

Progress in the Analysis of the Rare Earth Group

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For many years the analysis of the rare earth group for individual rare earth content proved to be one of the most difficult problems in rare earth chemistry. When we recall the great similarity in both the physical and chemical properties of their compounds we can readily understand why the analysis of this group has developed slowly.

The early analyst, restricted to methods of analysis which depended upon the chemical properties of the rare earths, reported only the total rare earth content of the ore or substance analyzed. Later when it was discovered that the rare earths could be separated into cerium and yttrium groups by means of the differences in the solubility of the double alkali sulfate, the percentages of these two groups were reported. In 1843 Mosander¹ found that cerium could be oxidized to a tetravalent state. This offers a means of estimating the amount of cerium present. Cerium in the tetravalent state is the least basic of the rare earths. Consequently if the cerium in a neutral rare earth solution is oxidized, hydrated cerio oxide precipitates upon boiling the solution. The cerium may then be determined gravimetrically. The advent of a number of suitable oxidation-reduction indicators had made it possible to determine the cerium volumetrically. Willard and Young² give a good review of the literature concerning the volumetric determination of cerium and have established the best conditions for the determination. With the exception then of a few isolated cases in which the lanthanum and didymium content, as determined by long-continued fractionation, was reported, the early analysis included only total rare earth, percentage of cerium earths and yttrium earths, and cerium content.

Within recent years the rare earth chemist has had at his disposal both physical and chemical means of analysis. Quantitative analysis based on physical measurements include the use of the x-ray and arc spectra, the magnetic susceptibility, atomic weight determinations, and solubility relationships. With the exception of the x-ray and arc spectra the physical methods are usually confined to binary or at the most tertiary mixtures. Our most important means for a complete analysis depend therefore upon the use of X-ray or arc spectra.

I. Noddack³ has employed the x-ray spectra for the analysis of rare earth ores and artificial mixtures. The method consists essentially of measuring photometrically the intensity of certain line pairs of the spectra of rare earth and an internal standard. The intensity ratios between the selected line pairs are plotted against known concentrations of each rare earth. A spectogram is then taken of the sample and the intensity ratios determined. By referring to the graphs one may obtain the percentage of each earth present. The method is one of the most accurate of those we now possess.

B. S. Hopkins and co-workers⁴ studied the use of the arc spectra as a means of analysis. The method is similar to that employed by Noddack. That is, the intensity ratios between the selected line pairs of rare earth and internal standard lines are determined by means of the microphotometer. These ratios are plotted logarithmically against concentration.

As previously mentioned, cerium has been determined for a long time by taking advantage of its anomalous valence. In 1930 Yntema⁵ showed that europium and ytterbium could be reduced electrolytically in aqueous solution. This contribution to rare earth chemistry has prompted other chemists to investigate the chemistry of those rare earths which may be

reduced to the divalent state. McCoy⁶ found that europium could be determined quantitatively by means of the Jones reductor. An acidified rare earth solution is reduced by zinc and passed into a standard iodine solution. The excess iodine is then determined by means of sodium thiosulfate. If the reduced europium is passed into a sulfate solution, insoluble europous sulfate precipitates. The precipitation however is not quantitative, consequently the volumetric method is preferred to the gravimetric. Brukl⁷ by taking advantage of the anomalous valence of ytterbium has worked out a method for the determination of the ytterbium content of rare earth mixtures. The ytterbium is reduced electrolytically in an inert atmosphere. The reduced solution is then treated with an excess of ferric ammonium sulfate. The reduced iron is then determined by means of potassium permanganate.

Thus far chemical analysis has been confined to cerium, europium, and ytterbium. These methods depend upon the anomalous valences of the rare earths. Praseodymium for example may assume the quadrivalent state, samarium may be reduced to the divalent state. Valuable contributions to rare earth chemistry will be made when conditions are found in which these elements are stable in their anomalous valences. We will then have five members of the rare earths which may be determined chemically but what is more important we will have five members which may be separated from the complex of complexes—the rare earths.

¹ Mosander, *J. Prakt. Chem.* 30 276 (1843).

² H. H. Willard and P. Young, *J. Am. Chem. Soc.* 50 1379 (1928).

³ I. Noddack, *Zeit. für anorg. Chemie* 225 337 (1935).

⁴ B. S. Hopkins, et al., *Ind. Eng. Chem.* 30 184 (1938).

⁵ Yntema, *J. Am. Chem. Soc.* 52 2782, 4264 (1930).

⁶ McCoy, *J. Am. Chem. Soc.* 58 1577 (1936).

⁷ Brukl, *Angew. Chem.* 50 25 (1937).