X-Ray Spectroscopic Determination of Lanthanum, Neodymium and Gadolinium in the Presence of Other Rare Earth Elements.

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(Received January 10, 1938.)

As is known, the separation of the rare earth elements from one another is, except cerium, so difficult and tedious that the usual chemical methods of analysis fail entirely when applied to the quantitative determination of each component in a rare earth mixture. Although some indirect methods proposed may be used for the analysis of a rare earth mixture of only a few components, most of them can not be applied to a complex mixture of the rare earths such as extracted from a natural mineral. The only reliable one that can be used even in such a case may be probably the X-ray spectroscopic method.[1]

(1) cf. A. Hadding, *Z. anorg. allgem. Chem.*, **122** (1922), 195; V.M. Goldschmidt and L. Thomassen, "Geochemische Verteilungsgesetze der Elemente," III, Kristiania (1924); P. Günther and G. Wilcke, *Z. physik. Chem.*, **119** (1926), 219; H. Schreiber, *Z. Physik*, **58** (1929), 619; P. Günther, A. Kotowski, and H. Lehl, *Z. anorg. allgem. Chem.*, **200** (1931), 287; I. Noddack, *Z. anorg. allgem. Chem.*, **225** (1935), 337; E. Minami, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, Fachgruppe IV, N.F. **1** (1935), 155.

The present author intends to estimate the amount of each of the rare earth elements in their mixture by comparing the intensity of their X-ray spectral lines with that of the reference elements. The method is in its principle quite similar to the one which was first proposed and investigated by G. von Hevesy, D. Coster, Y. Nishina and others[2] for the determination of hafnium content in zirconia-hafnia mixtures. The experimental results obtained with lanthanum, neodymium and gadolinium will be given in the present report.

The Determination of Lanthanum.[3]

For the determination of lanthanum in a mixture of the rare earths, the intensity of the $L\beta_2$ line of lanthanum is compared with that of the $L\beta_3$ line of cerium which is taken as the reference element. As the wavelength difference of the said two lines is only 8 X-Units, which corresponds to about 0.5 mm. on the photographic plate, the error of the estimation of the relative intensities due to the wrong exposure is practically eliminated.

Although cerium is an element that belongs to the rare earth group, it is comparatively easy to separate cerium alone from other rare earth elements by some chemical methods,[4] and there is no difficulty in ascertaining its amount present in a given sample, or in preparing a sample free from it. Since cerium can be completely precipitated from a solution with other rare earth elements in the form of hydroxide or oxalate, thorough mixing of the sample with the added reference substance can be easily attained without that tedious procedure of weighing and grinding which we have to follow when an element of quite different chemical properties is taken as the reference.

To a given sample of rare earth mixture is added a known quantity of cerium oxide, or lanthanum oxide if the cerium line of the original sample is stronger. The quantity added is to be varied until the two lines under consideration show an equal intensity on the photographic plate. If we know the concentration ratio CeO_2/La_2O_3 which makes the said two lines equally intense, we can easily calculate the amount of lanthana in the original sample from that of ceria present.

The actual procedure followed is given below.

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(2) Hevesy and Coster, *Nature*, **111** (1923), 182; Coster, *Chem. News*, **127** (1923), 65; Coster and Nishina, *ibid.*, **130** (1925), 149; Kimura, *Z. physik. Chem.*, **128** (1927), 394.

(3) Read before the Chemical Society of Japan, April 3, 1930 and July 11, 1931, and published in Japanese in *J. Chem. Soc. Japan*, **54** (1933), 213.

(4) e.g. C. James and L. A. Pratt, *J. Am. Chem. Soc.*, **33** (1911), 1326; Paul H.M.-P. Brinton and C. James, *ibid.*, **41** (1919), 1080.

Materials and Experimental Procedure. The intensity of the lanthanum $L\beta_2$ line was compared with that of the cerium $L\beta_3$ line by using the oxide mixtures of lanthanum and cerium. The mixtures were prepared from cerium chloride and lanthanum chloride, which had been carefully purified, the former by the bromate method, the latter by the fractionation.

The high purity of the cerium salt used was shown by the X-ray spectroscopic analysis. It did not contain the detectable amount of any of other lanthanide elements.

It was also revealed by the X-ray method that the lanthanum salt prepared was free from neodymide elements. Although a few spectral lines of cerium and praseodymium were observed very faintly on the plate, the $L\beta_3$ line of cerium was not detected under the same experimental conditions that were followed in the case of the comparison of the relative intensities of the said two lines. Besides, the absorption bands due to some other rare earth elements were not observed with the concentrated solution of the lanthanum chloride used. Both the hydrogen peroxide test and the iodate test failed also to show the presence of cerium in it. Therefore, for the present purpose, the material may be assumed to be a pure lanthanum salt.

Solutions with appropriate known concentrations of lanthanum chloride and of cerium chloride were prepared. The proper volumes of each solution were pipetted and mixed thoroughly. By the addition of ammonium chloride and ammonia, the hydroxides of lanthanum and cerium were precipitated from the solution, filtered off, and ignited to oxides, which were used as a standard sample for the comparison of the relative intensities of the lanthanum $L\beta_2$ and the cerium $L\beta_3$ lines.

When a sample to be analysed was given, a mixture that could be used for the X-ray analysis was prepared from it by the following procedure. The original sample, if it consisted of rare earths only, was dissolved in dilute hydrochloric acid after fusion with sodium bisulphate if necessary, and a solution with the known concentration was prepared. But, if it contained some other elements which were precipitated with ammonia, the rare earths should be first extracted from it. By precipitation with oxalic acid, the rare earth elements and thorium could be separated from the other members of the analytical group of ammonia, such as iron, aluminium, zirconium, uranium, etc. Thorium in the oxalate precipitate was removed by applying the hydrogen peroxide method and thus a solution which contained the rare earth elements only was obtained. After the determination of the contents of cerium and total rare earth elements of the solution thus prepared, a definite volume of it was pipetted. To

it was added a known amount of the solution of cerium chloride, or that of lanthanum chloride according to the ratio CeO_2/La_2O_3 of the original sample. From this solution, the hydroxides of the rare earth elements were precipitated by the addition of ammonia, filtered off, and ignited to oxides.

With the oxide mixture thus prepared, the lanthanum $L\beta_2$ and the cerium $L\beta_3$ lines were photographed, using a metal X-ray tube and a vacuum spectrograph of Siegbahn's type. Calcite was used as the crystal. The width of the slit of the spectrograph was about 0.1 mm. The sample was put on the copper plate of the anticathode, which had been changed before each exposure. The X-ray lines were excited by cathode rays from the hot cathode of tungsten wire. The photograph was taken by 41 minutes' exposure at the applied tension of 15 kilo-volts (effective) and the current of about 2 milliamperes. During the exposure, the crystal was slowly rotated through an angle of 0.2 degree.

The spectral lines on the plates were examined under the magnifying glass. Instead of estimating the intensity ratio of the two lines under consideration, the quantity of the element added was varied until the said two lines became equally intense.

The photograph was taken repeatedly with the same sample, and the reproducibility of experiments was confirmed.

Experimental Results. (a) The relative intensities of the lanthanum $L\beta_2$ and the cerium $L\beta_3$ lines were compared by using $La_2O_3 - CeO_2$ mixtures as the samples. In Table 1 are given the results obtained, from which we know that the two lines under consideration show an equal intensity when the ratio CeO_2/La_2O_3 in weight is equal to 2.5(5).

(b) The presence of other rare earth elements might have some effects on the value of the balance ratio which was just determined to be 2.55 in the case of the mixture of lanthanum oxide and cerium oxide.

For the disturbing effects of a third element present in a sample, the following four cases were mentioned by G. von Hevesy[5]: (i) the case when a third element present has a stronger absorption effect on the line of longer wave-length; (ii) the case when a third element present has an absorption edge situated between the two lines to be compared; (iii) the case when a line of a third element present is situated between the absorption edges which correspond respectively to the two lines under comparison; (iv) the case when a line of a third element present lies near and on the short wave-length side of the absorption edges above mentioned.

(5) Hevesy, "Chemical Analysis by X-Rays and its Applications," 117, New York (1932).

In the present case there is no element of the rare earth group which has the absorption effects mentioned in (i) and (ii). As the wave-length difference of the absorption edges corresponding to the two lines to be compared is fairly large, some rare earth elements which have the excitation effects mentioned in (iii) and (iv) may come into consideration. But, as is seen in the following examples, these disturbing effects, if there be any, are generally very small and may be neglected in actual analyses.

Table 1.

CeO_2/La_2O_3 in weight	Intensity of La $L\beta_2$ compared with Ce $L\beta_3$
3.69	Weaker
3.06	Weaker
2.92	Weaker
2.81	Weaker
2.70	Weaker
2.65	Weaker
2.61	A little weaker
2.60	A little weaker
2.59	A little weaker
2.55	Nearly equal
2.54	Nearly equal
2.50	A little stronger
2.45	Stronger
2.39	Stronger
2.37	Stronger
2.20	Stronger
1.97	Stronger
1.80	Stronger
1.79	Stronger
0.87	Stronger

(c) As the examples, the amount of lanthanum oxide in several samples was determined. Sample No. 1 mainly consisted of the oxides of lanthanide elements of lower atomic numbers and was free from ceria. Sample No. 2 was a mixture of cerium earths, rich in neodymium and praseodymium. The amount of ceria in it was determined to be 29.35%. Sample No. 3 contained 49.6% of ceria, and less than 10% of yttrium earths; the remainder was cerium earths rich in neodymium. Sample No. 4 was a mixture of the rare earths; it contained 22.2% of ceria and about 10% of yttrium earths. It was rich in samaria.

Cerium oxide was added to Samples No. 1, No. 2, and No. 4, while lanthanum oxide was added to Sample No. 3 which was already rich in ceria. The relative intensities of the lanthanum $L\beta_2$ and the cerium $L\beta_3$ lines were compared with the results shown in Table 2.

Table 2.

(1) Sample No. 1.

$\frac{CeO_2 \text{ added}}{\text{Sample taken}}$ (%)	Intensity of La $L\beta_2$ compared with Ce $L\beta_3$
114	Stronger
120	Stronger
128	Nearly equal
137	Weaker
139	Weaker

(2) Sample No. 2.

$\frac{CeO_2 \text{ added}}{\text{Sample taken}}$ (%)	Intensity of La $L\beta_2$ compared with Ce $L\beta_3$
8.6	Weaker
7.7	Nearly equal
5.45	Nearly equal
3.9	Nearly equal
2.8	Stronger
2.5	Stronger
0.0	Stronger

(3) Sample No. 3.

$\frac{La_2O_3 \text{ added}}{\text{Sample taken}}$ (%)	Intensity of La $L\beta_2$ compared with Ce $L\beta_3$
44.3	Stronger
22.2	Stronger
17.7	Nearly equal (a little stronger)
15.5	Nearly equal
8.2	Weaker
4.4	Weaker
0.0	Weaker

(4) Sample No. 4.

$\frac{CeO_2 \text{ added}}{\text{Sample taken}}$ (%)	Intensity of La $L\beta_2$ compared with Ce $L\beta_3$
0.0	Stronger
2.29	Weaker
4.57	Weaker

If the balance ratio 2.55 which was determined with $La_2O_3-CeO_2$ mixtures also held true of these samples, the amount of the lanthanum oxide present in them might be easily calculated. Thus, the amount of the lanthanum oxide present in Sample No. 1 would be 128/2.55%, that in Sample No. 2, (5.45 + 29.35)/2.55%, that in Sample No. 3, (49.6/2.55 − 16)%, that in Sample No. 4, (22.2 + 2.29/2)/2.55%. But, if the presence of other rare earths had some disturbing effects, the value of the balance ratio which could be used for each sample respectively should be determined.

To know the effects of the other rare earth elements present and to determine the balance ratio for each sample, the following method which was similar to the one proposed by the present author[6] in the case of

(6) Kimura, *Z. physik. Chem.*, **128** (1927), 394.

the determination of hafnia in a mixture of the oxides of the elements precipitated by ammonia was tried.

Let x denote the percentage of lanthanum oxide to be determined, then

$$\frac{a}{x} = k \qquad (1),$$

where a is the amount of cerium oxide required to make the two lines under comparison equally intense, and k is the balance ratio CeO_2/La_2O_3 yet unknown.

To the sample is added first a known quantity of lanthanum oxide, and then cerium oxide is added until the lanthanum $L\beta_2$ and the cerium $L\beta_3$ lines again show an equal intensity. Let b denote the amount of lanthanum oxide added to the sample, and c, the amount of cerium oxide required to make the said two lines equally intense after the addition of b of lanthana. Then,

$$\frac{c}{x+b} = k \qquad (2).$$

From (1) and (2), we get

$$k = \frac{c-a}{b} \qquad (3).$$

If the value of k thus obtained were equal to or nearly equal to 2.55, i.e. the balance ratio determined with the oxide mixture of lanthanum and cerium, then the effects of the other rare earth elements in the sample should be negligible. If the value of k from (3) were different from 2.55, then we could use that value as the balance ratio special to the sample and thus the effects of the other rare earths could be eliminated automatically.

The value of k thus obtained for each sample is shown in Table 3.

Table 3.

Sample	a (%)	b (%)	c (%)	k found
No. 1	128	33.0	214	2.61
No. 2	34.8	9.9	59.7	2.52
No. 3*	49.6*	10.6*	76.2	2.51
No. 4	23.4	6.0	38.2	2.48

* Instead of x, $x+16$ was used.

As was seen from Table 3, the value of k thus found agreed with the balance ratio previously obtained for the mixtures of lanthanum oxide and cerium oxide within the error of experiments. Thus, the disturbing effects were almost negligible in these cases.

The amount of lanthanum oxide found by using the value of the balance ratio, k, obtained for each sample was given in Table 4 together with the amount determined by assuming it to be 2.55.

Table 4.

Sample	k	La_2O_3 (%)	La_2O_3 (%) $_{k=2.55}$
No. 1	2.61	49	50
No. 2	2.52	13.8	13.6
No. 3	2.51	3.8	3.5
No. 4	2.48	9.4	9.2

The Determination of Neodymium.[7]

For the determination of neodymium in a mixture of the rare earths, the intensity of the $L\alpha_1$ line of neodymium is compared with that of the $L\beta_1$ line of cerium, which is taken as the reference element. As the wavelength difference of the said two lines is only 14 X-Units, which corresponds to about 0.9 mm. on the photographic plate, the error of the estimation of the relative intensities due to the wrong exposure is practically eliminated.

Materials and Experimental Procedure. The relative intensities of the neodymium $L\alpha_1$ and the cerium $L\beta_1$ lines were compared by using the oxide mixtures of neodymium and cerium, which were prepared from their chlorides.

The solution of the cerium chloride which was prepared for the experiments with lanthanum was also used here. As for neodymium salt, two different samples were used, the one contained no lanthanide element except the negligible amount of lanthanum and cerium, the other, no lanthanide element except a trace of praseodymium. The amount of impurities was so small in both cases that they might be assumed for the present purpose to be pure neodymium salts.

(7) Read before the Chemical Society of Japan, June 14, 1930 and July 11, 1931, and published in Japanese in *J. Chem. Soc. Japan*, **54** (1933), 220.

As the procedure to prepare a sample to be put on the anticathode was quite similar to the one given already in the part of lanthanum of this report, its description will be omitted here. It must be mentioned only that the mixtures of the rare earths free from thoria and other oxides were used as the samples throughout this work.

The experimental conditions for the exposure were also the same as in the previous case, i.e. the photograph was taken by 41 minutes' exposure at the applied tension of 15 kilo-volts (effective) and the current of about 2 milliamperes.

Experimental Results. (a) With the oxide mixtures of neodymium and cerium, the relative intensities of the neodymium $L\alpha_1$ and the cerium $L\beta_1$ lines were compared. In Table 5 are shown the results obtained, from which we know that the two lines under consideration become equally intense when the ratio CeO_2/Nd_2O_3 in weight is equal to 0.71.[8]

Table 5.

CeO_2/Nd_2O_3 in weight	Intensity of Nd $L\alpha_1$ compared with Ce $L\beta_1$
1.98	Weaker
1.85	Weaker
1.76	Weaker
1.13	Weaker
0.99	Weaker
0.895	Weaker
0.804	Weaker
0.802	Weaker
0.710	Nearly equal
0.708	Nearly equal
0.702	Nearly equal
0.607	Stronger
0.503	Stronger
0.496	Stronger
0.401	Stronger

(b) It is somewhat peculiar that the balance ratio is less than unity. According to the experiments carried out by Y. Nishina and the

(8) The intensity ratio of the said two lines was also estimated by a microphotometer. In this case a little higher value 0.78 was obtained as the balance ratio CeO_2/Nd_2O_3.

present author, in which the intensity of the $L\beta_1$ line of a rare earth element of even atomic number was compared with that of the $L\alpha_1$ line of the element of atomic number higher by two by using the mixtures of the oxides of the two elements under consideration, the amount of the former element was generally greater than that of the latter when the said two lines showed an equal intensity. For examples, the balance ratio Gd_2O_3/Dy_2O_3 was equal to 2.1 for the gadolinium $L\beta_1$ and the dysprosium $L\alpha_1$ lines, the balance ratio Sm_2O_3/Gd_2O_3 was 2.5 for the samarium $L\beta_1$ and the gadolinium $L\alpha_1$ lines, and the balance ratio Nd_2O_3/Sm_2O_3 was 1.8 for the neodymium $L\beta_1$ and the samarium $L\alpha_1$ lines.

Only for the cerium $L\beta_1$ and the neodymium $L\alpha_1$ lines, as was shown by the experiments mentioned above, the balance ratio CeO_2/Nd_2O_3 was less than unity. The origin of this singular result might be traced back to the rapid disappearance of neodymium atoms from the surface layer of the anticathode spot compared with cerium atoms under the bombardment of the cathode rays. To ascertain this, the photographic plates different in time of exposure were compared. The plates taken with the samples remained on the anticathode after the bombardment of the cathode rays were also compared with the regular one. The tendency that the intensity ratio changed in favour of the cerium $L\beta_1$ line with the time of exposure was observed sometimes when the plates quite different in time of exposure were compared. But, the effect was not so clear as seen in the case of the comparison of the relative intensities of the barium $L\alpha_1$ and the titanium $K\alpha_1$ lines, investigated by M. Ishibashi.[9]

(c) The experiments were also carried out to know the effects of the presence of other rare earth elements. The absorption effects are expected by no element of the rare earth group. As for the excitation effects, only samarium and terbium may be mentioned. But as is seen in the following examples these effects are, if there be any, very small.

The following three samples were taken for the examples: Sample No. 5 mainly consisted of the oxides of lanthanide elements of lower atomic numbers and free from ceria; Samples No. 1 and No. 4 were the same as those which were used in the case of lanthanum.

Cerium oxide was added to Samples No. 1 and No. 5, while neodymium oxide was added to Sample No. 4 which was already rich in ceria.

The relative intensities of the neodymium $L\alpha_1$ and the cerium $L\beta_1$ lines were compared with the results shown in Table 6.

If the balance ratio 0.71 which was determined with $Nd_2O_3-CeO_2$ mixtures also held true of these samples, the amount of the neodymium

(9) Ishibashi, *Z. anorg. allgem. Chem.*, **202** (1931), 372.

Table 6.

(1) Sample No. 1.

CeO_2 added / Sample taken (%)	Intensity of Nd $L\alpha_1$ compared with Ce $L\beta_1$
34.19	Weaker
31.63	Weaker
30.74	Weaker
23.09	Weaker
20.70	Nearly equal (a little weaker)
18.89	Nearly equal (a little stronger)
11.40	Stronger

(2) Sample No. 5.

CeO_2 added / Sample taken (%)	Intensity of Nd $L\alpha_1$ compared with Ce $L\beta_1$
32.82	Weaker
26.47	Weaker
25.47	Weaker
22.70	Weaker
20.40	Weaker
18.21	Weaker
18.11	Weaker
16.40	Weaker
15.04	A little weaker
14.29	A little stronger
13.99	Stronger
13.74	Stronger
13.63	Stronger
11.82	Stronger
11.76	Stronger

(3) Sample No. 4.

Nd_2O_3 added / Sample taken (%)	Intensity of Nd $L\alpha_1$ compared with Ce $L\beta_1$
41.2	Stronger
25.5	A little stronger
23.1	A little weaker
20.6	Weaker
16.5	Weaker

oxide in them might be found by simple calculation. Thus, the neodymia content in Sample No. 1 would be $(20.70 + 18.89)/2 \times 0.71\%$, that in Sample No. 5, $(15.04 + 14.29)/2 \times 0.71\%$, and that in Sample No. 4, $\{22.2/0.71 - (25.5 + 23.1)/2\}\%$.

To see the effects of the presence of the other rare earths, the value of the balance ratio was determined for each sample by the method described in the case of lanthanum. The results obtained are shown in Table 7, where a denotes the amount of cerium oxide required to make the two lines under comparison equally intense, b, the amount of neo-

Table 7.

Sample	a(%)	b(%)	c(%)	k found
No. 1	19.8	64.13	66.28	0.73
No. 5	14.7	12.84	23.91	0.72
No. 5	14.7	25.67	32.86	0.71
No. 4*	22.2*	12.0*	30.2	0.67

* Instead of x, $x+24.3$ was used.

dymium oxide added to the sample and c, the amount of cerium oxide required to make the said two lines again equally intense after the addition of b of neodymia.

As was seen from Table 7, the value of k thus found agreed with the balance ratio obtained for the mixtures of neodymium and cerium oxides within the error of experiments.[10] Thus, the disturbing effects of the other rare earths were not observed in these cases. In Table 8, the amount of neodymium oxide found by applying to k the value obtained from the above experiments was compared with that calculated by assuming it to be 0.71.

Table 8.

Sample	k	$Nd_2O_3(\%)$	$Nd_2O_3(\%)_{k=0.71}$
No. 1	0.73	27.	28.
No. 5	0.72	20.	21.
No. 5	0.71	21.	21.
No. 4	0.67	8.8	7.0

The Determination of Gadolinium.[11]

For the determination of gadolinium in a mixture of the rare earths, the intensity of the $L\alpha_1$ line of gadolinium is compared with that of the $L\beta_2$ line of neodymium, which is taken as the reference element. As the wave-length difference of the said two lines is only 10.5 X-Unites, which corresponds to about 0.7 mm. on the photographic plate, the error of the estimation of the relative intensities due to the wrong exposure is practically eliminated.

The neodymium content of a sample given should be previously estimated by the method described already in this report.

Materials and Experimental Procedure. The intensity ratio of the gadolinium $L\alpha_1$ and the neodymium $L\beta_2$ lines was determined with the mixtures of oxides of gadolinium and neodymium, which were prepared from their chlorides. Gadolinium chloride which did not show the presence of other lanthanide elements by the X-ray spectroscopic method was used for this work. The purity of neodymium chloride used was already given in the part of neodymium of the present report.

(10) The relatively low value of k found in the case of Sample No. 4 might be due to the excitation effect of samarium which was richly present in the sample, although it could not be yet confirmed.

(11) In collaboration with Mr. Yoshio Tsunoda. Read before the Chemical Society of Japan, July 14, 1934, and published in Japanese in *J. Chem. Soc. Japan*, **56** (1935), 81.

As the procedure of preparation of a sample to be put on the anti-cathode was quite similar to the one given already in the case of lanthanum, the description of it will be omitted here. It must be only mentioned that the mixtures of the rare earths free from thoria and other oxides were used throughout this work.

The apparatus used was the same as that described before. The photograph was taken by 41 minutes' exposure at the applied tension of 16 kilo-volts (effective) and the current of 2–5 milliamperes. The relative intensities of the lines were compared by a microphotometer with a photo-cell and a string-electrometer. The balance method used in the previous cases was also tried. Both results found agreed with each other.[12]

Experimental Results. (a) By using the mixtures of oxides of gadolinium and neodymium, the intensity of the gadolinium $L\alpha_1$ line was compared with that of the neodymium $L\beta_2$ line. The relative intensities of spectral lines were estimated by microphotometry.

The results obtained are shown in Table 9, where A_b denotes the deflection of the string of the electrometer expressed in divisions of the scale accessory to it at the background of the photographic plate, A_{Gd}, the deflection due to the gadolinium $L\alpha_1$ line, and A_{Nd}, that due to the neodymium $L\beta_2$ line. The density of the gadolinium $L\alpha_1$ line, denoted in Table 9 as D_{Gd}, can be expressed by $\log \frac{A_b}{A_{Gd}}$, while that of the neodymium $L\beta_2$ line, D_{Nd}, by $\log \frac{A_b}{A_{Nd}}$, and the intensity ratio of the said two lines, by D_{Nd}/D_{Gd} or $\log \frac{A_b}{A_{Nd}} : \log \frac{A_b}{A_{Gd}}$.

Table 9.

(1) Exposure at the current of 3 milliamperes.

Nd_2O_3/Gd_2O_3 in weight	A_b	A_{Nd}	A_{Gd}	D_{Nd}/D_{Gd}	D_{Nd}/D_{Gd} (Mean)
4.00	45.2	32.4	29.3	0.77	0.80
	45.2	32.2	30.0	0.83	
4.40	43.2	27.4	26.2	0.91	0.90
	42.7	28.0	26.4	0.88	
4.50	40.7	23.2	24.0	1.06	1.06
	40.7	23.4	24.2	1.06	

(12) In the case of neodymium given in this report and also in some other cases, a slight discrepancy was observed between the value obtained by microphotometry and that by the balance method. This was not the case with gadolinium.

Table 9.—(*Concluded*)

Nd_2O_3/Gd_2O_3 in weight	A_b	A_{Nd}	A_{Gd}	D_{Nd}/D_{Gd}	D_{Nd}/D_{Gd} (Mean)
5.00	41.7	14.4	16.2	1.13	1.13
	42.2	14.6	16.4	1.12	
6.00	36.7	27.2	29.0	1.27	1.27

(2) Exposure at the current of 5 milliamperes.

Nd_2O_3/Gd_2O_3 in weight	A_b	A_{Nd}	A_{Gd}	D_{Nd}/D_{Gd}	D_{Nd}/D_{Gd} (Mean)
4.40	39.8	20.3	19.3	0.93	0.92
	39.7	19.7	18.3	0.91	
4.50	41.3	27.0	29.3	1.24	1.20
	41.8	27.2	28.9	1.16	

(3) Exposure at the current of 2–3 milliamperes.

Nd_2O_3/Gd_2O_3 in weight	A_b	A_{Nd}	A_{Gd}	D_{Nd}/D_{Gd}	D_{Nd}/D_{Gd} (Mean)
4.40*	42.6	36.3	36.0	0.95	0.96
	42.3	35.3	35.1	0.97	
4.50**	42.3	32.3	32.8	1.06	1.07
	42.3	31.5	32.1	1.07	

* The photometer curve is shown in Fig. 1.

** The photometer curve is shown in Fig. 2.

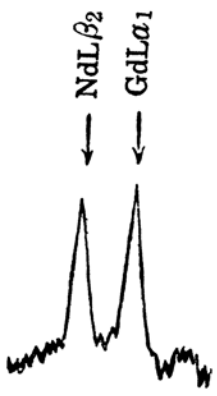

Fig. 1. $Nd_2O_3/Gd_2O_3 = 4.40$.

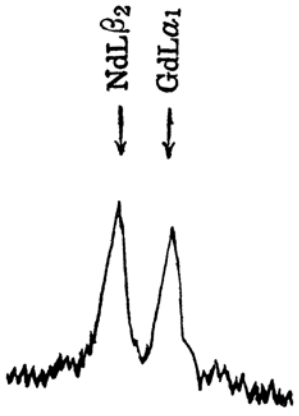

Fig. 2. $Nd_2O_3/Gd_2O_3 = 4.50$.

The balance ratio Nd_2O_3/Gd_2O_3, i.e. the ratio that makes D_{Nd}/D_{Gd} equal to 1.00, was found to be 4.46 from Table 9 (1), 4.43 from Table 9 (2), and 4.44 from Table 9 (3).

The photograph was also taken with the samples that remained on the anticathode after the bombardment of the cathode rays. The results are shown in Table 10. The balance ratio obtained was 4.47 and no sign of the change of the relative intensities was observed.

Table 10.

Nd_2O_3/Gd_2O_3 in weight	A_b	A_{Nd}	A_{Gd}	D_{Nd}/D_{Gd}	D_{Nd}/D_{Gd} (Mean)
4.40	39.9	23.3	21.4	0.86	0.87
	40.8	24.3	22.5	0.87	
4.50	39.8	24.7	25.3	1.05	1.05
	39.8	24.1	24.7	1.05	

From these experiments, the value 4.45 was taken as the balance ratio. A trial experiment with a sample which consisted of neodymium oxide and gadolinium oxide in the proportion of 4.45 to 1.00 showed, as was seen in Table 11, that the value was correct.

Table 11.

Nd_2O_3/Gd_2O_3 in weight	A_b	A_{Nd}	A_{Gd}	D_{Nd}/D_{Gd}	D_{Nd}/D_{Gd} (Mean)
4.45	39.0	26.3	26.6	1.03	1.01
	40.8	31.8	31.8	1.00	

(b) The experiments were also carried out to know the effects of other rare earth elements. The absorption effects are expected by no element of the rare earth group. As the wave-length difference of the absorption edges corresponding to the said two lines under comparison is fairly large, some rare earth elements may have the excitation effects.

The following three samples were used for the examples: Sample No. 6 consisted of the rare earths obtained from so-called gadolinium oxalate on sail which was not naturally pure and contained various rare earth elements; Sample No. 7 was a mixture of the rare earths rich in the elements of yttrium group; Sample No. 8 was the rare earths extracted from gadolinite found in Gihu Prefecture, Japan.

Various quantities of neodymium oxide were added to these samples respectively and the intensity ratio of the two lines under comparison was determined with the results shown in Table 12.

Table 12.

(1) Sample No. 6.

Nd_2O_3 added / Sample taken (%)	A_b	A_{Nd}	A_{Gd}	D_{Nd}/D_{Gd}	D_{Nd}/D_{Gd} (Mean)
0					0.59
11.4	43.5	34.0	36.0	1.30	1.28
	43.2	34.0	36.0	1.25	
9.8	39.8	33.3	33.3	1.00	1.00
	39.8	33.3	33.3	1.00	
8.6	40.5	35.0	34.2	0.86	0.88
	40.5	34.4	33.8	0.90	

(2) Sample No. 7.

Nd_2O_3 added / Sample taken (%)	A_b	A_{Nd}	A_{Gd}	D_{Nd}/D_{Gd}	D_{Nd}/D_{Gd} (Mean)
0					0.75
4.5	42.3	35.3	33.8	0.81	0.79
	41.8	35.1	33.3	0.77	
5.4	39.3	32.5	32.5	1.00	1.00
	38.8	31.3	31.3	1.00	
9.7	43.3	36.8	38.3	1.33	1.31
	43.3	37.5	38.7	1.28	

(3) Sample No. 8.

Nd_2O_3 added / Sample taken (%)	A_b	A_{Nd}	A_{Gd}	D_{Nd}/D_{Gd}	D_{Nd}/D_{Gd} (Mean)
0					0.54
12.2	42.3	34.1	37.3	1.71	1.66
	42.3	34.9	37.3	1.53	
9.2	41.2	33.0	34.4	1.23	1.29
	40.7	32.2	34.2	1.35	
7.4	42.8	38.0	38.1	1.02	1.01
	43.8	37.3	37.3	1.00	
6.1	37.3	27.3	25.8	0.85	0.82
	37.3	27.5	25.3	0.79	

From Table 12 (1), we knew that the addition of 9.4% of neodymium oxide to Sample No. 6 would make the said two lines equally intense. After the addition of this amount of neodymium oxide to the original sample, various quantities of neodymium oxide and gadolinium oxide were added in the proportion, $Nd_2O_3/Gd_2O_3 = 4.45$, and the relative intensities of the said two lines were compared. An example of the results obtained is shown in Table 13 (1).

Samples No. 7 and No. 8 were treated in a similar way. After the addition of 5.4% of neodymium oxide to Sample No. 7 or 7.4% of it to Sample No. 8, various quantities of neodymium oxide and gadolinium oxide were added in the proportion, $Nd_2O_3/Gd_2O_3 = 4.45$, respectively, and the relative intensities of the said two lines were compared. An example for each case is shown in Table 13 (2) and in Table 13 (3) respectively.

Table 13.

(1) Sample No. 6.

A_b	A_{Nd}	A_{Gd}	D_{Nd}/D_{Gd}	D_{Nd}/D_{Gd} (Mean)
37.8	27.3	27.7	1.05	1.01
37.8	26.9	26.7	0.98	

(2) Sample No. 7.

A_b	A_{Nd}	A_{Gd}	D_{Nd}/D_{Gd}	D_{Nd}/D_{Gd} (Mean)
30.3	25.7	25.9	1.03	1.01
30.3	24.5	24.5	1.00	

(3) Sample No. 8.

A_b	A_{Nd}	A_{Gd}	D_{Nd}/D_{Gd}	D_{Nd}/D_{Gd} (Mean)
40.3	24.6	26.0	1.13	1.13
40.3	24.6	26.0	1.13	

From the above experiments, we knew that the balance ratio 4.45 which was determined with the mixture of gadolinium and neodymium oxides also held true of Samples No. 6 and No. 7, and the effects of the other rare earth elements were not observed in these cases. A little low value 4.4 was obtained for Sample No. 8.[13] As the content of neodymium

(13) This might be due to the excitation effect of dysprosium richly present in the sample, although it could not yet be confirmed.

oxide in this sample was estimated to be 19.4% by the method described in the previous part of this report, the content of gadolinium oxide would be 6.1% if we took 4.4 for the balance ratio. It would be 6.0% if we assumed the balance ratio to be 4.45.

Table 14.

Allanite from Oyama.

MgO	1.29%
CaO	10.42
MnO	1.22
FeO	4.76
Fe_2O_3	9.70
Al_2O_3	16.03
La_2O_3	0.63
Ce_2O_3	5.96
Pr_2O_3	0.57
Nd_2O_3	3.80
Sm_2O_3	1.92
Gd_2O_3	1.02
Y_2O_3 etc.	4.19
ThO_2	2.11
SiO_2	34.65
H_2O	1.58
Total	99.85%

Applications.

These methods, combined with the other methods,[14] were applied in this laboratory to the analyses of chemical preparations as well as of minerals containing rare earth elements. As an example, the result of the analysis of allanite found in Oyama, Ehime Prefecture, Japan is given in Table 14.[15]

Summary.

(1) Lanthanum in a rare earth mixture can be determined by comparing the intensity of its $L\beta_2$ line with that of the cerium $L\beta_3$ line.

(2) Neodymium in a rare earth mixture can be determined by comparing the intensity of its $L\alpha_1$ line with that of the cerium $L\beta_1$ line.

(3) Gadolinium in a rare earth mixture can be determined by comparing the intensity of its $L\alpha_1$ line with that of the neodymium $L\beta_2$ line.

In conclusion, the author wishes to express his hearty thanks to Professor M. Katayama and to Professor Y. Shibata for their kind interests during the work. It is also the author's pleasant duty to acknowledge the valuable advice offered by Dr. Y. Nishina.

A part of the cost of this investigation was defrayed from the grant of the Nippon Gakujutsu Shinko-kwai (the Japan Society for the Promotion of Scientific Research) for which also the present author wishes to record his thanks.

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(14) For the determination of praseodymium, the intensity of the praseodymium $L\beta_2$ line was compared with that of the neodymium $L\beta_3$ line; vid. S. Shinoda, *J. Chem. Soc. Japan*, **56** (1935), 76. For the determination of samarium and also of neodymium, the intensity of the samarium $L\alpha_1$ line was compared with that of the neodymium $L\beta_1$ line by the wedge method proposed by S. Shinoda of this laboratory; vid. S. Shinoda, *J. Chem. Soc. Japan*, **56** (1935), 1483; *ibid.*, **58** (1937), 989.

(15) M. Ikawa, *J. Chem. Soc. Japan*, **58** (1937), 1261.