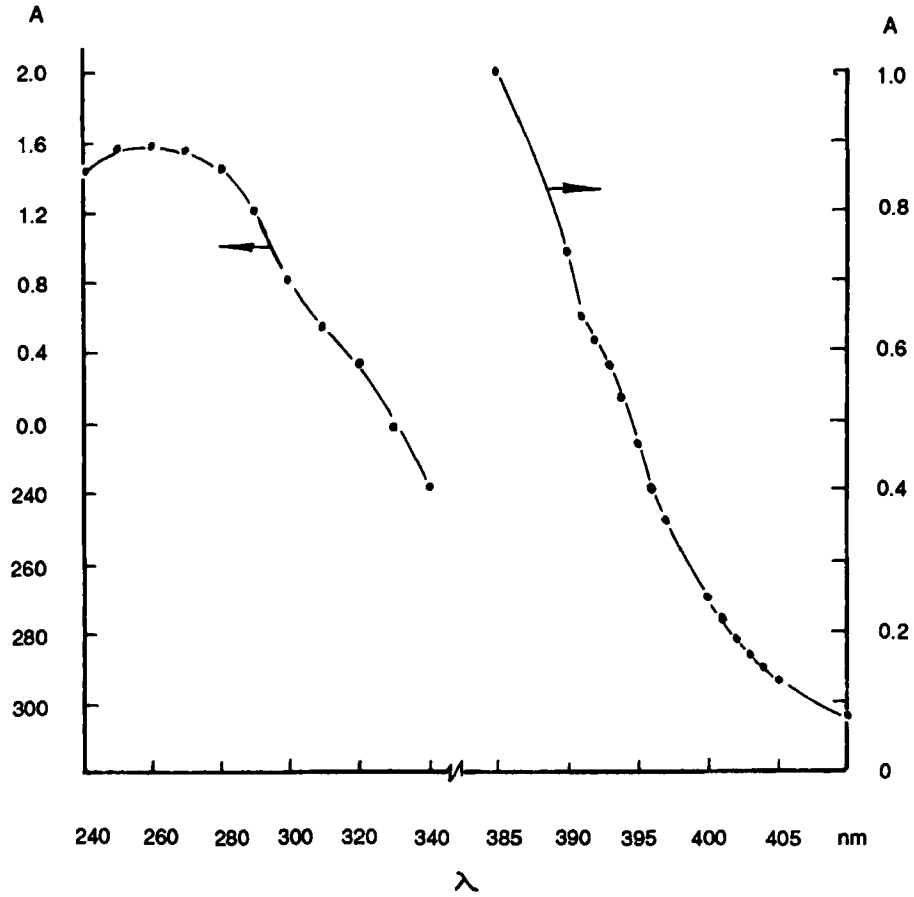

FIG. 6. The absorption spectra of the immediately dissolved precipitate.

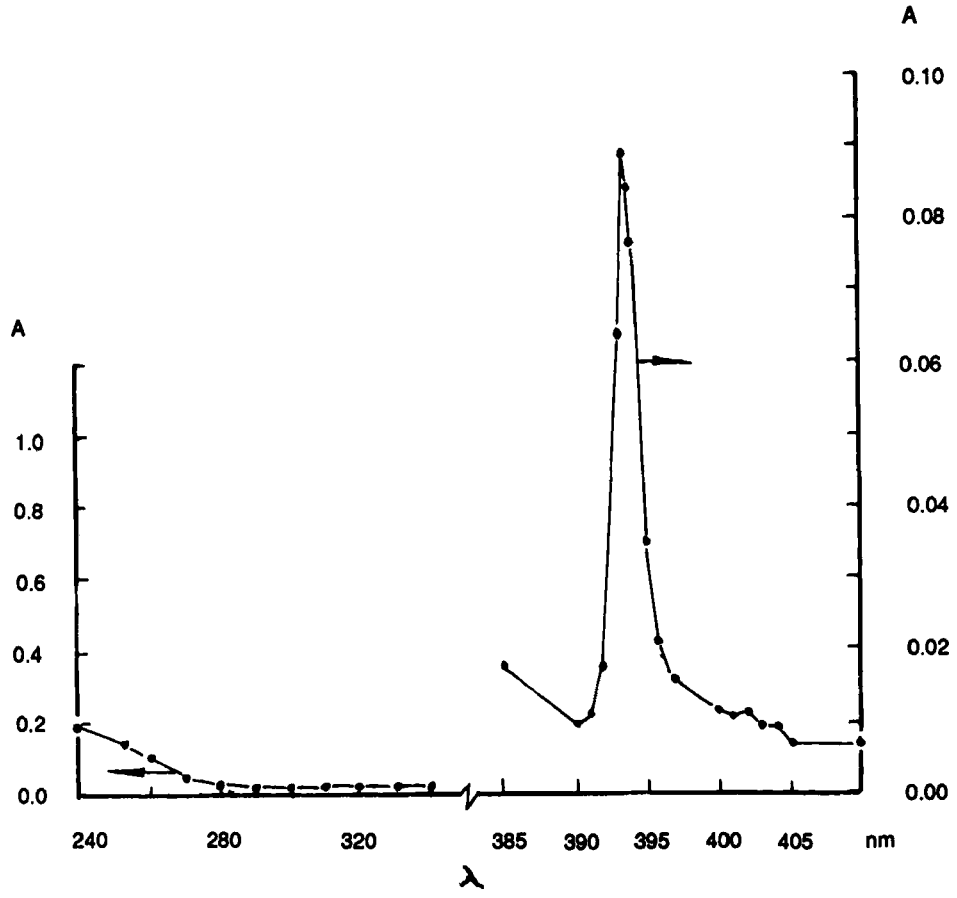

FIG. 7. The absorption spectra of the immediately dissolved precipitate after oxidation by H_2O_2.

TABLE 2[a]
Photoreduction Results in a Two-Component System (Sm,Eu)Cl_3

No.	$[RECl_3]_0$ (mol/L)	$[EtOH]_0$ (vol%)	$\beta_{Sm/Eu}$	Yield of Eu(II) (%)
II-03-5	$EuCl_3$ (0.0199) $SmCl_3$ (0.0752)	40	~960	80.0
II-03-6	$EuCl_3$ (0.0186) $SmCl_3$ (0.0702)	50	~900	79.4

[a]Mercury lamp: 125 W. Irradiation time: 10 min. IS: 10 mL.

TABLE 3
The Influence of $[HCl]_0$ on β and on the Yield of Eu(II)[a]

No.	$[HCl]_0$ (mol/L)	$\beta_{Sm/Eu}$	Yield of the Eu(II) (%)
II-04-1	10^{-5}–10^{-6}	320	85.1
II-04-2	0.125	~940	82.4
II-04-3	0.250	180	85.9
II-04-4	0.498	90	88.9

[a]Mercury lamp: 125 W. Irradiation time: 90 min. IS: 10 mL. $[EtOH]_0$ = 40%. Total concentration of $ReCl_3$: 0.0931 mol/L.

Influence of the Initial H_2O Content in IS

It seldom happens that the rare-earth chlorides crystallized out of the aqueous solution are without crystal water. On the other hand, the high water content in IS is not beneficial to the yield of Eu(II) owing to the solubility. The data in Table 4 show that the initial water content in IS influences not only the $\beta_{Sm/Eu}$ but also the yield of Eu(II). It is preferable to control the water content in IS at ≤2%. The separation coefficient depends on the appropriate conditions of precipitation, and the yield of Eu(II) depends mainly on the water content in IS.

Influence of the Initial Relative Concentration of the Two Alcohols

The influence of the initial relative concentration of EtOH and isopropanol on β and on the yield of Eu(II) is shown in Table 5. The preferable initial relative concentration of EtOH and isopropanol for obtaining higher $\beta_{Sm/Eu}$ and yield of Eu(II) is 50–50 vol%.

When the concentration of EtOH is 50 (vol%) in the mixture of the EtOH–isopropanol, the solubility of $RECl_3$ is 0.14 mol/L; when $[HCl]_0$ is about 0.125 mol/L and the water content in the system is ≤2 vol%, the $\beta_{Sm/Eu}$ is approximately 1000 and the yield of Eu(II) is not less than 95%. The absorption spectra of test II-6-3 (see Table 5) are shown in Fig. 9.

3. Comparison Test between Pretreatment Processes I and II

By using the industrial concentrate material of Sm, Eu, and Gd, two initial irradiation solutions (IS) were prepared separately by Processes I and II, and then the photoreduction test was carried out. The results are shown in Table 6.

From the data in Table 6 it can be seen that the results of Process I are slightly better than for Process II. But Process II, in which less reagents are used, is simpler. In general, Process II is more suitable for industrial

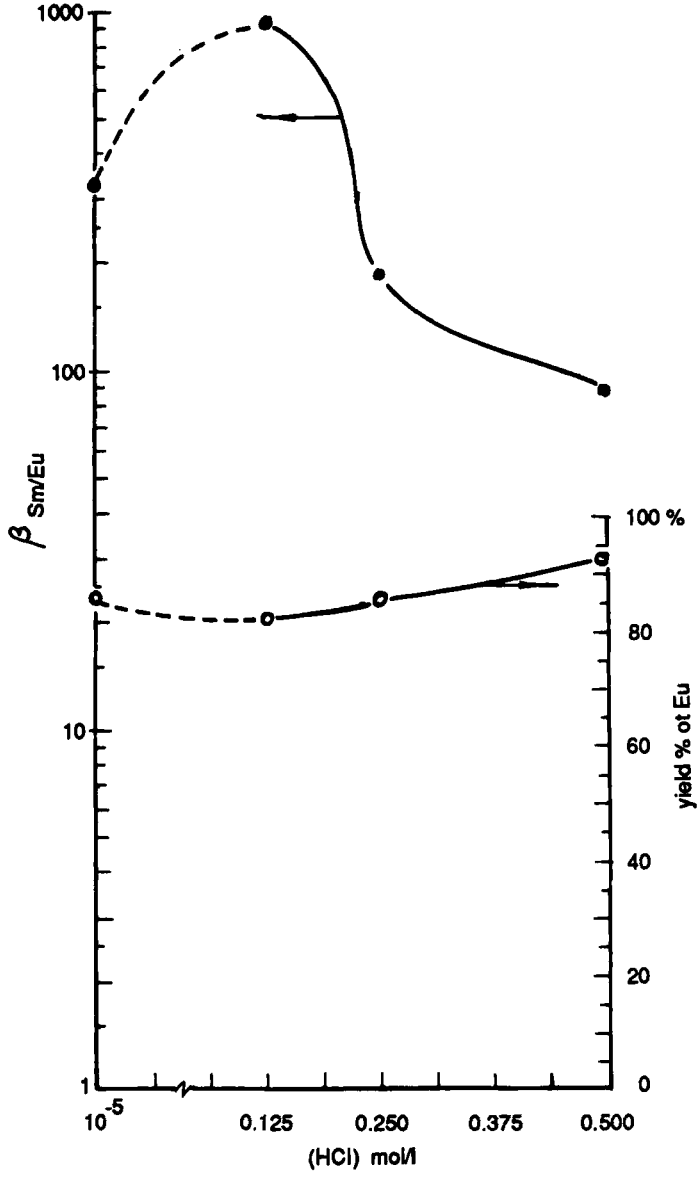

FIGURE 8.

TABLE 4
The Influence of the Initial Water Content on Photoreduction[a]

No.	$[H_2O]_0$ (vol%)	$\beta_{Sm/Eu}$	Yield of Eu(II) (%)	Phenomenon observed
II-05-1	~0	160	92.3	Bubbles, turbid
II-05-2	2	~860	85.6	Bubbles, precipitate
II-05-3	5	—	—	Bubbles, no precipitate
II-05-4	10	—	—	Bubbles, no precipitate

[a]Mercury lamp: 125 W. IS: 10 mL. Irradiation time: 90 min. $[EuCl_3]_0$ = 0.0112 mol/L. $[SmCl_3]_0$ =0.0418 mol/L. $[GdCl_3]_0$ = 0.0403 mol/L. $[EtOH]_0$ = 40%.

applications. Therefore, the IS used for the later tests were all prepared from the Sm, Eu, and Gd concentrate material with pretreatment Process II.

4. Influencing Factors on the Photoreduction Separation of Eu from the Industrial Concentrate Material of Sm, Eu, and Gd

Influence of the Solvent Composition

From Table 7 it is clear that when the $[EtOH]_0$ percentage is 50, the results are preferable. By comparing Table 5 with Table 7, it can also be seen that it is easier to separate Eu from the mixture of Sm, Eu, and Gd prepared artificially than from the industrial concentrate material. This is due to the fact that in the industrial concentrate material there are rare-earth elements other than Sm, Eu, and Gd, and this causes more components to compete with Eu to absorb the light.

TABLE 5
The Influence of the Initial Relative Concentration of EtOH and Isopropanol on Photoreduction[a]

No.	$[RECl_3]_0$ (mol/L) Eu	Sm	Gd	$[EtOH]_0$ (vol%)	$\beta_{Sm/Eu}$	Yield of Eu(II) (%)
II-6-1	0.0366	0.1391	0.1338	100	790	23.8
II-6-2	0.0305	0.1160	0.1115	80	880	66.6
II-6-3	0.0172	0.0652	0.0626	50	~1000	95.0
II-6-4	0.0050	0.0189	0.0186	30	140	86.7
II-6-5	0.0017	0.0066	0.0065	0	97	76.9

[a]Mercury lamp: 125 W. IS: 10 mL. Irradiation time: 63 min. 35–40°C.

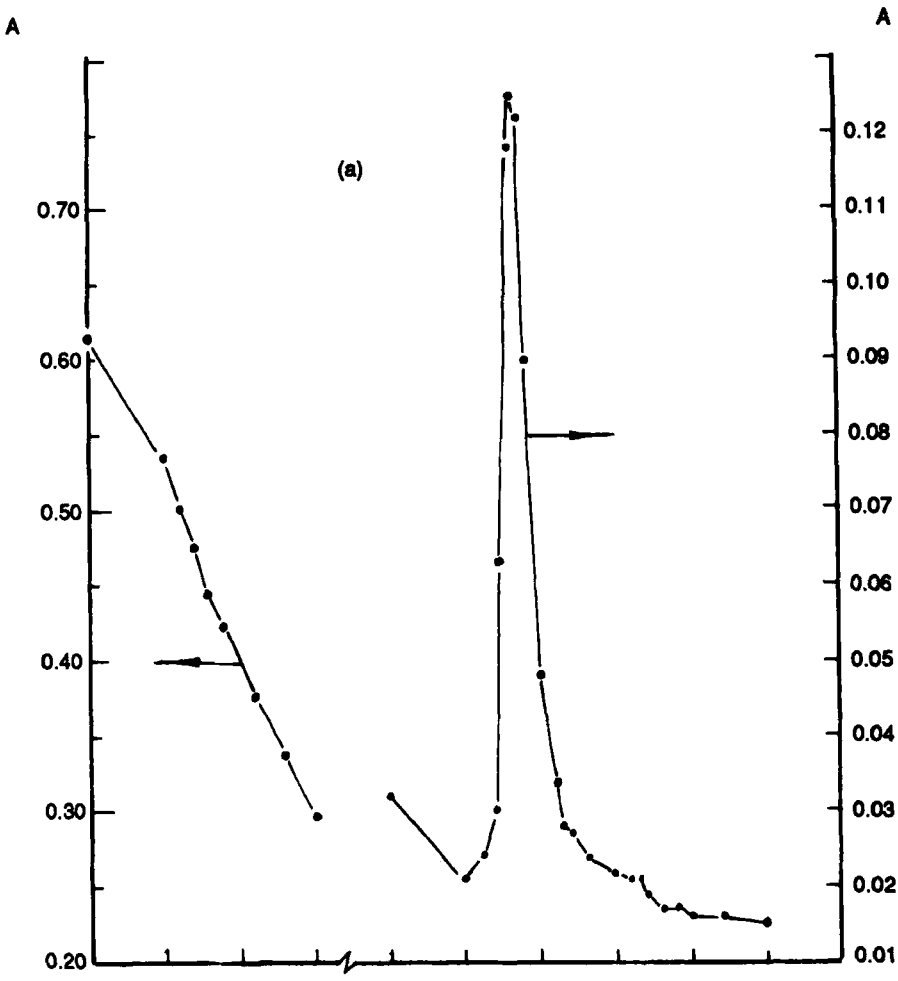

FIG. 9. The photoreduction effect of the artificially prepared IS of Sm, Eu, and Gd. (a) Precipitate.

Influence of the Irradiation Time and the Lamp Power on the Yield of Eu(II)

Table 8 indicates that when the power of the lamp is fixed, the yield of Eu(II) increases with an increase of the irradiation time. However, with an increase of time, the time effect gradually decreases. When the density of the electrical energy of the IS increases, the photoreduction rate is faster, and for the same yield of Eu(II), the irradiation time needed is less.

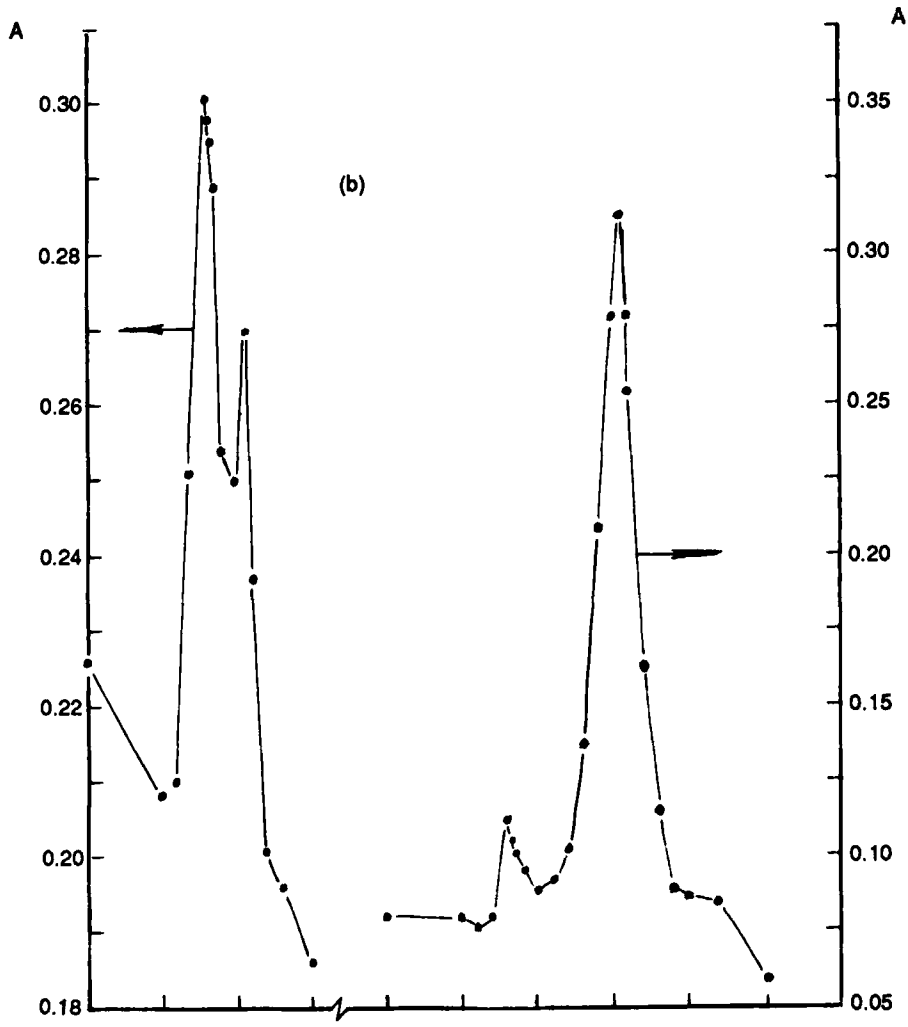

FIG. 9. The photoreduction effect of the artificially prepared IS of Sm, Eu, and Gd. (b) IS.

The optimum conditions to realize the separation of Eu from the Sm, Eu, and Gd concentrate material are as follows: By using the apparatus shown in Fig. 4, the saturated IS of the Sm, Eu, and Gd concentrate in the alcohol mixture was prepared by pretreatment Process II. The $[Re(III)]_0$ was equal to 0.14 mol/L in IS, the power of the high-pressure

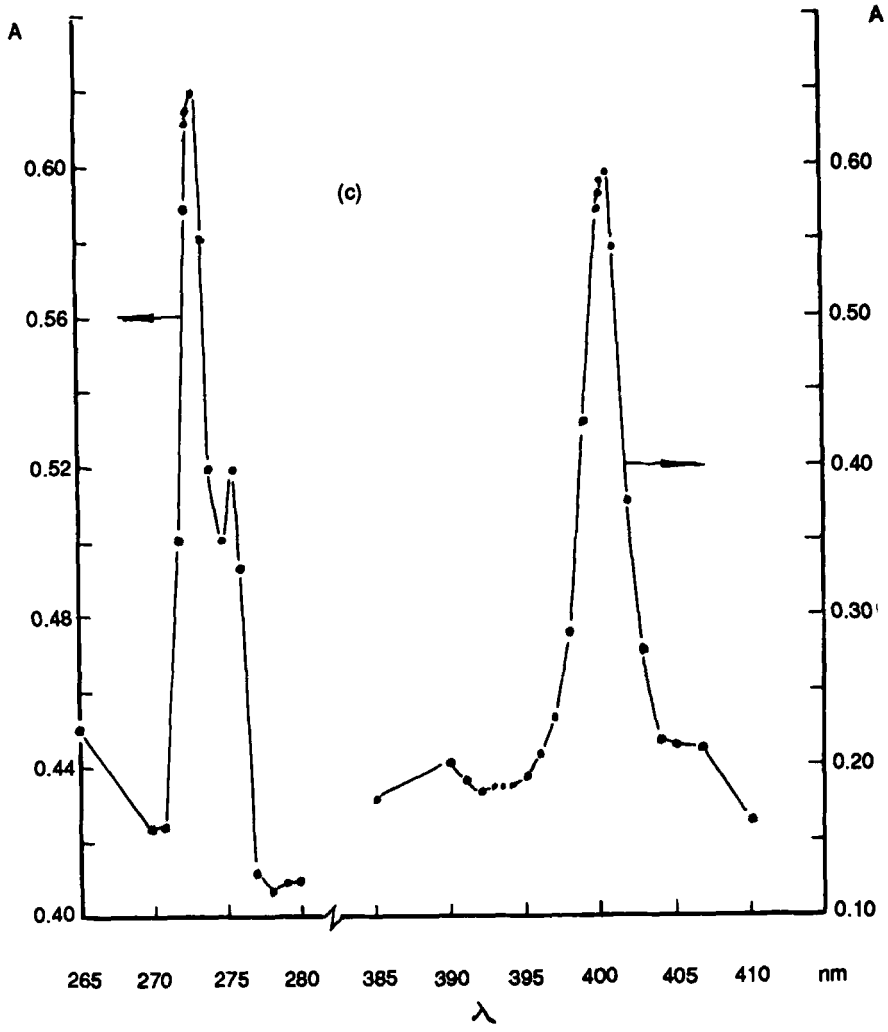

FIG. 9. The photoreduction effect of the artificially prepared IS of Sm, Eu, and Gd. (c) Remainder solution.

mercury lamp was 250 W (the density of electrical energy was 1.35 W/mL), the irradiation time was 60 min, the temperature was maintained at 40–43°C, and the precipitate obtained was separated by centrifugation and then washed individually by 50% EtOH–50% isopropanol and isopropanol.

TABLE 6
Comparison between Processes I and II[a]

No.	$[EtOH]_0$ (vol%)	Yield (%) of Eu(II)		$[RECl_3]_0$ (mol/L)	
		I	II	I	II
III-2-6,5	70	60	34	0.2265	0.2277
III-2-3,4	60	94	87	0.1941	0.1952
III-2-2,1	50	96	92	0.1294	0.1626

[a]Mercury lamp: 125 W. IS: 8 mL. Irradiation time: 90 min.

TABLE 7
The Influence of Relative Concentration of EtOH and Isopropanol on the Separation Effect[a]

No.	$[EtOH]_0$ (vol %)	$\beta_{Sm/Eu}$	Yield of Eu(II) (%)
III-5-1	70	—	34.0
III-5-2	60	—	86.2
III-5-3	50	360	86.0
III-5-4	40	180	86.0
III-5-5	30	30	95.1

[a]Mercury lamp: 125 W. IS: 10 mL. Irradiation time: 90 min.

TABLE 8
The Influence of Lamp Power and Irradiation Time on the Yield of Eu(II)[a]

No.	Power (W)	Volume of IS (mL)	Density of electrical energy (W/mL)	Temperature (°C)	Time (min.)	Yield of Eu(II) (%)
III-4-1	125	10	0.67	34–36	30	33.5
III-4-2,5	125	10	0.67	34–36	60	61.1
III-4-3	125	10	0.67	34–36	90	78.7
III-7-1	250	10	1.35	40–43	30	82.8
III-7-2	250	10	1.35	40–43	60	97.4
III-7-3	250	10	1.35	40–43	90	98.5
III-7-4	250	15	0.90	40–43	30	81.8
III-7-5	250	15	0.90	40–43	60	86.9
III-7-6	250	15	0.90	40–43	90	88.3

[a]The $[EtOH]_0$ percentage in the IS is 50.

The absorption spectra of the samples of IS, the remainder liquid, and the precipitate were measured (see Fig. 10), and the $\beta_{Sm/Eu}$ and the yield of Eu(II) were also calculated.

$\beta_{Sm/Eu}$ = 960; the yield of Eu(II) = 97.4%;

The purity of Eu, as analyzed by x-ray fluorimetry, was 92%.

Therefore, it is possible to separate Eu from the industrial concentrate material of Sm, Eu, and Gd by photoreduction.

V. CONCLUSION

1. The solubility curve of the Sm, Eu, and Gd chloride concentrate in EtOH–isopropanol system was roughly determined.

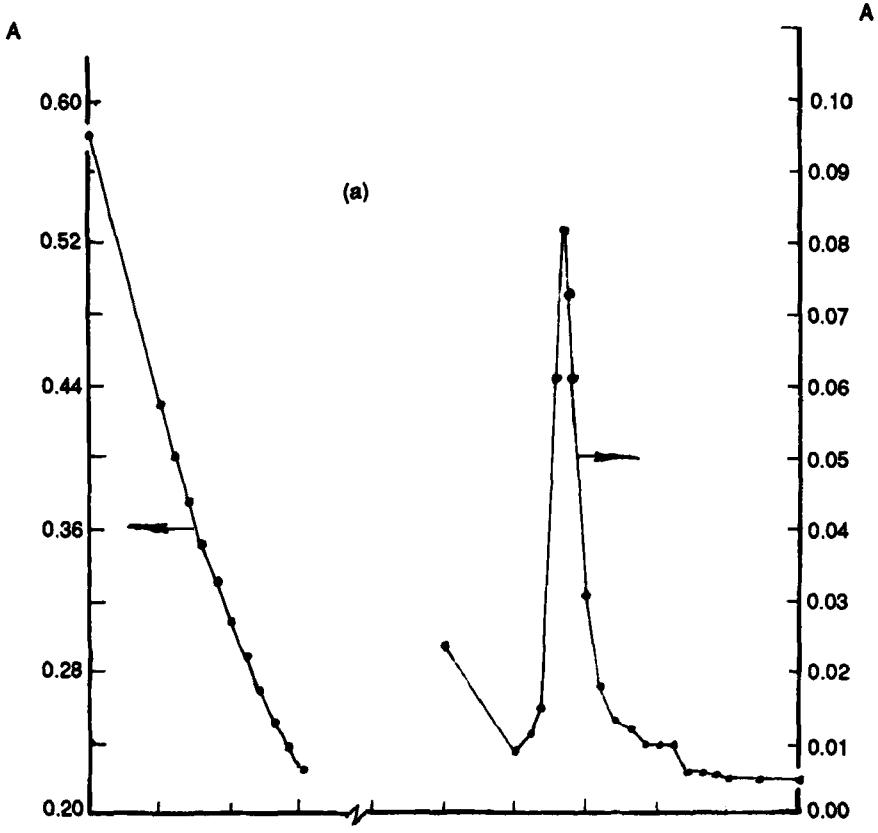

FIG. 10. The photoreduction effects of Sm, Eu, and Gd concentrate material (Test III-7-2). (a) Precipitate.

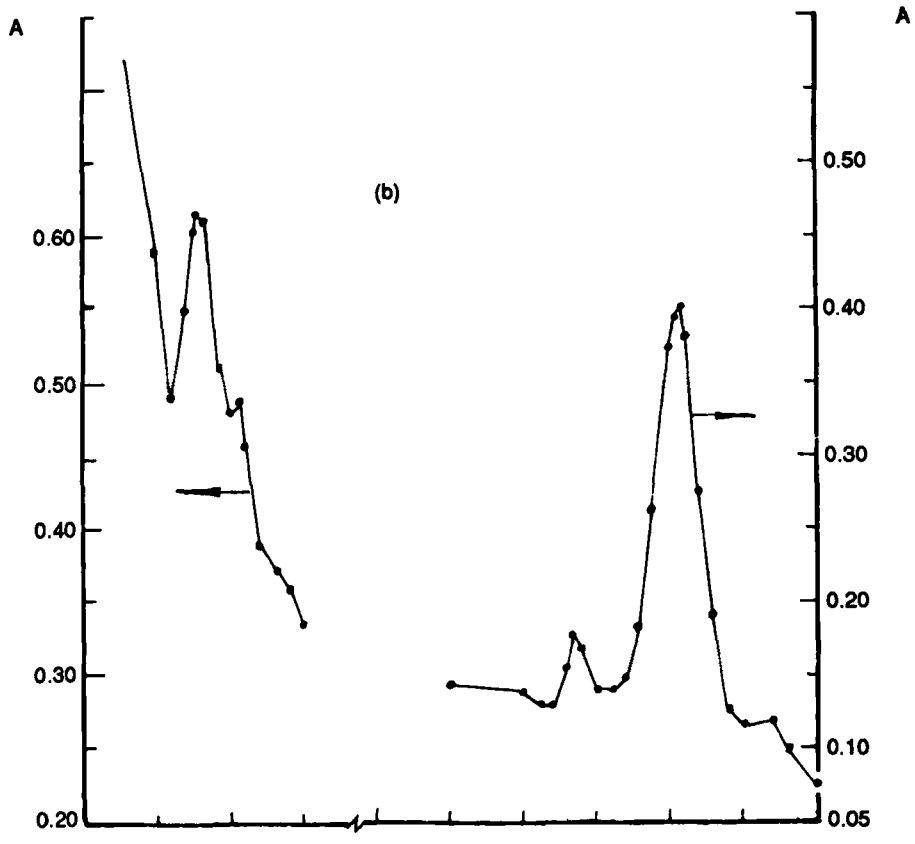

FIG. 10. The photoreduction effects of Sm, Eu, and Gd concentrate material (Test III-7-2). (b) IS.

2. By using a high-pressure mercury lamp as the light source, the influencing factors in the photoreduction process in the artificially prepared ($SmCl_3$, $EuCl_3$, $GdCl_3$)–EtOH–isopropanol system were investigated, such as $[HCl]_0$, $[H_2O]_0$ and [EtOH–isopropanol] of IS.

3. By using a high-pressure mercury lamp as the light source, the influencing factors in the photoreduction separation of Eu from the Sm, Eu, and Gd concentrate material in the EtOH–isopropanol system were investigated, such as [EtOH–isopropanol], irradiation time, the power of lamp, etc., and the optimum technological conditions were determined.

The separation coefficient $\beta_{Gd/Eu} > \beta_{Sm/Eu} = 960$.

The yield of Eu(II) $\geq 95\%$.

The purity of Eu obtained was 92%.

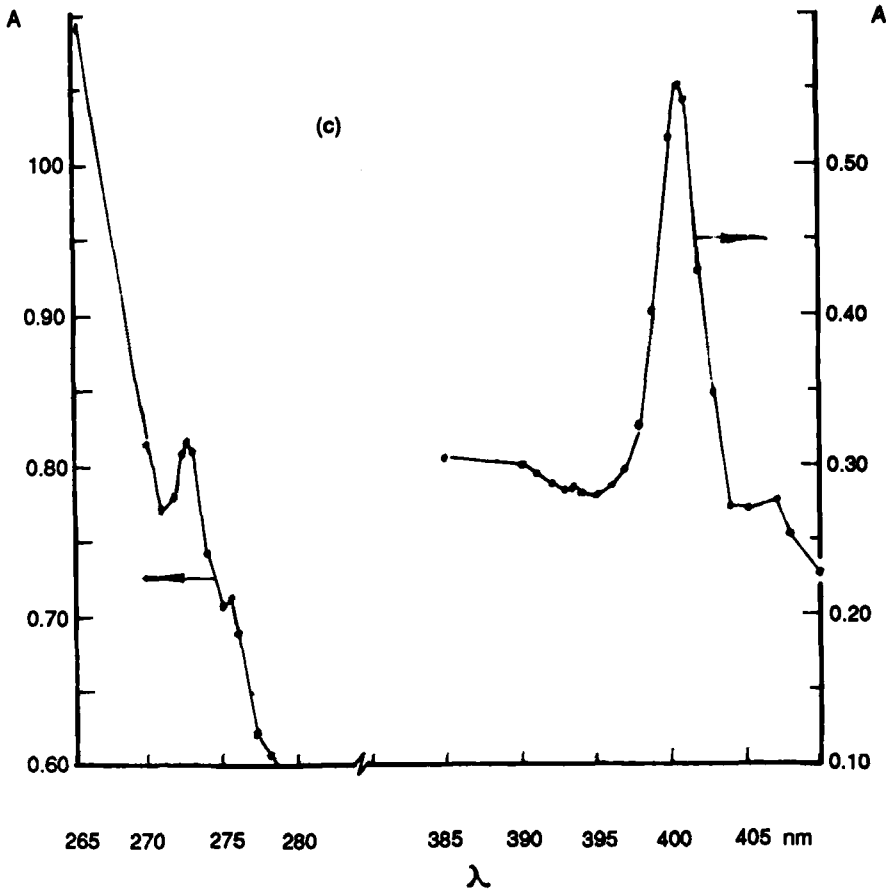

FIG. 10. The photoreduction effects of Sm, Eu, and Gd concentrate material (Test III-7-2). (c) Remainder solution.

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