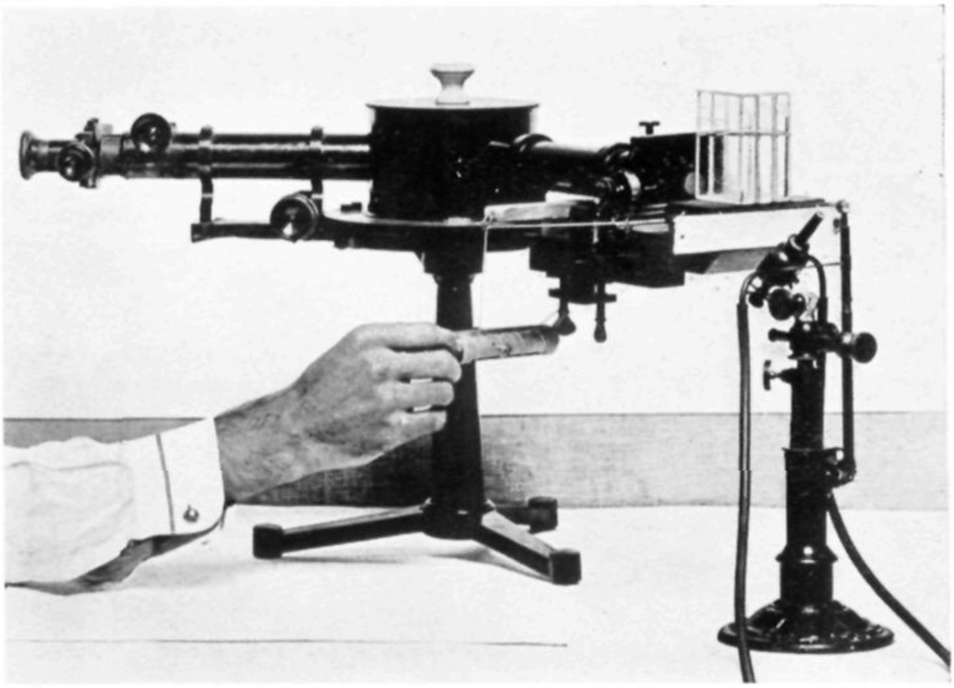

Fig. 1.

FRACTIONAL CRYSTALLIZATION OF THE PICRATES OF THE RARE EARTHS.

By L. M. Dennis and C. W. Bennett.

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Earlier work in this laboratory having shown that the picrates of the rare earths may easily be prepared, and that they crystallize readily from aqueous solutions, the investigation described below was undertaken to ascertain whether these salts could be utilized to advantage in the separation of the rare earths. If the results had shown that the method gives the usual gradual separation of the earths that is characteristic of most methods of fractional crystallization, the process would scarcely have merited description, for advances in this field are chiefly to be looked for in methods that will accelerate the separation of the earths. The picrates of the rare earths appear to facilitate the rapid concentration of certain groups of earths, and for this reason the details of the method and the results that it yielded are here briefly described.

Material.—In this first trial of the method it was thought advisable to use mixtures of earths containing members of the yttrium, erbium and didymium groups. Consequently a residue that was in hand and that contained chiefly earths of the didymium group was mixed with the earths obtained from xenotime. Both portions of the material contained cerium and thorium, which were removed by chlorination and treatment with a 10% solution of hydrogen dioxide. The earths were then precipitated from slightly acid solution with oxalic acid. The oxalates were washed with boiling water on a Büchner filter, were dried, and were then ignited in quartz trays about 32 cm. long, 15 cm. wide and 3 cm. deep, which were heated in a muffle furnace. The total weight of the oxides thus obtained was about 1500 grams.

Since the oxides of the rare earths do not dissolve readily in picric acid, they were converted into the hydroxides by solution in hydrochloric acid and precipitation with ammonium hydroxide. Before precipitation as the hydroxides a portion of the solution was treated with hydrogen sulfide, but no precipitate resulted. The rare earth hydroxides were repeatedly washed by decantation with water. After the last washing the supernatant liquid was siphoned off, and a hot solution of picric acid was poured upon the moist hydroxides. The material was actively stirred by a blast of air, and in this manner solution of the hydroxides was rapidly effected. The addition of the solution of picric acid was continued until most of the hydroxides had been dissolved and until the solution, after thorough stirring, failed to turn Congo-red paper blue. The solution was then separated from the residual hydroxides by filtration, and the residue was again treated with picric acid, the filtrate from this treatment being added to the main portion. There was finally obtained a residue of reddish brown color that was insoluble in picric acid, and that was found to consist chiefly of ceric hydroxide. This point is of interest in that it shows that rare earth material which has been freed from cerium so completely as to show no trace of that element when tested with hydrogen dioxide will disclose further amounts of cerium upon treatment of the hydroxides with picric acid.

Fractional Crystallization of the Picrates.—The neutral solution of the picrates of the rare earths, obtained as above described, was then subjected to fractional crystallization in enameled iron pans holding from 20 to 25 liters each. Six of these pans were used in the beginning, but as soon as the fractions were sufficiently reduced in size, the crystallization was continued in large porcelain evaporators. Two hundred and sixty-three fractional crystallizations were made, which yielded, following the usual method of uniting the crystals on the one hand and the mother liquors on the other, a series of 25 final fractions.

The absorption spectra of the final fractions were plotted, and the atomic weights of these fractions were determined by precipitating the earths as oxalates and ascertaining the $R_2O_3 : 3\ C_2O_3$ ratio.

In the examination of the absorption spectra of the fractions, the picrates were precipitated with oxalic acid, the oxalates were thoroughly

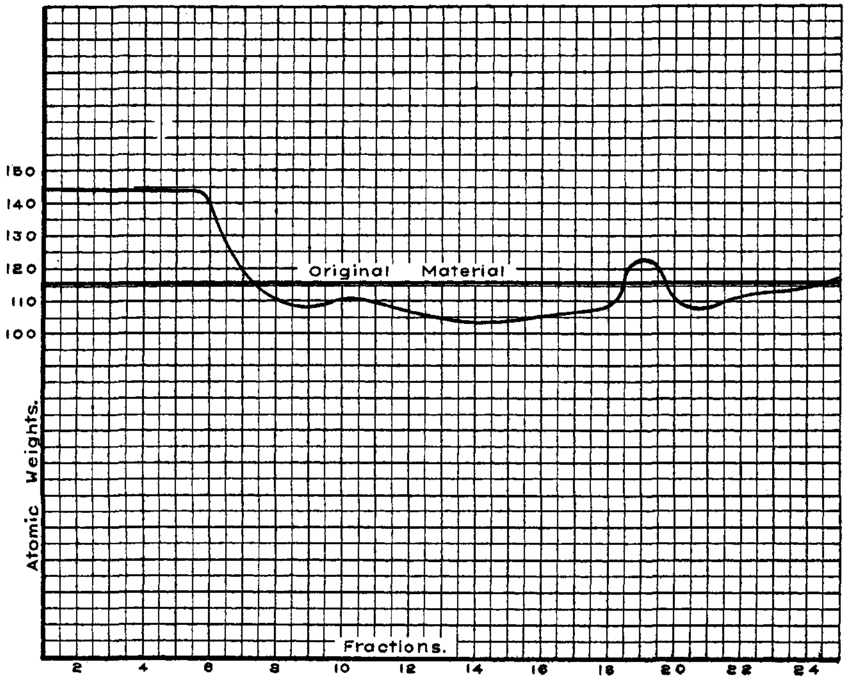

Fig. 2.

washed with boiling water, dried, and ignited to the oxide. These oxides were then dissolved in hydrochloric acid to solutions of uniform strength containing 20% R_2O_3. A Krüss spectroscope was used, and this was calibrated against the Fraunhofer lines of the sun spectrum and the spectrum of the mercury lamp. The thickness of the chloride solution was 47 mm. The absorption bands were plotted in the usual manner on the basis of their width and intensity. It was further attempted, however, to obtain an approximate idea of the concentration of each solution in respect to those earths that give absorption bands by measuring the *relative* intensities of the bands in successive fractions. To permit of the accomplishment of this object the arrangement of apparatus shown in Fig. 1 was devised. Three cells, containing three separate fractions to be compared, were placed in front of the slit on a grooved wooden block that could easily be moved to the left and right across the field. To the ends of this block was attached a cord that could be drawn to the right or left by rotating with the fingers of the right hand the small cylinder shown in the figure. The source of light was an oxy-hydrogen flame impinging on a disk of zirconium oxide.

The results of the fractionation are shown in Figs. 2 and 3. Fig. 2 gives the changes in the atomic weights in the final 25 fractions, while

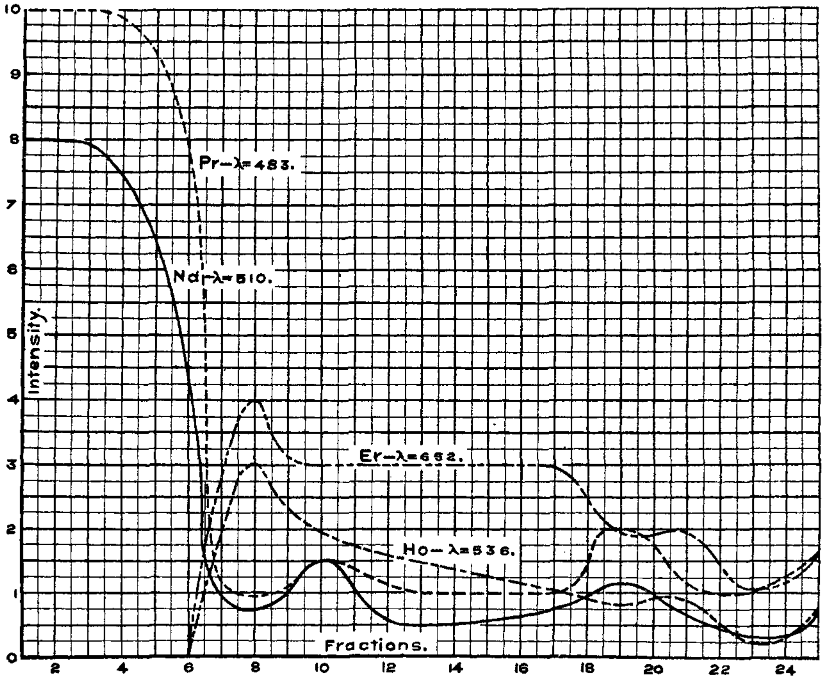

Fig. 3.