≪Original≫ # Determination of Individual Lanthanide Elements by Neutron Activation Using a New Comparator Technique

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Abstract

The contents of the individual lanthanide elements are determined by neutron activation using a new comparator technique, which employs the short-lived radio-isotope of ^{56}Mn as a neutron flux monitor. The total rare earths are separated as a group from the monazite sample before irradiation. After irradiation the rare earths are separated from each other by gradient elution with ammonium alpha-hydroxyisobutyrate using a cation-exchange column. The contents of 14 individual rare earths, from lutetium to lanthanum, are determined.

요   약

중성자 선속 모니타로써 단 수명 방사성 동위원소인 ^{56}Mn 을 이용한 새로운 비교법 을 사용하여 모나자이트중에 함유된 개개 회토류원소의 함량을 중성자 방사화법으로 정량하였다. 전회토류원소를 군으로 분리하고 난 다음 중성자 조사를 하였으며 개개 회토류 원소는 양이온 교환수지통을 통하여 알파 하이드록써 부탈산으로 구배 용출시 킴으로서 분리하였다. 루데슘으로 부디 란타늄까지 14개의 회토류원소를 정량하였다.

1. Introduction

The present authors have reported the determination of three heavy lanthanide elements in monazite using the neutron activation[1]. This paper is the continuation of the previous work for the determination of the individual lanthanide elements in monazite, in this case fourteen elements, from lanthanum to lutetium, were determined.

The single comparator technique was proposed by Girardi[2] and was applied by Hoste[3] to the determination of rare earths in gadolinite and tantalocolumbite. In these methods, cobalt was used as a flux monitor. Girardi used the cobalt wire(1% Co, 9% Mg, and 90% Al). This method has the disadvantage that the cobalt wires are left to decay for about one day for the activity due to the reaction $^{27}Al(n, \alpha)$ ^{24}Na to decay. Hoste used the cobalt solution

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as flux monitor which is less convenient than the metal wire to handle. As an alternative we have studied the use of commercial iron wire(about 0. 05 cm dia. , obtained in the Korean market), which contains sufficient manganese to produce a short-lived ^{56}Mn activity. In the present work, the iron wire has been applied as a flux monitor to the determination of the rare earth elements.

2. Experimental

Reagents and Apparatus

One N and 3 N hydrochloric acid, A. R., which were standardized with 0. 1N sodium hydroxide solution. These solutions were stocked in the Pyrex glass bottles. If the soda glass bottles were used, potassium from soda glass seriously interferes because it is eluted between terbium and gadolinium peaks. The first cation exchange resin column, Dowex, 50W X8, 200-400 mesh, 6 cm long by 5 mm diameter, was used for the group separation of rare earths. The second cation exchange resin column, Dowex, 50W X8, -400 mesh, 13 cm long by 5 mm diameter, was used for the individual rare earth separation. The resin was previously washed in the following sequence, *i.e.*, 6 N hydrochloric acid, distilled water, 6 N nitric acid, distilled water, 6 N ammonium hydroxide, and finally with distilled water until alkali free.

A pH meter, Beckman, Zeromatic, a frac-

tion collector Instrumentation Specialities Company, and a well type scintillation counter, Tracerlab Versa/Matic V, were used. A 100 channel gamma ray pulse height analyzer, TMC 102 Model, Technical Measurement Corporation, was connected with 2″ x 2″ NaI(TI) crystal.

Rare Earths Standards

Stock solution of standard rare earths: About 100 mg of each rare earth oxides(spec. pure, Johnson and Matthey) were exactly weighed, dissolved in about 2 ml. of hot concentrated nitric acid, and finally diluted to ca. 1. 6 mg of rare earth oxides/ml.

Standard solution of individual rare earth: Two ml. of each standard rare earth stock solution were pipetted into a 25 ml of volumetric flask and diluted with water to the volume (80μg rare earth oxides/ml).

Standard solution of rare earth mixture: A portion of standard rare earth stock solution or individual rare earth standard solution was pipetted into a volumetric flask of 25 ml and diluted to the volume.

Separation of the Rare Earth Group

An appropriate amount of strontium nitrate, A. R., were weighed exactly and dissolved with distilled water, and about 0. 5 ml of this solution, 2 mg Sr/ml, were taken into a polyethylene vial of ca. 1 ml capacity.

The vial was irradiated for 10 min. in the nuclear reactor via pneumatic tube. 250λ of

Table I.   The γ-energies selected

Isotope	Half-Life	Selected Energy	Isotope	Half-Life	Selected Energy
^{177}Lu	6. 8 d	208 Kev	^{152}Eu	9. 2 hr	961 Kev
^{175}Yb	4. 2 d	396 Kev	^{153}Sm	46. 7 hr	103+70 Kev
^{170}Tm	127　d	84 Kev	^{149}Nd	1. 73hr	240+220+266 Kev
^{171}Er	7. 8 hr	296+308 Kev	^{142}Pr	19. 2 hr	1. 58 Mev
^{166}Ho	27. 3 hr	1. 36 Mev	^{143}Ce	33　hr	294 Kev
^{165}Dy	2. 35hr	361 Kev	^{140}La	40. 2 hr	1. 60 Mev
^{165}Tb	72　d	880+970 Kev			
^{159}Gd	18　hr	364 Kev	^{56}Mn	2. 58hr	845 Kev

Table II. Elution with I N hydrochloric acid

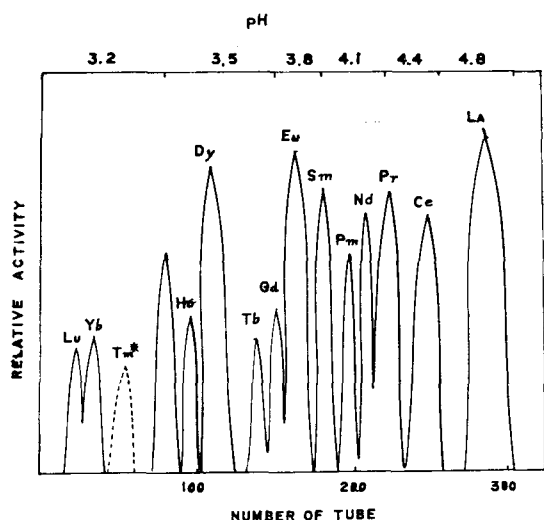| Element \ vol. of HCl (10ml)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Sr	0	0	0	0	0	0	0	0	4.1	20.1	41.1	24.9	6.4	2.6	0.6	0
Lu	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Fig. I. Elution curve of rare earths

*Tm curve, appeared in the case of the synthetic mixture

Sr solution which contains radioactive ^{87}Sr induced by the reaction ^{86}Sr(n, r) ^{87}Sr were loaded on the 1st cation exchange colum which has been pre-equilibrated by eluting with ca. 10 ml of 1N hydrochloric acid. This column was then eluted with 16 x 10 ml aliquots of 1 N hydrochloric acid. The elution rate was regulated by air compressor to 0. 33 ml/min.. Each eluate was analysed by counting the radioactivity with 2"×2" well type scinillation counter. The results, which are shown in Table II, indicate that strontium was not eluted before 80 ml of 1N hydrochloric acid, but that it was completely eluted with the additional 70 ml of 1N hydrochloric acid. In order to check the elution behavier of rare-earths, standard lutetium solution was prepared by dissolving appropriate amounts of lutetium oxide in concentrated nitric acid and by diluting with distilled water(1. 85 mg of Lu$_2$O$_3$/ml).

About 0. 5 ml of this solution was irradiated for 5 min. and 100λ of the irradiated solution containing ^{177}Lu, was loaded on the same resin column, which was then eluted with 1 N hydrochloric acid. Lutetium was not eluted with 150 ml of this solution as shown in Table II.

It has been reported that strontium(II) has the highest distribution coefficient after barium (II) among alkali and alkaline earth metals[4, 12] Therefore it is reasonable to expect that all these elements are completely eluted either before or together with strontium. Accordingly strontium was chosen as the tracer in this experiment. Since the distribution coefficients of rare earth elements on the cation exchange column decrease in the followieg sequence[12],

Table III. Counts of rare earth per min. per 10μg

Element	Counts of Synthetic Mixture	Counts of Pure Rare Earth (expected value)
Lu	3, 506($\pm$5. 6%)	3, 710($\pm$4. 2%)
Yb	683($\pm$8. 8%)	743($\pm$7. 6%)
Tm	244($\pm$5. 2%)	220($\pm$6. 0%)
Er	10, 862($\pm$6. 0%)	11, 514($\pm$5. 7%)
Ho	415($\pm$8. 4%)	380($\pm$9. 0%)
Dy	132, 105($\pm$8. 5%)	143, 702($\pm$7. 8%)
Tb	401($\pm$5. 5%)	378($\pm$4. 4%)
Gd	910($\pm$5. 6%)	961($\pm$7. 1%)
Eu	295, 510($\pm$9. 1%)	316, 905($\pm$5. 4%)
Nd	823($\pm$1. 0%)	820($\pm$1. 0%)
Sm	179, 780($\pm$1. 1%)	176, 680($\pm$2. 1%)
Pr	421($\pm$2. 1%)	430($\pm$1. 9%)
Ce	111($\pm$5. 4%)	117($\pm$5. 5%)
La	910($\pm$5. 6%)	961($\pm$2. 1%)

i.e., La^{+3}, Ce^{+3}, Pr^{+3}, Nd^{+3}, Pm^{+3}, ..., Tm^{+3}, Yb^{+3}, Lu^{+3}, and also from Table II which indicates that lutetium was not eluted by 150 ml of 1N hydrochloric acid, it was concluded that all the rare earth elements were not eluted from the column during the elution. The above results indicate that the whole elements which are contained in the monazite, with the exception of Th(IV) and rare earth elements(III), are eluted from the column with 150 ml of 1 N hydrochloric acid. The present authors have reported[5] that the rare earth elements can be separated from the thorium by eluting with 60 ml of 3 N hydrochloric acid.

Standardization of Rare Earth

About 0. 5 ml of each standard solution containing individual rare earth was taken into the polyethylene vial(capacity of 1 ml), which was then fused with a flame. The iron wire weighing about 10-15 mg was attached to the outside wall of the vial with the Scotch tape. The vial was irradiated for 1 hr. in the TRIGA MARK II reactor via the pneumatic tube. Neutron flux was about 3×10^{12} neutron cm^{-2} sec^{-1}. After irradiation, the exact amout, 100λ, of each irradiated solution were pipetted into a 25 ml volumetric flask and diluted to the volume with water. Using the gamma rays in Table I, the activity of each solution was measured with 100 channel analyzer. The irradiated iron wire was attached on the center of a aluminium plate and was measured with the analyzer under the 0. 84 Mev peak at about 2 hours after the end of irradiation. The activity of rare earth was corrected for the decay of two hours from the end of irradiation, and stand ardized against the activity of the manganese comparator. The corrected activity of each rare earth are shown in the 3rd column in Table III.

About 0. 5 ml of standard solution of rare earth mixture which was prepared as described above was irradiated along with iron wire in

Table IV. Rare earths contents in Koksung monazite

Element	1st Determination(%) (a)	2nd Determination(%) (b)	The Previous Results(%)
Lu	0. 0099(±3. 1%)	0. 0096(±2. 9%)	0. 0065[1]
Yb	0. 083 (±4. 8%)	0. 079 (±5. 2%)	0. 040[1]
Tm	—	≤0. 006	
Er	0. 12 (±4. 8%)	0. 11 (±5. 3%)	
Ho	0. 084 (±6. 7%)	0. 096 (±3. 0%)	
Dy	0. 44 (±3. 5%)	—	0. 54[1]
Tb	0. 12 (±9. 2%)	0. 099 (±8. 9%)	
Gd	1. 4 (±7. 7%)	1. 3 (±5. 0%)	
Eu	0. 074 (±3. 0%)	0. 079 (±4. 2%)	
Sm	1. 6 (±14%)	1. 2 (±12. 5%)	
Nd	9. 9 (±1. 0%)	—	
Pr	2. 3 (±4. 2%)	2. 5 (±2. 5%)	
Ce	28 (±3. 6%)	29 (±3. 5%)	22. 0[1]
La	10. 0 (±1. 0%)	9. 9 (±2. 1%)	

(a) 250λ(1. 65 mg) of rare earth sample were taken.
(b) 2 ml(13. 20 mg) of rare earth sample were taken.

the identical condition. After irradiation, the exact amount, 100λ, of the irradiated solution of synthetic rare earth mixture was loaded on the second ion exchange column. The column was eluted sequentially with 0. 25 M alpha-hydroxyisobutyrate solution at controlled gradient pH as follows; 16. 8 ml at pH 3. 20, 16. 8 ml at pH 3. 50, 9. 60 ml at pH 3. 80, 6. 60 ml at pH 4. 40. and 10. 0 ml at pH 4. 70. During the elution, air compessor was applied to maintain the elution rate to 0. 3 ml per min.

The eluate in fraction of 6 drops was taken into the test tube by means of the fraction collector. The activity of each tube was measured for 30 seconds with a well type scintillation counter, and was plotted against the number of the test tube as shown in Fig. I. The eluted portion of each rare earth was collected into a volumetric flask of 25 ml. Each test tube was washed three times with

water and the washed solutions were added to each volumetric flask, and the content of the flask was diluted to the volume. Each solution in the volumetric flask was measured with 100 channel analyzer. The counts were corrected for the decay of two hours from the end of irradiation. Neutron flux variation was corrected with the activity of iron wire which was measured similarly with 100 channel analyzer. A correction was also made for the loss of each activity of Lu, Yb, and Gd under the respective interferring peak as described below under the section of "Separation of Individual Rare Earth". The corrected activity of rare earth mixture solution are shown in the second column of Table III.

Separation of Individual Rare Earth

As shown in Fig. I, a cross contamination of lutetium and ytterbium was observed when eluted with 0. 25 M alpha-hydroxyisobutyrate at pH 3. 20. A correction was made for lutetium activity lost under the ytterbium peak and also for ytterbium activity lost under lutetium peak respectively according to the method by Said[6] and Hoste[7]. The fractional recoveries obtained for letetium and ytterbium were 0. 91 and 0. 98 respectively. The separation of thulium was complete at pH 3. 20.

In order to elute erbium, pH was increased to 3. 50. At this pH, erbium, holmium, dysprosium and terbium were separated from each other quantitatively. When the elution peak of gadolinium began to appear, pH was increased from 3. 50 to 3. 80. At this pH the separation of gadolinium from europium was nearly complete. A small correction was thus made by the above method for Lu and Yb. The fractional recovery of gadolinium was 0. 98. A slight contamination of europium in gadolinium portion was estimated by repeating measurement and thus the gadolinium activity was graphically determined. Europium lost under the gadolinium peak was negligibly small.

After eluting europium at pH 3. 80, pH was increased to pH 4. 10 for the quantitative separation of samarium, promethium, and neodymium, While praseodymium was being eluted, pH was increased to 4. 40 in order to separate praseodymium and cerium. After elution of cerium, pH was finally increased to 4. 70 for the separation of lanthanum.

Determination of Rare Earths in Sample (1)

About 0. 1g of the finely ground monazite (dried at 110°C) was accurately weighed into a platinum crucible fitted with a cover. The content was digested with 1 ml of concentrated sulfuric acid for 3 hours on hot plate at ca. 250°C. When cool, the digested mass was quantitatively transferred with a jet of water into a 150 ml beaker containing ca. 60 ml of water. The solution was filtered into a 100 ml volumetric flask through a hardened filter (Whatman No. 542) using gentle suction. The clear filtrate was diluted to 100 ml with water. 50 ml of the solution were loaded on the first column for the group separation of rare earths. The whole elements, except rare earths and thorium, were eluted out by eluting the column with 150 ml of 1 N hydrochloric acid. The rare earth were then eluted with 60 ml of 3 N hydrochloric acid and the eluate was collected into a 100 ml beaker. The solution was evaporated to near dryness under an infrared lamp. The residue was digested with 1 ml of concentrated nitric, acid, and the digested solution was evaporated to near dryness. The digestion and evaporation were repeated once more. Finally the residue was dissolved with distilled water. The solution was transferred quantitatively into a 10 ml volumetric flask and diluted to the volume. About 0. 5 ml of above sample solution was taken into a ca. 1 ml polyethylene vial. A weighed iron wire was attached on the outside wall of the vial. The vial was irradiated for 1 hour in the identical condition as described

under the section of "Standardization of Rare Earths". The exact amout, 250λ, of the irradiated rare earth sample solution were loaded on the second resin column for the individual separtion of rare earths. The column was then eluted as described above under "Standardization of Rare Earts". Each test tube was counted for 30 sec. and an elution curve was obtained as Fig. I by plotting the activity of each test tube vs. the test tube number. The eluted portions of each rare earth were collected into a 25 ml volumetric flask and the activity was counted with 100 channel analyzer at the respective γ-energy as described in Table I. The content of each rare earth in monazite sample was calculated by comparing the activity of each rare earth with the corresponding value in the second column of Table III. The rare earth contents thus obtained are shown in the second column of Table IV.

Determination of Rare Earths in Sample (2)

In the present work 250λ of the irradiated solution(1. 65 mg of monazite) were used for the determination of rare earth content as described under the section of "Determination of Rare Earths in Sample(1)". As the result of this, thulium activity was too low to be detected, while the other rare earths showed enough activities for the quantitative determination. In order to determine thulium, the following experiments were made.

About 2 ml of monazite sample solution in a 3 ml polyethylene vial were irradiated along with the iron wire comparator in the identical condition. The exact amout, 2 ml(13. 20 mg of monazite), of the irradiated sample solution, which contains 8 times larger amount of rare earths than in the previous case, were pipetted into a test tube. About 0. 2 ml of a slurry of purified Dowex, 50W X 8, —400 mesh, was added to the sample solution. Several minutes were taken for the rare earths to be adsorbed and for the resin to settle. The resin was with-

drawn with a transfer pipette taking as little solution as possible, and transferred to the liquid above the second column which was pre-equilibrated with 0. 25 M alpha-hydroxyisobutyrate at pH 3. 20. The added resin was swirled to ensure uniform settling. These adsorption and transfer steps, which are similar to the method by Marsh[9], were repeated twice with the additional small portions of resin. After thesesteps, no activity was detected in the sample solution, thus confirmed the complete trans ferrance of rare earths to the column. The contents of rare earths in monazite were calculated as described above and are shown in the third column of Table IV.

3. Results and Discussion

Massart and Hoste[3] have reported the radioactivation analysis of rare earths using ^{60}Co as a single comparator. This method requires that, for identical irradiation time, the same ratio between the activities of the comparator and the individual rare earths should always be obtained. Since the excitation functions of the rare earths and the comparator are not identical, this can only be the case if the neutron spectrum is constant over the whole series of irradiations. In the present work, the iron wire was used as the comparator, which homogeneously contains sufficient manganese to produce a suitable ^{56}Mn activity as desribed in the previous report[8]. Therefore, the errors induced by shifts in the neutron spectrum depend on the fraction of the total activation due to epithermal activation of the manganese comparator and the rare earths[4]. This fraction is represented by the cadmium ratio. The higher the differences of cadmium ratios between rare earth and the manganese comparator, the larger will be the error.

In order to evaluate the validity as well as the over-all precision of the present method using the manganese comparator was experimentally proved as described above under the

section of "Standardization of Rare Earths".

The extreme percentage difference over 4 determinations are given in Table III. As shown in this Table, the data in the second and third column are well agreed each other within the experimental errors. From these agreements it may be concluded that the iron wire could be used as a single comparator, and also that the precision of the present method for the determination of individual rare earth element is satisfactory. From this agreement it may also be concluded that the possible errors, *i. e.*, from the self shielding effect and from the interferring nuclear reaction such as $^{176}Yb(n, \beta: \gamma)$ ^{177}Lu are negligibly small.

As shown in the Table IV, two values in the second and third column, *i. e.*, one determined using $250\lambda(1.65$ mg of monazite) and another determined using 2 ml(13.20 mg of monazite), also showed a good ageement each other. Although the precision of the present method was confirmed once again by this agreement, thulium was still not detected in this experiment.

Therefore, the thulium content seems to be less than 0.006% by the following calculation as described by Curie[10]. $Ld=2.71+4.655\mu_B$, where μ_B is the limiting mean of blank.

^{90m}Y nuclide which could be produced from yttrium by $^{89}Y(n, \gamma)$ ^{90m}Y reaction was not detected in this work. It is thought that yttrium is eluted in the same eluting fraction of dysprosium and that the higher activity of dysprosium completely covers the ^{90m}Y activity,

The possible interference of the fission products from uranium and thorium in the sample could give rise to positive error in the rare earth determination. In the present work, however, these two elements have been separated prior to irradiation.

References

1) K. S. Chung and C. Lee, J. Nucl. Sc., Korea 5, 53–57 (1965)

2) F. Girardi, G. Guzzi and J. Pauly, Anal. Chem. 37, 1085 (1965)

3) D. L. Massart and J. Hoste, Anal. Chim. Acta 42, 21–28 (1968)

4) F. W. E. Strelow, Anal. Chem. 32, 1185 (1960)

5) C. Lee and K. S. Chung, J. Korean Chem. Soc. 15, 5–9 (1971)

6) A. S. Said, J. Gas Chromatog. 2, 60 (1964)

7) D. L. Massart and J. Hoste, Anal. Chim. Acta 12, 15–20 (1968)

8) M. Sanker Das, W. I. Kim and C. Lee, Int. J. Appl. Radiation and Isotopes, 20, 746–747 (1969)

9) S. F. Marsh, Anal. Chem. 39, 641–645 (1967)

10) L. A. Currie, Anal. Chem. 40, 586–593 (1968)

11) K. S. Chung, Ph. D. Thesis, Univ. of Liverpool, England, 1962.

12) The Rare Earths, *ed.* by F. H. Spedding and A. H. Daane, p 58, John Wiley and Sons, *Inc.* 1961.