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《**Original**》

Ion Exchange Separation and Spectrofluorometric Determination of Lanthanides in Nuclear Grade Material

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이온 교환수지 및 형광분석법에 의한 핵급물질 중 희토류원소의 분리정량

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Abstract.

Distribution coefficients between cation exchange resin(Dowex 50W×8) and α-hydroxyisobutyric acid (α-HIBA) are measured in order to separate traces of Sm, Eu, Gd and Dy from nuclear material. Individual separations are performed by pH gradient technique with 0.40M α-HIBA from 3.40 to 3.60 in cation exchange resin after a group separation. Each of separated elements is determined with a fluorometric method except Gd by colorimetry. The results are applied to analyze Sm, Eu, Gd and Dy in magnesium diuranate (yellow cake).

요 약

핵급물질에 함유된 미량 희토류원소인 Sm, Eu, Gd, Dy를 개별 분리하기 위해 Dowex50Wx8 양이온교환수지와 α-hydroxyisobutyric acid (α-HIBA) 사이에서 분배계수를 측정하였다. 양이온교환수지를 이용하여 우라늄매질로부터 미량희토류원소를 군분리한 후 0.40Mα-HIBA용리액의 pH를 3.40에서 3.60까지 변화시키면서 개별분리하였다.

Sm, Eu, Dy은 형광분석법으로 Gd은 비색법으로 정량하였으며 실험결과를 토대로하여 magnesium diuranate (yellow cake) 중의 Sm, Eu, Gd, Dy를 각각 정량하였다.

I. Introduction

Some of lanthanides, such as Sm, Eu, Gd and Dy, in nuclear material must be controlled at minimum level for the neutron economy because of their very high thermal neutron absorption cross-section.[1] Generally, colorimetric

method[2,3], EDTA titration method[4] and flame emission spectrometry[5] are used for the determination of high concentration of lanthanides, however, fluorometric method could be used due to its high selectivity and low detection limit. When trace and ultra-trace amounts of lanthanides in uranium matrix are determined with fluorometry, the elements are always to be separated prior to determination to prevent uranium interference as well as quenching effect of lanthanides each other. Many separation methods[6-9] have been developed according to variation of concentration. When large amounts of lanthanides are to be separated as a group, oxalate precipitation[10,11] and solvent extraction method[12-15] are applied, however, when in trace, separation by ion exchange resin is reported more effective.[16-20] To analyze various components of rocks or trace of lanthanides in nuclear material, mass spectrometry[17,21], X-ray fluorescence spectrometry,[22,23] flameless atomic absorption spectrophotometry[24], emission spectrographic analysis[18] and activation analysis[25-27] have been widely used.

But when none of above techniques are available, lanthanides are separated as a group or individual for the determination (for the better accuracy). Individual separations using cation exchange resin has been studied since 1940's[28,29] and the use of organic complexing agents[20] like α-hydroxycarboxylic acid or aminopolyacetic acid has improved the separation factor. Lanthanides in fission products are separated by hydroxide and fluoride precipitation method as a group first and determined by γ-ray detection after individual separation using pH gradient technique of 0.5M α-HIBA.[19] Trace amounts of lanthanides in monazite are separated first as a group with cation exchange resin and then individual separations with 0.25M α-HIBA eluent are followed using same resin as above.[27] F.W.E. Strelow et al. have determined ultra-trace amounts (nanogram order) of lanthanides in rocks with spark source mass spectrometry after group separation by cation exchange resin.[17] High performance liquid chromatography (HPLC) can make individual separation more effective with pH gradient technique using α-HIBA eluent.[30,31] Anion exchange resin[32-35] is used to separate lanthanides as a group or individual like cation exchange resin. For the lanthanides having low fluorescence intensity, β-diketone chelating agents such as thenoyltrifluoroacetone (TTA) or hexafluoroacetylacetone (HFA) is used to enhance fluorescence intensity.[36-39] In this experiment, ion exchange resin separation and spectrofluorometry have been tried to analyze four of lanthanides, i.e., Sm, Eu, Gd and Dy, in uranium matrix and the chelating agents used in fluorometry were HFA and sodium tungstate.

2. Experiment

Reagent and Apparatus

Dy_2O_3, Gd_2O_3, Sm_2O_3 (Yokosawa, G.R.) and Eu_2O_3 (Merck, G.R.) were dissolved in nitric acid and standardized. α-HIBA solution (Pfaltz and Bauer) was used as eluent after confirmed by IR spectrum[40] and standardized with NaOH solution. Cation exchange resin (Dowex 50W×8, 100-200 mesh, NH_4^+ form) and anion exchange resin (Dowex AG1×8, 200-400 mesh, NO_3^- form) were obtained from Sigma Co. and Bio-Rad Co., respectively. Hexafluoroacetylacetone (HFA) and trioctylphosphine oxide (TOPO) from Ishizu were used as a chelating agent and an extractant, respectively, and sodium tungstate and uranium acetate from Merck, G.R. were used. Absorbance was recorded on a Jobin Yvon Duospac 203 spectrophotometer and fluorescence spectra were obtained by a Jobin Yvon 3 fluorometer. Fraction collector used was product of Eldex Co. Group separation of lanthanides was

performed on the lst column with 26cm resin bed height and 1.7cm i.d., and on the second column with 7.0cm resin bed height and 0.5cm i.d. For the individual separation of Dy, Gd, Eu and Sm, the 3rd column with 6.3cm resin bed height and 0.38cm i.d. was used.

Procedure:

To 0.1 grams of anion exchange resin, 400μg of lanthanide and 22ml of nitric acid-methanol (1/10;V/V) solution were added and the mixture was stirred for five hours. Distribution coefficients were obtained by determination of each lanthanide in solution using Arsenazo-III method.[2,3] 0.05 grams of cation exchange resin, 10ml of α-HIBA and 100μg of lanthanide were mixed and treated same as above to measure the distribution coefficients. α-HIBA concentrations were 0.25M, 0.30M, 0.35M, 0.40M and pH of each solution was adjusted to 3.00, 3.20, 3.40, 3.60 and 3.80 using ammonium hydroxide solution, respectively.

An appropriate amount of cation exchange resin was filled in 3rd separation column and the column was preconditioned by passing excess of α-HIBA solution. The height of resin bed was adjusted to 6.3cm. Each 10μg of Eu(III), Gd(III), Dy(III) and Sm(III) was loaded on the resin and the element was eluted with 0.35M or 0.40M α-HIBA solution. Elution rate was regulated with needle valve stop cock. For a group separation of lanthanides, a small portion of solution containing 1mg of Ca(II), 200μg of Dy(III) and Sm(III) in each was passed through the lst separation column. The Ca(II) was eluted first with 1.75M HCl and then Dy(III) and Sm(III) were eluted with 4.0M HCl. The 2nd separation column was loaded by 200μg of Ca(II) and 100μg of Dy(III). 1.0M HCl and 4.0M HCl solutions were used for the separation of Ca(II) and Dy(III), respectively. From lst column, each 25ml-fraction was collected and from 2nd column, each 10ml-fraction was collected and determined (Table 2). Flow rates of 2.4±0.1ml/min. and 1.0±0.05ml/min. were maintained for the lst and 2nd separation columns, respectively. Dy(III)[41], Eu(III) and Sm(III)[37] were determined by spectrofluorometry while Gd(III) by colorimetry. Synthetic solution was prepared from four Lanthanides and uranium.

Sample Analysis

About 3~5 grams of magnesium diuranate was weighed accurately and dissolved in 100ml of 1:1 HNO_3. After filtration, insoluble materials were fused with sodium carbonate and borax in platinum dish at 1100 °C for an hour, dissolved in dilute nitric acid solution and combined with mother liquor. The acid was removed by evaporation and residue was dissolved in 20ml of 1.0M HCl. Group separation of lanthanides on the lst and 2nd separation columns was performed first and each of four lanthanides was eluted with α-HIBA on 3rd separation column. α-HIBA solution was removed by evaporation and the residue was further heated to remove carbonized impurity at 400°C for an hour in furnace. Finally, the residue was treated with concentrated nitric acid and dilute HCl solution, and then chemical analysis with fluorometry and colorimetry was followed.

3. Results and Discussion

Distribution coefficients both in cation exchange resin and anion exchange resin have been measured in order to apply to an individual separation of lanthanides. Distribution coefficients between HNO_3-methanol mixture and anion exchange resin are too close together to separate each of lanthanides as shown in figure 1. Table 1 shows distribution coefficients of each lanthanide with variation of concentrations and

Table 1. Distribution Coefficients of Lanthanides with α-HIBA in Dowex 50w×8 100-200 Mesh Size Resin

conc. of α-HIBA	elem.	pH of α-HIBA				
		3.00	3.20	3.40	3.60	3.80
0.25M	Sm(Ⅲ)	11748.5	4009.5	1000.4	199.2	69.3
	Eu(Ⅲ)	7951.9	2848.6	461.8	153.5	72.1
	Gd(Ⅲ)	4867.2	1829.3	346.8	96.7	—
	Dy(Ⅲ)	2532.0	504.6	124.2	72.9	—
0.30M	Sm(Ⅲ)	8612.7	3478.8	971.1	198.7	70.2
	Eu(Ⅲ)	7617.1	2475.6	568.3	118.0	68.5
	Gd(Ⅲ)	4779.6	1774.6	352.7	90.2	63.2
	Dy(Ⅲ)	1499.2	492.4	121.9	68.3	—
0.35M	Sm(Ⅲ)	8120.5	810.9	171.0	86.3	59.1
	Eu(Ⅲ)	7674.7	499.9	121.0	77.4	52.8
	Gd(Ⅲ)	3122.9	341.8	103.7	68.5	64.3
	Dy(Ⅲ)	820.6	158.2	100.0	52.5	50.2
0.40M	Sm(Ⅲ)	2550.6	794.2	155.6	56.5	32.4
	Eu(Ⅲ)	2174.9	434.1	106.6	46.6	37.2
	Gd(Ⅲ)	1452.5	283.3	59.3	32.0	25.4
	Dy(Ⅲ)	532.2	99.5	48.7	49.3	24.1

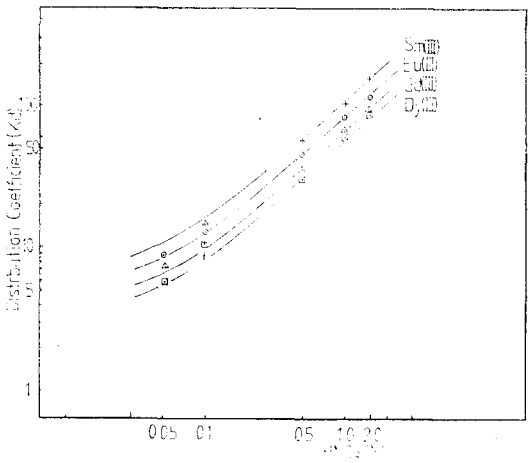

Fig. 1. Variation of Distribution Coefficient with Acid Molarity in Mixture of Nitric Acid and Methanol as 1/10 (v/v), Dowex AG 1 ×8 200-400 Mesh Size Resin

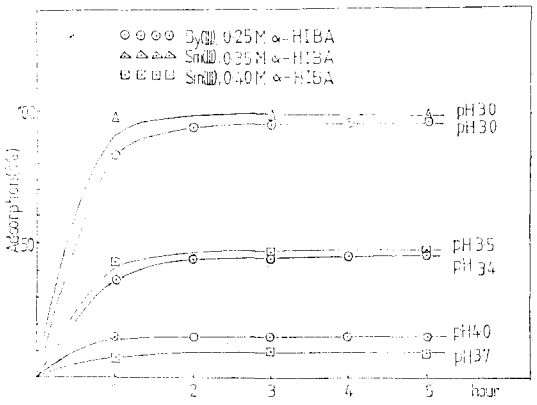

Fig. 2. Adsorption Percentage of Dy(III) and Sm(III) on Resin as Function of Time, Dowex 50w×8 100-200 Mesh Size Resin

pH of α-HIBA solution in cation exchange resin used. Figure 2 indicates that it takes about 4~5 hours to obtain an equilibrium and the data were useful for measurement of distribution coefficients. As in Table 1 and Fig. 2, adsorption of Dy(III), Sm(III), Gd(III) and Eu(III) on the resin depends on α-HIBA concentration and on pH of the solution. It was explained that complex stability of the element in α-HIBA solution[47] and NH^+_4 ion liberated by the increase of pH were main reason for this phenomena.[6] The optimum separation condition was obtained as in Fig. 3. In this experiment, Dy(III) and Sm(III) were completely separated from others while Gd(III) and Eu(III) were partially overlapped each other as shown in

Table 2. Elution of Ca(II) and Dy(III) with Hydrochloric Acid

elem. \ frac.* no		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
I	Ca(Ⅱ), μg	0	0	0	0	0	0	0	0	0	0	3.7	4.0	5.0	7.4	22.6	61.6	140	260	200	155
	Dy(Ⅲ), μg	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

elem. \ frac. no		21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
I	Ca(Ⅱ), μg	81.6	38.6	14.8	3.7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Dy(Ⅲ), μg	0	0	0	0	0	0	0.5	0.7	8	30	80	31	10	5	2	1.0	0	0	0	0

elem. \ frac.** no		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ⅱ	Ca(Ⅱ), μg	0	0	0.3	11.8	37.0	28.2	11.7	4.5	2.3	1.2	0	0	0	0	0	0	0	0	0	0
	Dy(Ⅲ), μg	0	0	0	0	0	0	0	0	0	0	0	80	20	0	0	0	0	0	0	0

Ⅰ, no 1-25 1.75M HCl
26-40 4.0M HCl * each fraction 25ml
Ⅱ, no 1-11 1.0M HCl
12-20 4.0M HCl ** each fraction 10ml

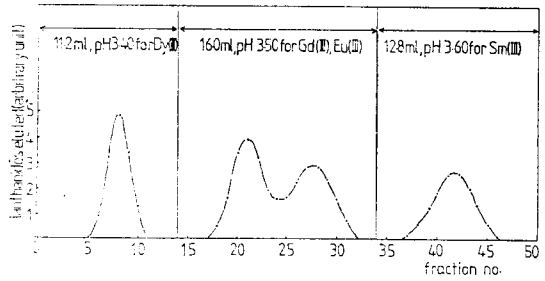

Fig. 3. Elution Curve for Dy(III), Gd(III), Eu (III) and Sm(III). Resin, Dowex 50w×8 100—200 mesh size. Resin bed, 6.3cm(l)× 0.38cm(id). Eluent, 0.40Mα-HIBA pHgradient. Flow rate, 0.05±0.002ml/min.

Figure 3. When lst separation column is used with 1.75M HCl solution, most of the cations except lanthanides, i.e., Fe(III), Ti(IV), Mg (II), Mn(II), U(VI) etc. are eluted at the same time or ahead of Ca(II).[42,43] Thus Ca(II) was to be chosen as a monitoring element in a group separation of lanthanides.[17,18,44,45] Table 2 indicates that Ca(II) and Dy(III) can be separated each other, and U(VI) was eluted far ahead of Ca(II) in lst and 2nd separation columns. When a large amount of uranium(VI) are present in the sample, 2nd separation column is required to separate all of lanthanides from uranium which is still remained in the tail portion of lst separation column. In a group separation of lanthanides, Zr, Hf, Ba and Sr are presumably eluted with lanthanides[42,43,45] but these elements could be isolated by individual separation.[48] Dy(III) was determined in sodium tungstate matrix with excitation at 275nm and measuring fluorescence at 478nm. When Dy(III) is mixed with same amount of Ho(III) and Tb(III), about 10% quenching effect is involved in analysis.[41] HFA is used as a chelating agent of Sm(III) and Eu(III). Sm(III)-HFA complex shows two fluorescence peak at 560nm and 600nm when excited at 330nm in HFA/TOPO layer. Detection limit is down to 6×10^{-2}ppm for Sm(III). When Eu (III) is present with Sm(III), absorption band at 600nm is interfered for the determination of Sm(III) due to very strong fluorescence intensity of Eu(III) at 615nm. Eu(III) alone can be determined using either 594nm or 615nm bands and its detection limit is further down to 1.6×10^{-4}ppm. Gd(III) content was calculated from combined absorption intensity, measured by Arsenazo-III colorimetry, of Gd(III) and Eu(III) using following equations because Gd (III) has low fluorescence sensitivity.[46]

$$A_{Eu}=a_{Eu}bc_{Eu}$$

$$A_{Gd}=a_{Gd}bc_{Gd}$$

Table 3. Recovery Yields of Synthetic Sample and Analysis Data of Magnesium Diuranate

elem.	recov.	synthetic sample						magnesium diuranate (ppm)
		1	2	3	4	5	recovery yields (%)	
Sm	added	10	2	2	2	2		
	found	9.29	1.71	2.05	1.93	1.74	92.9± 6.3	0.36±0.03
Eu	added	10	2	2	2	2		
	found	9.45	1.70	1.92	1.81	1.87	91.9± 3.9	0.18±0.01
Gd*	added	10	2	2	2	2		
	found	9.14	1.23	2.50	2.34	2.09	99.9±22.3	0.78±0.15
Dy	added	10	2	2	2	2		
	found	9.60	1.90	1.96	1.97	1.95	97.0± 1.3	0.40±0.01

unit μg * det. by Arsenazo-Ⅲ

$A_{tot.}=a_{Eu}bc_{Eu}+a_{Gd}bc_{Gd}$

Where, A is absorbance, a is molar absortivity, b is light path length and c is concentration. Recovery yields of lanthanides from synthetic sample and concentrations of four lanthanides in magnesium diurante (n=3) are summarized in Table 3. Table 3 shows that Gd determinations in both synthetic and magnesium diuranate sample have relatively larger standard deviations than those of other three because of using both fluorometry and colorimetry together. In the present work, trace amounts of Sm, Eu, Dy and Gd in uranium matrix could be analyzed by the cation exchange resin, spectrofluorometry and colorimetry.

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