Summary.

A satisfactory radiomicrometer, having a half-period of 10 seconds and a sensibility of 5 per square millimeter of exposed vane (candle and scale being at a meter's distance) was constructed.

Making use of the radiomicrometer and the grating spectroscope, a radiometric method was worked out for the determination of the ionization constants of indicators. This method is freer from objections and limitations than any method previously used. It serves as well for a two-colored indicator as for a one-colored indicator.

Very small concentrations of colored components were determined, and it has been shown that minute concentrations of hydrogen and hydroxyl ions can be quickly and accurately estimated by means of radiometric measurements.

Satisfactory constants were obtained for the ionization of methyl orange as a base. The value found is 2.1×10^{-11}.

The ionization and hydrolysis constants for phenolphthalein considered as a monobasic acid are far from being satisfactory.

From the known ionization constant of methyl orange and from radiometric measurements, the ionization constant of a very weak base and the hydrolysis constant of one of its salts have been roughly determined. The method can likewise be applied for the determination of the ionization constants of very weak acids, and the hydrolysis constants of the salts formed by these acids. Work is now in progress in this laboratory on other indicators, from this same standpoint, and the results will soon be published in THIS JOURNAL.

JOHNS HOPKINS UNIVERSITY, BALTIMORE, MD.,
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

THE FRACTIONAL CRYSTALLIZATION OF THE PICRATES OF THE RARE EARTHS OF THE DIDYMIUM GROUP.

BY L. M. DENNIS AND F. H. RHODES.

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The salts of the rare earths with picric acid form well-defined crystals, are much more soluble in hot water than in cold, and crystallize very well from solution. For these reasons, the fractional crystallization of the picrates naturally suggests itself as a method for the separation of the rare earths. Holmberg[1] made a brief examination of this method in the attempt to separate the earths of the terbium group. By the fractional crystallization of the picrates of gadolinium and terbium containing 25 g. of the earths he obtained a rapid concentration of terbium in the first mother liquors and an accumulation of gadolinium in the crystals which

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[1] *Z. anorg. Chem.*, 53, 80 (1907).

separated first from the solution. James[1] tried to purify thulium by the fractional crystallization of the picrates, but found that the method is not satisfactory for this purpose.

The work of Holmberg and of James on the fractional crystallization of the picrates was done with small amounts of material and with rare earth mixtures that contained unusual components, and was more or less incidental to other researches. The applicability of the method to the general problem of the separation of the rare earths was investigated systematically for the first time by Dennis and Bennett,[2] who fractionated a mixture of the picrates of the didymium, erbium, and yttrium groups containing about 1500 g. of the oxides. Fractional crystallization of the neutral solution of the picrates of this material yielded a series of twenty-five final fractions. They determined the atomic weights of the earths in these final fractions and made a comparative study of the absorption spectra of solutions of the chlorides of the earths. They summarized their results as follows:

> ". . . . with an original material of an atomic weight of 116, containing earths of the didymium, erbium, and yttrium groups, fractional crystallization of the picrates from aqueous solution yields the following results:
>
> "(1) A concentration of praseodymium and neodymium in the first fractions followed by a rapid decrease of these two elements after the sixth fraction.
>
> "(2) A peculiar increase in the amounts of praseodymium and neodymium in the tenth and nineteenth fractions.
>
> "(3) A sudden concentration of erbium and holmium in the eighth fraction and an entire absence of these two elements in the first six fractions of the series.
>
> "The fractional crystallization of the picrates of the rare earths appears to furnish excellent means of effecting a rapid concentration of praseodymium and neodymium practically free from erbium and holmium, and concentration of erbium and holmium with but relatively small amounts of the members of the didymium group. The peculiar rise in the concentration of praseodymium and neodymium in the tenth and nineteenth fractions is under further investigation."

The work here to be described was undertaken with the object of making careful investigation of the apparently abnormal behavior of the earths of the didymium group upon the fractional crystallization of their picrates.

The original material used in this work consisted of about 25 kg. of the double sodium sulfates of the rare earths obtained as a byproduct in the extraction of thorium from monazite sand and which was kindly presented to us by Dr. H. S. Miner. This material was particularly suited to our purpose because of the relatively large amounts of the earths of the didymium group that it contained. A qualitative analysis of the crude double sulfates revealed the presence of sodium, cerium, and the rare earths, with small amounts of iron, calcium, and silica. No thorium was present. An examination of the absorption spectrum of a concentrated solution of

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[1] This Journal, 33, 1332 (1911).

[2] *Ibid.*, 34, 7 (1912).

the chlorides of the rare earths from the double sulfates showed that the material contained large amounts of neodymium and praseodymium. None of the absorption bands of samarium, erbium, or holmium could be detected, even on examining a syrupy solution of the chlorides that was 15 cm. thick.

The difficultly soluble double sulfates of the rare earths were decomposed and converted into the chlorides by the method suggested by Browning and Blumenthal.[1] The material was mixed with about five times its weight of coke dust, and the mixture was placed in large graphite crucibles which were then heated to bright redness for about one hour in crucible assay-furnaces. The reduction of the sulfates took place readily at this temperature, and large volumes of carbon monoxide were evolved. When the reduction was complete, the crucibles were withdrawn and allowed to cool. The mixture of coke dust and sulfides was treated with an excess of commercial concentrated hydrochloric acid. The sulfides of the rare earths dissolved readily with the copious evolution of hydrogen sulfide. As soon as the first vigorous reaction had ceased, the mixture was heated rapidly to boiling to drive off the hydrogen sulfide. The resulting solution of the chlorides of the rare earths was diluted with about six times its own volume of water, allowed to stand until most of the undissolved material had settled out, and then filtered through a Büchner filter. The mass of carbon at the bottom of the cylinder was transferred to the filter, washed thoroughly with hot water, and drained as completely as possible. The finely divided carbon remaining on the filter paper was dried and used for the reduction of further amounts of the crude double sulfates. The oxalates of the rare earths were precipitated by the addition of a solution of oxalic acid to the filtrate after the removal of the carbon. These oxalates were washed, filtered, dried, and ignited to the oxides in bowls of fused quartz heated in a muffle furnace. About 10 kg. of the crude oxides of the rare earths and cerium was obtained. Cerium was next removed by the chlorination method of Mosander. After the material had been subjected to four chlorinations, a solution of the chlorides of the earths from the final filtrate was tested for cerium by making the solution *very faintly* alkaline with ammonium hydroxide and adding hydrogen peroxide. Since no yellow color was produced, cerium was present in no more than minute traces.

From the final solution, after the removal of the cerium, the rare earths were precipitated as the oxalates, which were converted to the oxides by ignition. About 6 kg. of the purified oxides was obtained. The oxides were then dissolved in hydrochloric acid, and the solution was filtered, transferred to large precipitating cylinders, and treated with a slight excess of ammonium hydroxide. The precipitated hydroxides were washed

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[1] *Z. anorg. Chem.*, 72, 358 (1911).

by decantation with water until the supernatant liquid was free from chlorides. A qualitative analysis of the washed hydroxides showed the absence of salts of iron, calcium, and ammonium. The average atomic weight of the mixture of rare earths in the purified material was determined by the oxalate method and was found to be 141.48.

There was thus obtained a mixture of the hydroxides of the rare earths of the didymium group, containing small amounts of the earths of the erbium and yttrium groups, but free from cerium, thorium, and the common elements. To convert the hydroxides into the picrates, the suspension of the hydroxides was heated almost to boiling in large pans of enameled ware and a hot solution of picric acid was added in small amounts at a time. In order to insure the formation of a neutral solution of the picrates, the hydroxides were kept always in excess, and the addition of the picric acid was discontinued while a small amount of the hydroxides remained yet undissolved.

The solution of the picrates of the rare earths was diluted with water until it was just saturated at room temperature. The saturated solution was then subjected to fractional crystallization. The first few series of fractionations, involving the concentration of large volumes of solutions, were made in enameled pans holding about forty liters each and heated by means of small gas stoves. As soon as the fractions became sufficiently reduced in size, the crystallization was continued in smaller pans of a capacity of from fifteen to twenty liters. Subsequent fractions of smaller size were concentrated in porcelain evaporators.

The plan of the fractionation is shown in Fig. 1. When an end fraction became too small for further separation it was set aside, and the adjacent fraction became the end fraction in the next series of recrystallizations. Fractions 58, 136, 278, 428, 610, 768, 944, 1008, 1140, 1352, 1504, and 1584 from the soluble end, and fractions 183, 461, 809, 925, 1115, 1323, and 1629 from the insoluble end, were thus removed from further fractionation. When forty-two series of crystallizations had been made, the fractionation was stopped and the fractions of the final series, together with the end fractions set aside during the progress of the fractionation, were examined to determine the nature and the relative amount of the rare earths contained in each.

A considerable difference in the appearance of the crystals and of the mother liquors from the various fractions was observed. The picrates from the less soluble portions of the material crystallized in large plates and columns of an orange-yellow color, while the crystals from the more soluble fractions separated as small bundles of yellow needles. The mother liquors from the less soluble fractions were yellow, while those at the soluble end were of a yellowish brown color. From the first mother liquor set aside from the fractionation at the soluble end, a gelatinous substance separated on standing. This jelly-like material was analyzed and was found to consist of silica, which had probably been introduced into the original mixture of rare earths from the quartz bowls in which the oxalates had been ignited.

In the examination of the fractions of the final series and of the end fractions set aside during the fractionation, the average atomic weight of

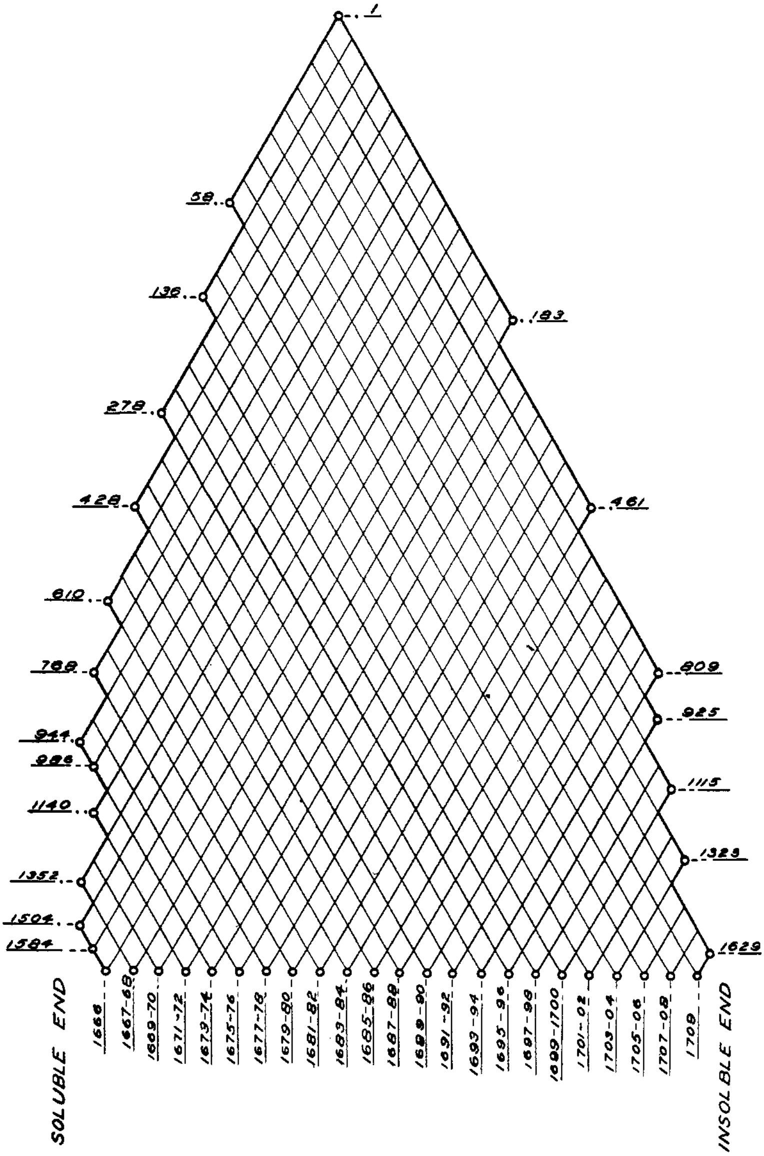

Fig. 1.

the earths in each fraction was determined, and an examination of the absorption spectrum of a solution of the chlorides from each fraction was made.

In the determination of the average atomic weights of the mixtures of rare earths from the various fractions the usual oxalate method was employed. The results of the determination of the average atomic weights of the rare earths from the various fractions were as follows:

Fraction number soluble end.	Atomic weight.	Color of. oxides.
58	128.06	Orange-yellow
136	118.41	Orange-yellow
273	114.67	Yellow
428	115.17	Yellow
610	118.34	Yellow
768	126.68	Yellow
944	127.88	Yellow
1008	143.97	Yellow
1140	148.25	Yellow
1352	151.48	Yellow
1504	152.12	Yellow
1584	153.18	Yellow
1666–67	154.59	Yellow
1668–69	152.52	Yellow
1670–71	151.65	Yellow
1672–73	149.12	Light yellow
1674–75	146.11	Light yellow
1676–77	144.01	Grey
1678–79	144.82	Grey
1680–81	143.47	Grey
1682–83	142.87	Grey
1684–85	142.12	Grey
1686–87	141.52	Grey
1688–89	141.67	Grey
1690–91	141.62	Grey
1692–93	141.67	Grey
1694–95	141.7	Grey
1696–97	141.67	Grey
1698–99	141.02	Grey
1700–01	141.53	Grey
1702–03	141.15	Grey
1704–05	141.59	Grey
1706–07	141.52	Grey
1708–09	141.53	Grey
1629	141.7	Grey
1323	141.98	Grey
1115	141.12	Grey
925	141.57	Grey
809	141.12	Grey
461	141.24	Grey
183	141.12	Grey

Fig. 2 shows the curve obtained by plotting the average atomic weights of the fractions against the positions of the fractions in the plan of fractionation.

It appears from these results that the average atomic weights remained almost constant at a value between 141 and 142 in all of the fractions removed from fractionation at the insoluble end, and throughout the less soluble fractions in the final series up to fraction 1684–85. From this point the atomic weights rose to a maximum value of 154.59 in fraction 1666–67, fell rapidly to a minimum value of 114.67 in fraction 278, and rose again slightly in fractions 136 and 58. By far the greater portion of the material was contained in the portions with an almost constant atomic weight of about 141.

In the examination of the absorption spectra of the earths from the various fractions, neutral solutions of the chlorides of equal concentrations were used. Weighed amounts of the oxides from the various fractions were dissolved in hydrochloric acid, the acid being added very gradually until the oxides just dissolved on boiling. The approximately neutral solutions of the chlorides of the rare earths thus obtained were diluted with water until each cubic centimeter contained 0.2 g. of the oxides and were then transferred to glass boxes 55 mm. in width. The absorption spectra were examined by means of a Krüss spectroscope previously calibrated by the use of the Fraunhofer lines, the spectrum of the mercury arc, and the emission spectra of potassium, lithium, and thallium. A disc of zirconium oxide heated to incandescence in the oxyhydrogen flame was used as the source of light. In comparing the intensities of the absorption bands of the solutions of the rare earths from the various fractions, the apparatus devised by Dennis and Bennett was used.[1]

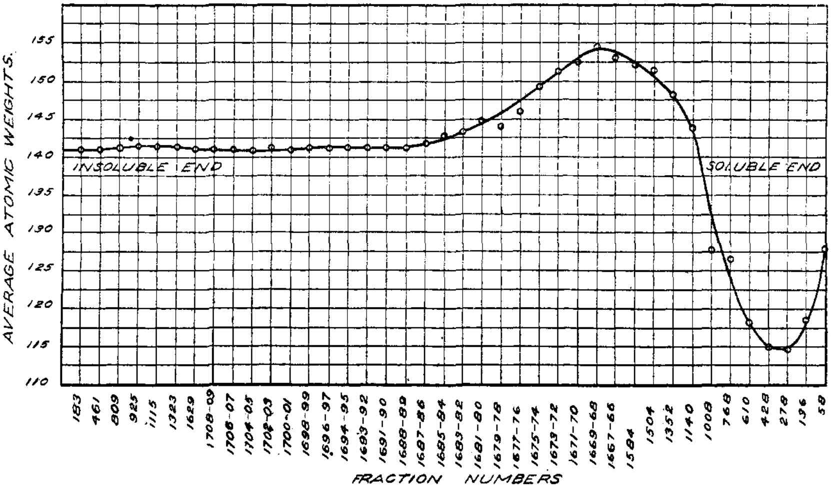

Fig. 2.

In Fig. 3 are shown the curves obtained by plotting the relative intensities of the characteristic lines of the absorption spectra of neodymium, praseodymium, erbium, and holmium in the various fractions against the positions of the fractions in the plan of fractionation.

The general course of the separation may be traced by the examination of the results of the comparison of the absorption spectra and the determination of the average atomic weights of the earths from the end fractions and from the fractions of the final series. The high and constant concentration of praseodymium and neodymium in the less soluble fractions and the fact that these fractions have an average atomic weight of between 141 and 142 proves that the less soluble portions of the material consisted of a mixture of the elements of the didymium group and that little or no

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[1] *Loc. cit.*

separation of the elements of this group had been effected. The increase of the concentrations of erbium and holmium beyond fraction 1678–79 explains the increase of the atomic weights to fraction 1584. That the atomic weights reached a maximum in fraction 1584 while the concentration of the erbium and holmium continued to increase until fraction 1008 was reached was probably due to the effect of the increasing concentration of yttrium in the more soluble fractions. The slight increase in the concentration of the neodymium and praseodymium in fractions 136 and 58 was in agreement with the rise in the atomic weight in these fractions and was due to the fact that they were removed from fractionation after comparatively few series of recrystallizations and therefore resembled more closely in composition the initial mixture of rare earths.

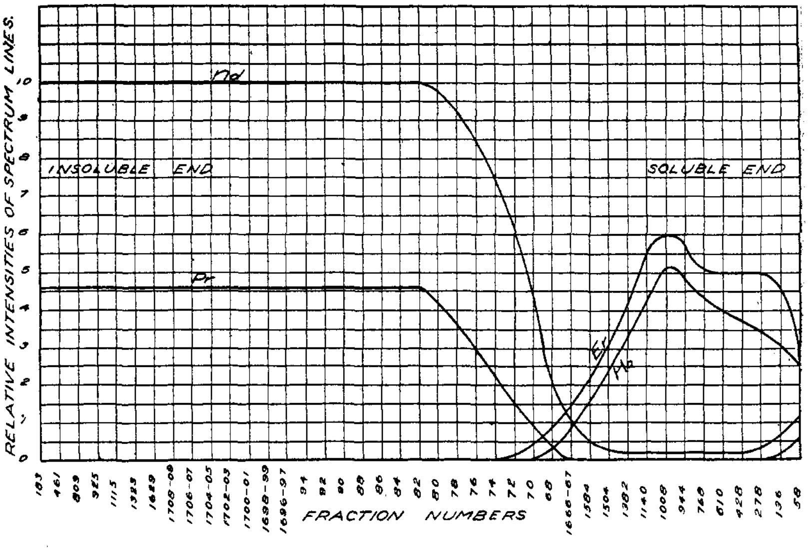

Fig. 3.

Dennis and Bennett, in their investigation of the fractional crystallization of the picrates of the rare earths, had observed a sudden and isolated concentration of neodymium and praseodymium in certain of the fractions of intermediate solubility. This observation was not confirmed in this present work. The earths of the didymium group were found to concentrate in the fractions at the insoluble end and in these fractions only. A portion of the material from one of the fractions of intermediate solubility from the final series of fractions obtained by Dennis and Bennett was analyzed and was found to contain considerable amounts of ammonium salts. Therefore it is probable that the results obtained by them in their work on the fractional crystallization of the picrates of the rare earths were due to the fact that they were fractionating a complex mixture of the simple and the double ammonium picrates of the various earths. It is evident that the results of the fractional crystallization of such a mixture would be the results of two simultaneous, superimposed fractionations, and that each earth present would tend to concentrate in two or more separate regions of the final series of fractions.

The fractional crystallization of the picrates does not give an efficient separation of the individual elements of the didymium group. The ratio of the intensity of the neodymium spectrum to the intensity of the praseodymium spectrum remains approximately constant throughout all of the fractions. As a method for the separation of the didymium group from the yttrium and erbium groups, however, the fractionation of the picrates promises very good results. About 200 g. of the oxides of the yttrium and erbium groups was obtained from the more soluble fractions, although no trace of erbium or holmium bands could be detected in the absorption spectrum of the original material. Even after a comparatively short series of recrystallizations, the mother liquor at the soluble end showed a marked increase in the concentration of erbium and holmium and a very great decrease in the concentration of neodymium and praseodymium. Therefore the picrate method should be especially useful for the separation of the elements of the didymium group from the other rare earths and for the isolation of the earths of the erbium or yttrium groups from material containing large amounts of the didymium elements. The fractional crystallization of the picrates also appears to afford a rapid method for the separation of the yttrium earths of the erbium group.

Summary.

A mixture of the picrates of the rare earths of the didymium group, containing small amounts of the elements of the yttrium and erbium groups, was subjected to 42 series of fractional crystallizations. The earths of the didymium group concentrated in the less soluble fractions, while the most soluble fractions showed a concentration of yttrium, and the elements of the erbium group accumulated in the fractions of intermediate solubility. No indications of a concentration of neodymium or praseodymium in any fraction of intermediate solubility were observed.

The fractional crystallization of the picrates does not effect a separation of the individual elements of the didymium group, but is an efficient method for removing small amounts of the elements of the erbium and yttrium groups from the earths of the didymium group and for separating yttrium from erbium and holmium.

ITHACA, N. Y.