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OBSERVATIONS ON THE RARE EARTHS.[1]

BY EDGAR W. ENGLE AND CLARENCE W. BALKE.

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I. Introduction.—One object of the present work was to study some separation methods which might be suitable for the isolation of the various individual rare earths, more particularly those of the yttrium group. This was undertaken preliminary to a later object which was to prepare dysprosium material of sufficient purity for atomic weight work, and to determine the atomic weight of that element. Oxides of the rare earths obtained from a previous investigation[2] furnished most of the material for this work. These were originally obtained from the following mineral sources: monazite, gadolinite, xenotime, euxenite, and fergusonite. From the gadolinite and xenotime material part of the yttrium had been previously removed in the investigation above referred to. The oxides were in the main those of the yttrium earths, though some portions contained appreciable quantities of the cerium earths.

II. Separation of Cerium and Yttrium Groups.—For the separation of the earths the scheme suggested by James[3] was used as a working basis. However, several deviations were made from this scheme. The method used for the separation of the yttrium earths from the cerium earths depends upon the fact that the cerium earths are but slightly soluble in a saturated solution of sodium or potassium sulfate, while, in the presence of the cerium earths, the yttrium earths are quite soluble in these solutions. This separation, which is approximate, and which serves to divide roughly the rare earths into the two groups, was carried out as follows: The oxides were dissolved in strong nitric or hydrochloric acid, a large excess of acid being avoided. The solutions were diluted with water so that there was a volume of about one liter for each hundred grams of dissolved oxide. Solid sodium or potassium sulfate was added and the solutions stirred from time to time until they were saturated with the alkali sulfate or until the absorption spectra showed the removal of most of the

[1] This paper represents part of the work done by Edgar W. Engle in fulfilment of the requirement for the degree of Doctor of Philosophy in the Graduate School of the University of Illinois.

[2] Egan and Balke, THIS JOURNAL, 35, 365 (1913).

[3] THIS JOURNAL, 30, 979 (1908); 34, 757 (1912).

cerium earths from solution. Ordinarily this process required three or four days. The solutions were kept cool in order to reduce to a minimum the amount of alkali sulfate required. One portion treated with sodium sulfate consisted of the chlorides from 3760 g. of oxides, mainly cerium group, obtained from oxalates furnished by the Welsbach Company. The solution was filtered, diluted and precipitated in the cold with oxalic acid. The precipitated oxalates, which probably carried down slight amounts of sodium oxalate,[1] were washed and ignited to oxides. The oxides weighed 490 g.

In most of the other portions treated the cerium group material formed only a small percentage of the whole, and the amounts precipitated by the alkali sulfates were less. The alkali sulfates carried down some yttrium group material with the cerium earth precipitate. When the precipitation was complete the solutions were decanted through a filter, the precipitate washed a few times with a saturated solution of the alkali sulfate and set aside for later treatment. The filtrates were diluted with water and the earths precipitated with a hot, saturated solution of oxalic acid. The oxalates obtained settled rapidly and could be washed easily by decantation. After having been washed until the alkali salts in solution were removed, the oxalates were sucked dry on a Büchner funnel. Part of the oxalates obtained in this way were ignited to oxides, dissolved in nitric or hydrochloric acid and reprecipitated with oxalic acid. The oxalates were washed again in order to remove alkali salts which might have been included in the first precipitate. If these are not removed they cause inconvenience in the later fractionation of the earths.

III. Fractionation of the Bromates.—For the preliminary separation of the yttrium group elements the bromate method, first proposed by James,[2] was chosen as being most satisfactory. The rare earth bromates are best prepared in quantity by the double decomposition of rare earth sulfates and barium bromate. The oxalates of the rare earths may be changed to sulfates either by igniting to oxide and dissolving the oxide in cold, dilute sulfuric acid, or by making the oxalates into a paste with a slight excess of concentrated sulfuric acid and igniting to drive off the excess of acid. The latter method was found more satisfactory. The sulfates obtained by this method were dissolved in ice-cold water by adding slowly with constant stirring. The sulfate solution was added slowly to an excess of hot barium bromate solution contained in a porcelain evaporating dish of sixty-five liters' capacity. The liquid in the dish was kept agitated by means of a mechanical stirring device. The solution containing the rare earth bromates, along with a slight amount of barium bromate, was drawn off from time to time and more barium bromate and

[1] Baxter and Daudt, THIS JOURNAL, 30, 563 (1908).

[2] THIS JOURNAL, 30, 182 (1908); *Chem. News*, 97, 61 (1908).

earth sulfate added as required. The bromate solution was pale pink in color and the solid bromates had a light pink color.

The bromates were fractionally crystallized for a long time, in the usual way. Eighteen-inch evaporating dishes were used for containers at first. However, as the number of fractions increased and the size of each became correspondingly small, smaller dishes were used, and as soon as size permitted the fractions were transferred to three-liter Jena flasks, Florence shape, and finally to smaller ones. In some of the later series of fractionation flasks of fifty cubic centimeters' capacity were used. For a rather large series flasks of seven hundred cubic centimeters' capacity were found very convenient to handle. Flasks have advantage over casseroles in that creeping of the material is eliminated, the solutions lend themselves more readily to spectroscopic examination, less space is required, the draining of the crystals is more easily accomplished, and there is less danger of contamination from laboratory dust. The loss due to breakage when using flasks was very small and was no greater than when casseroles were used. The dissolving of the crystals was carried out on the water or steam bath. At the temperatures attained there was no decomposition unless the solutions became very concentrated and then only in the more soluble fractions. A series could be fractionated once or twice a day.

According to James and Bissel[1] the order of solubility of the rare earth bromates is as follows, arranged in order of increasing solubility; Eu (least soluble), Gd, Tb, Dy, Ho, Y, Er, Tm, Yb, Lu, Ct, Sc. The order of increasing solubility of the cerium earth bromates, according to the same authors, is as follows: Eu, Sa, Nd, Pr, Ce, La. The solubility of neodymium bromate lies between that of gadolinium and terbium.

After about fifty series of crystallizations of the bromates had been carried out, during which time several small fractions had been set aside from the insoluble end as they contained, in the main, barium and potassium bromates, the colors of the fractions which were numbered 8 to 31, inclusive, were noted. This, together with a study of the absorption spectra, indicated a composition of the fractions as follows:

Fraction No.	Color.	Absorption shows.	Earths present.
8	almost colorless	Sa, Nd	Sa, Gd, Nd
9, 10, 11	pink	Sa, Nd	Sa, Nd, Gd
12, 13	flesh-pink	Nd, Pr, Dy, Ho	Nd, Pr, Dy, Ho
14, 15	yellowish pink	Nd, Pr, Dy, Ho	Nd, Pr, Dy, Ho, Y
16, 17	cream	Dy, Ho	Dy, Ho, Y
18, 19, 20, 21	pale pink	Er	Y, Er
22, 23, 24, 25, 26, 27	pink	Er	Y, Er
28	yellowish pink	Er, Tm	Y, Er, Tm
29, 30	greenish yellow	Er, Tm	Er, Tm
31	bright blue-green	Tm	Tm

[1] THIS JOURNAL, 36, 2060 (1914).

After the series had been fractionated for some time longer it became evident that the terbium collected with the praseodymium, and that ytterbium, lanthanum and cerium collected in the fractions more soluble than thulium. These observations are in close agreement with those of James and Bissel.

As the separation continued, fractions were set aside from both ends of the series from time to time, until enough had accumulated to start separate series. Some of the fractions from the soluble end were placed into a series which was being run from bromates obtained in earlier investigations in this laboratory. New series were started and fractions added to them in such a way as to make the number of earths in a given series as small as possible, and to concentrate each earth in a single series. The transfer of a fraction from one series to another was governed by its color and absorption spectrum. The above method of manipulation may be made more clear by a statement of the composition of some of the series run.

Series A contained mainly yttrium, with erbium at the soluble end and holmium at the insoluble end. The fractions in this series were almost colorless. Concentration of yttrium was sought in this series, which contained more material than any of the others.

Series B contained bromates somewhat less soluble than those in Series A. It contained mainly yttrium, with some holmium and traces of dysprosium and terbium. It was free from erbium. The fractions were almost colorless. Concentration of yttrium was sought in this series.

Series C contained bromates somewhat less soluble than those in Series B. It contained mainly yttrium, holmium and dysprosium bromates. It was entirely free from bromates more soluble than yttrium bromate, but contained small amounts of terbium, praseodymium and neodymium bromates, which are less soluble than dysprosium bromate. Concentration of holmium was sought in this series.

Series D contained earths of about the same solubility as dysprosium. It consisted mainly of dysprosium, with some holmium and terbium and traces of praseodymium and neodymium. Concentration of dysprosium was sought in this series.

Series E contained bromates less soluble than those in Series D. It consisted mainly of neodymium and dysprosium, with some praseodymium and terbium. Concentration of terbium and dysprosium was sought in this series.

Series F contained bromates somewhat more soluble than those in Series A. It consisted mainly of yttrium and erbium, with traces of thulium and more soluble bromates. It was entirely free from holmium and less soluble bromates. Concentration of erbium was sought in this series.

Series G contained the most soluble bromates. It contained considerable thulium, ytterbium, cerium and lanthanum. Concentration of thulium and ytterbium was sought in this series. The insoluble end fractions gave bluish green solutions and crystallized well, while the soluble end fractions formed colorless solutions and crystallized poorly.

In addition to the study of the absorption spectra of the various fractions, determinations of the average atomic weight aided in following the course of the separations. Two methods of analysis were used for this purpose, the permanganate method of Gibbs[1] and the sulfuric acid volumetric method. The methods were found to give almost equally satisfactory results for control work. The sulfuric acid volumetric method is much more rapid, though perhaps not of so general application. In this latter method a few tenths of a gram of the oxide are dissolved in standardized sulfuric acid, approximately tenth-normal. The earth is precipitated from solution by the addition of an excess of approximately half-normal potassium oxalate solution. If the color of the oxalate is such as to interfere with the indicator color, the oxalate should be filtered off, otherwise this is not necessary. The excess of acid is titrated with standardized sodium hydroxide solution, approximately tenth-normal, phenolphthalein being used as the indicator. This method is similar in principle to that used by Feit and Przibylla[2] in their atomic weight determinations, and is essentially the same as that used by Holden and James[3] in control work.

Analyses of two samples from separate yttrium earth mixtures, made by two workers in this laboratory, one using the permanganate method, the other using the sulfuric acid volumetric method, gave the following results:

Method used.	Atomic wt. No. 1.	Atomic wt. No. 2.
Permanganate.....	91.85	89.73
Sulfuric acid volumetric.....	91.52	89.43

A sample from another lot of material gave the value 90.36 by the permanganate method, and the value 90.78 by the sulfuric acid volumetric method.

After bromate Series A had been fractionated for about two and one-half years, several thousand crystallizations having been carried out, the fractions richest in yttrium were removed. There was obtained from these over a kilogram of oxide. The atomic weight according to the permangnate method, as determined by another worker in this laboratory, was 88.94. This was evidently yttrium material of very high purity.

[1] *Am. Chem. J.*, **15**, 546 (1893).
[2] *Z. anorg. Chem.*, **50**, 249 (1906).
[3] THIS JOURNAL, **36**, 638 (1914).

For the conversion of the bromates into oxalates the following method was found most suitable: To the saturated solution of the bromates is added a concentrated solution of barium chloride. This causes the precipitation of practically all the bromate radical as crystalline barium bromate, and leaves the rare earth chlorides in solution. The solution may be readily filtered and the earths precipitated with oxalic acid, after the addition of free mineral acid to prevent the precipitation of barium oxalate. In this way barium bromate is obtained in suitable condition for conversion of other rare earth material into bromates. Direct addition of oxalic acid to a solution of rare earth bromates should be avoided as it results in the evolution of free bromine and the decomposition of oxalic acid. It is a disagreeable operation as well as a wasteful one.

A sample of earth for analysis was taken from a fraction in a bromate series which had been run for the concentration of erbium for a very long time, until the method seemed to give only very slow further separation. The fraction analyzed was judged by its absorption spectrum to be the one richest in erbium, and to contain only erbium and yttrium. The atomic weight was found by the permanganate method to be 162.34, which indicated an erbium content of about ninety-three per cent. Several fractions from this series, of composition very close to that of the sample analyzed, were united, and from them were obtained eighty-five grams of a very dense, rose-colored oxide. This material was fractionated by sixteen series of fusions by the basic nitrate method. There were thus obtained eight fractions of which the one richest in erbium gave an atomic weight slightly above 164 (this determination was made by another worker in this laboratory and exact data are not available). This value indicated an erbium content of about 95%.

Series C and D, the bromate series which were being run for the concentration of holmium and dysprosium, respectively, proved very interesting. A study of the absorption spectra showed that a rather marked separation had taken place in Series C after it had been fractionated for a long time. Some fifty fractions had been set out of the insoluble end of this series and placed in series containing less soluble bromates. There remained in the series sixteen fractions. A sample from Fraction 54, the least soluble fraction, which contained a large percentage of dysprosium and holmium and small amounts of terbium, praseodymium and neodymium, was analyzed by the sulfuric acid volumetric method. The oxide was cream colored. The atomic weight found was 161.59. A sample from Fraction 64, which was judged to be richest in holmium, and which contained only traces of dysprosium, together with a large percentage of yttrium, was analyzed. The permanganate method gave the value 128.15 and the sulfuric acid volumetric method gave the value 128.28 for the atomic weight. Those values indicated a holmium content of about 50%.

A sample from Fraction 69, the most soluble fraction, which showed only holmium absorption and which gave a cream-colored oxide, was analyzed. The sulfuric acid volumetric method gave the atomic weight as 105.22, indicating a holmium content of about 22%.

A study of the fractions of bromate, Series D, after it had been fractionated for a long time in a similar manner to the preceding series, showed that it consisted almost entirely of dysprosium material. There were present small amounts of holmium, terbium, praseodymium and neodymium. A sample from Fraction 34, the least soluble in the series, which showed slight praseodymium and neodymium absorption bands in addition to those of dysprosium and which gave a light brown oxide, gave the atomic weight 161.19. A sample from Fraction 41 in the same series, which showed holmium absorption bands, but no neodymium, gave the atomic weight 161.92. It was evident from the values obtained, 161.19, 161.92 and 161.59, that the bromates of Series D and those from the insoluble end of Series C were of quite uniform composition. The absorption spectra indicated the presence of but slight amounts of earths other than dysprosium. It was decided to purify further this material for the purpose of securing dysprosium material of sufficient purity for accurate atomic weight determinations and to determine the atomic weight of the element.

IV. **History of Dysprosium.**—There is but little regarding dysprosium to be found in the literature. In 1886, Lecoq de Boisbaudran[1] announced that he had been able to divide the earth, known as holmia, into two earths. He made the separation by fractionating with potassium sulfate and alcohol. He gave the name dysprosium, from a Greek word meaning "difficult to approach," to the earth which gave the following absorption maxima in solution; $\lambda = 753, 475, 451.5, 427.5$. Boisbaudran[2] did not succeed in freeing the new earth from terbia.

In 1906 Urbain[3] announced the isolation of about fifty grams of the dysprosium of Boisbaudran. He studied the absorption in the ultraviolet region, gave the atomic weight as 162.49, and stated that the characteristics of its compounds range it in the rare earth series between terbium and holmium. He found no evidence of the complexity of the element. He recommended the fractionation of the ethyl sulfates and of the simple nitrates as being most suitable for the separation of yttrium and terbium from dysprosium. However, neither of these methods was very satisfactory for the separation of holmium from dysprosium.

In the same year, Urbain and Demenitroux published a series of determinations[4] of the atomic weight of dysprosium. As a result of twelve

[1] *Compt. rend.*, 102, 1003 (1886); *Chem. News*, 53, 265 (1886).
[2] *Ibid.*, 102, 1005 (1886); *Ibid.*, 53, 265 (1886).
[3] *Compt. rend.*, 142, 785 (1906).
[4] *Ibid.*, 143, 598 (1906).

determinations, which gave values from 162.29 to 162.75, they give 162.54 as the most probable value for the atomic weight. Their determinations were made by transforming the octohydrated sulfate $Dy_2(SO_4)_3.8H_2O$ into the oxide Dy_2O_3 by calcination at white heat. Few details are given. In 1908, Urbain[1] mapped the spark spectrum of dysprosium and determined the magnetic susceptibility of its oxide, Dy_2O_3. Bourion[2], Urbain and Jantsch,[3] Jantsch and Ohl,[4] have prepared and studied several compounds of dysprosium. Moseley,[5] in his table of the elements, in which the arrangement is based upon the high frequency spectra, gives the atomic number of dysprosium (symbol given as Ds) as 67, placing it between holmium (66) and erbium (68). Dushman[6] mentions the fact that in Moseley's table the order of atomic numbers in the case of dysprosium and holmium is apparently the reverse of that of the atomic weights.

V. Fractionation of the Simple Nitrates for the Separation of Dysprosium.—Fractionation of the bromates showed that the last traces of praseodymium and terbium could be removed from dysprosium but very slowly, if at all, by this method. Accordingly, it was decided to convert the dysprosium rich material from Series D and from the insoluble end of Series C into nitrates and ethyl sulfates, and fractionate these salts. From the least soluble fractions in Series D were obtained eighty-six grams of a light brown oxide, containing dysprosium, with small amounts of neodymium, praseodymium and terbium, and a faint trace of holmium. The atomic weight as determined by the sulfuric acid volumetric method was between 161.2 and 161.9. The oxide was dissolved in nitric acid. Bismuth nitrate was added and the fractional crystallization carried on in nitric acid solution of about 60% nitric acid. According to Urbain,[7] bismuth nitrate is very slightly less soluble than terbium nitrate, dysprosium nitrate is more soluble than terbium nitrate, and neodymium nitrate is more soluble than dysprosium nitrate in nitric acid solution. The nitrates crystallize well and the mother liquors are easily drained off. There is considerable tendency towards the formation of supersaturated solutions unless seeding is resorted to or a slight amount of the solid left undissolved when solution for recrystallization takes place. This is also true of the bromates. The nitrates were run through about fifty series of crystallizations. As a result of these crystallizations the absorption spectra and the color of the oxides showed that but slight change was

[1] *Compt. rend.*, **146**, 922 (1908).
[2] *Ibid.*, **145**, 243 (1907); *Ann. chim. phys.*, [8] **381**, 21, 77 (1910).
[3] *Compt. rend.*, **146**, 127 (1908).
[4] *Ber.*, **44**, 1274 (1911).
[5] *Phil. Mag.*, **27**, 703 (1914).
[6] *Gen. Elec. Rev.*, **18**, 614 (1915).
[7] *Compt. rend.*, **149**, 37 (1909).

taking place. Neodymium concentrated somewhat at the soluble end.[1] It was decided to change the earth nitrates into ethyl sulfates, since an ethyl sulfate series being fractionated at the same time was found to be giving a good separation. The nitrate fractions were united, with the exception of five fractions at the soluble end, which were set aside as most of the neodymium had concentrated in them. Bismuth was removed from the united fractions by dilution and by precipitation with hydrogen sulfide. The earths were precipitated with oxalic acid. The oxalates obtained were ignited to oxides. The weight of the oxides was between seventy-five and eighty grams.

VI. Fractionation of the Ethyl Sulfates for the Separation of Dysprosium.—The oxides obtained from the simple nitrate series were dissolved in the calculated amount of ethyl sulfuric acid, N. F. = 0.63.[2] The oxides dissolved quite readily though it was difficult to get them to neutralize the solution completely. As the ethyl sulfates decompose quite readily it was not considered safe to heat very much in order to hasten solution. The neutral solution finally obtained was evaporated under reduced pressure, with gentle warming, until quite concentrated, after which air was blown over the surface until solution was evaporated sufficiently for crystallization. This series was fractionated, using absolute alcohol as a solvent. It was hoped that this would prevent hydrolysis of the ethyl sulfates, which takes place readily in aqueous solution, especially if there is present a trace of free acid.[3] The ethyl sulfates were found to be quite stable under the conditions of fractionation. Care was taken not to heat the fractions any hotter than was necessary to dissolve the crystals. This dissolving was done on a steam bath kept at a temperature no hotter than the hand could bear with comfort. The ethyl sulfates did not form supersaturated solutions as did the bromates and nitrates. This adds much to the convenience of the fractionation. The slight amounts of neodymium and praseodymium present in the series concentrated rapidly in the least soluble fractions. The terbium concentrated in the less soluble fractions also, but not nearly so rapidly as did the neodymium and praseodymium. The dysprosium, with the slight trace of holmium present, concentrated in the middle and most soluble fractions. This series will be referred to later as the first ethyl sulfate series.

The bromates from the more soluble fractions of Series D, having an atomic weight of 161.6 to 161.9 as determined by the sulfuric acid volumetric method, were converted to the oxides. The yield was seventy-three grams of buff-colored oxide. This was mainly dysprosium, with 1 or 2% of holmium and slight amounts of praseodymium and terbium,

[1] Demarcay, *Compt. rend.*, 130, 1019 (1900).

[2] Urbain, *J. chim. phys.*, 4, 31 (1906).

[3] *Loc. cit.*

and a trace of neodymium. From the method used in fractionating the bromates and from the small percentage of holmium present, it was regarded that this material was free from yttrium though there was no positive, direct evidence of this. The oxide was converted into ethyl sulfate in the manner recommended by James.[1] The procedure was as follows: The oxide was dissolved in hydrochloric acid to neutral solution. This solution was concentrated and treated with an alcoholic solution of sodium ethyl sulfate. The precipitated sodium chloride was filtered off and the series was fractionated similarly to the preceding one. This method of preparing the ethyl sulfate was not nearly so satisfactory as that of dissolving the oxide in ethyl sulfuric acid. Considerable sodium salts remained in solution and were troublesome to remove in the final purification of the material for analysis. As the fractionation progressed the neodymium and praseodymium rapidly concentrated in the least soluble fractions, which were removed from the series from time to time. After the series had been run about twenty times a sample from the soluble end was analyzed. The oxide was cream colored. Check analyses by the sulfuric acid volumetric method gave the values 162.62 and 162.41 for the atomic weight. A sample from an insoluble end fraction gave the value 163.01 by the same method. This series will be referred to later as the second ethyl sulfate series.

Since it appeared that, with the material at hand, dysprosium might readily be isolated with no impurity other than a small amount of holmium, which was not sufficient to affect the atomic weight more than one or two points in the second decimal place, and for which a correction might be made, based on the intensity of the absorption spectrum, it was decided to attempt to determine accurately the atomic weight of dysprosium. With this end in view, the fractionation of the ethyl sulfates was continued. It was decided to study the ratio $Dy_2O_3 : 2DyCl_3$ by a method similar to that used for the determination of the atomic weight of yttrium by Egan and Balke.[1]

VII. Preparation of Reagents Used in the Atomic Weight Determinations.—*Water.*—The ordinary distilled water was redistilled, after the addition of alkaline potassium permanganate, from the still used in this laboratory for conductivity water.

Oxalic Acid.—Chemically pure oxalic acid was dissolved in hot water. The slight, insoluble residue was filtered off and the acid crystallized twice from dilute nitric acid, and twice from conductivity water. After each crystallization the product was sucked dry on a Büchner funnel.

Nitric Acid.—Chemically pure nitric acid was distilled from a quartz container, through a quartz condenser into a quartz receiver. The middle third was reserved for use.

[1] *Loc. cit.*

Hydrochloric Acid Solution.—This was prepared by heating the concentrated chemically pure hydrochloric acid and passing the gas into conductivity water. Quartz vessels were used throughout.

Hydrogen Chloride Gas.—This was prepared by dropping chemically pure concentrated sulfuric acid on chemically pure concentrated hydrochloric acid. It was dried by passage through two vertical drying towers, each one meter high and two and one-half centimeters in diameter. The towers were filled with solid glass beads wet with chemically pure concentrated sulfuric acid. The entire apparatus was of glass and was continuous.

Ammonia.—This was made as used by warming the chemically pure concentrated aqueous solution.

Nitrogen.—Air was mixed with ammonia and passed through a quartz tube containing copper gauze heated to redness, then bubbled through dilute sulfuric acid. The nitrogen thus obtained was purified and dried as follows: The gas was passed through a tower, sixty centimeters high, two and one-half centimeters in diameter, containing solid glass beads moistened with dilute sulfuric acid, next through a similar tower in which the beads were moistened with a 5% silver nitrate solution, next through a similar tower in which the beads were moistened with chemically pure concentrated sulfuric acid, next through a tower seventy-five centimeters high, three and eight-tenths centimeters in diameter, loosely packed with solid potassium hydroxide, next through a sulfuric acid tower similar to the preceding one, and finally through a tube forty centimeters high, two centimeters in diameter, containing glass wool interspersed with phosphorus pentoxide which had been redistilled directly into the tube. The gas was passed upward through each tower. The purifying and drying train was constructed entirely of glass and was continuous.

Air.—Air was purified and dried in the same way as nitrogen.

The hydrogen chloride, nitrogen, and air trains were all mounted compactly on a wooden support.

Vessels of platinum, quartz, or Jena resistance glass were used in all cases where the use of less resistant containers would have been likely to contaminate the material.

VIII. Preparation of Dysprosium Oxide.—The material for analysis was converted from the ethyl sulfate into the oxide as follows: The alcoholic solution was diluted with water, a little dilute sulfuric acid added, the solution heated to boiling and filtered. The object of adding the sulfuric acid was to precipitate any barium which might have been in solution. In the preparation of ethyl sulfuric acid, barium carbonate had been added to remove sulfuric acid. A slight amount of barium ethyl sulfate, which is soluble, was formed here. The dysprosium material was obtained and purified by alternate precipitations with ammonia and oxalic acid, the last precipitation, in every case, being as oxalate.

The precipitation with ammonia was carried out by passing ammonia gas into the hot solution diluted to from one to one and one-half liters, until all the dysprosium was precipitated. The hydroxide was filtered with suction, washed and dissolved in considerable excess of nitric acid, the solution diluted to from one to one and one-half liters, heated to boiling, and an excess of a hot solution of oxalic acid added. This was allowed to stand until cool, after which it was filtered and washed with hot water. Precipitated in this way, the oxalate filtered readily and was easily washed. The oxalate was then dried, ignited in an electric furnace in platinum, and the oxide dissolved in nitric acid if another precipitation was desired. Each sample analyzed was precipitated two or more times with ammonia and two or more times with oxalic acid in the manner described. In addition Sample number 3 was precipitated with ammonium sebacate.[1] The oxalate finally obtained was ignited for several hours in a platinum crucible, to bright redness in an electric resistance furnace. The oxide was then used for the atomic weight determination.

IX. Ratio of Dysprosium Oxide to Dysprosium Chloride.—The above ratio was obtained by converting a weighed amount of the oxide to the anhydrous chloride and determining its weight. The method of procedure was quite similar to that used by Egan and Balke[2] in their study of a similar ratio for yttrium. The oxide, while still hot, was transferred to the weighed quartz reaction flask. The bulb of the flask used in this work had a capacity of twenty-five cubic centimeters. After addition of the oxide the caps were adjusted over the inlet and outlet tubes and the flask placed in a desiccator to cool over solid sodium hydroxide. After having cooled one of the joints was loosened for an instant, in order to allow the pressure to equalize. The flask was then hung in the balance case for several hours, after which it was weighed. The oxide was then dissolved by the addition of a slight excess of hydrochloric acid, with gentle warming. The solution took place slowly and quietly, and without spattering. The flask was next attached to the gas train by means of ground glass joints. The gas train was so arranged that either air, nitrogen, hydrogen chloride, a mixture of air and hydrogen chloride, or a mixture of nitrogen and hydrogen chloride could be passed through the flask at will. Air was first passed in while the solution was heated in an electric oven to 100–105°. When the solution had become quite concentrated the air current was stopped and a current of hydrogen chloride passed in while the solution was allowed to cool somewhat. Dysprosium chloride separated from the strong hydrochloric acid solution in a well-crystallized form. Air was again passed in and the temperature gradually raised. At this stage care had to be taken in the heating of the flask

[1] Whittemore and James, THIS JOURNAL, 34, 772 (1912); 35, 127 (1913).

[2] *Loc. cit.*

and in the regulation of the gas current in order to prevent, on the one hand, the solution of the chloride, and on the other, the formation of an almost impermeable crust of chloride on top of the solution. In order to prevent this latter, the entering gas was preheated by passage through a coil of glass tubing enclosed in the oven, and the solution was heated from above by means of a suitable heating coil. When the temperature reached 110° the air current was replaced by nitrogen, and when it had reached 120° hydrogen chloride was mixed with the nitrogen. This was done in order to eliminate the danger of formation of basic chloride. The temperature was allowed to rise to 125°, where most of the water of crystallization came off. The temperature was allowed to remain at 125° until water ceased coming off, after which it was raised to 200°. Between 125° and 200° no water was given off. Nitrogen was replaced entirely by hydrochloric acid gas when the temperature reached 200°. At 200° water began coming off again and this temperature was held until most of the water was expelled. A small resistance furnace, with alundum core, was now placed around the bulb of the flask, the temperature raised slowly to 350° and kept there for about one and one-half hours after all visible water had been expelled. The furnace was then allowed to come to dull red for a few minutes. It was then removed. A protecting shield of asbestos was placed just above the bulb of the flask to prevent undue heating of the neck during fusion. The current of hydrogen chloride was stopped and the chloride fused with the flame of a Bunsen burner. According to Bourion[1] the chloride fuses at 680°. As soon as fusion had taken place the flame was removed and as the flask cooled the hydrogen chloride was replaced by nitrogen, which in turn was replaced by air. While the flask was at room temperature, and while the air was yet passing, the cap was adjusted on the outlet tube. This caused a slight back pressure in the flask which prevented moist air entering the flask while the cap was being quickly adjusted on the inlet tube. The time required for converting a sample of oxide into anhydrous chloride was twenty-five to thirty hours. The flask was hung in the balance case for several hours and weighed.

Dysprosium chloride prepared in the manner just described formed a crystalline, olive-green mass which did not wet the flask. There was no indication of volatilization during the fusion period. The chloride dissolves slowly and completely in cold water to a clear solution, with evolution of considerable heat. The solution is almost neutral to litmus. There is perhaps a faint trace of acidity. The solution obtained in analys is number 2 was tested with several indicators with the following results: Blue litmus paper was changed to red-violet. Red litmus paper was unchanged. The solution was neutral to methyl orange, acid to

[1] *Loc. cit.*

methyl red, and acid to phenolphthalein. This slight acidity was probably due to hydrolysis, as dysprosium is a relatively weak base[1] in the rare earth series.

Five consecutive determinations have been made. Samples 1 and 2 were obtained from two fractions near the middle of the second ethyl sulfate series after it had been run about sixty-five times. These fractions were united and the oxide obtained as previously described. The two samples had the same treatment, with the exception that the oxide of Sample 2 had been ignited eight hours longer than that of Sample 1. The magnetic susceptibility of the oxide from these two samples was determined by Mr. O. A. Randolph of the Physics Department of the University of Illinois, whom the authors wish to thank for this work. Determinations were made on two portions of oxide. The values obtained for $X.10^{-6}$ per unit mass were 291.1 at 24° and 290.6 at 23°. Urbain[2] gives the value for dysprosium oxide as 290. He does not state the temperature.

Sample 3 was taken from near the middle of the second ethyl sulfate series after it had been run about sixty times. A test of the purity of this sample was made by passing hydrogen sulfide, for one-half hour, into the aqueous solution of the chloride obtained at the end of the determination. No precipitate was formed and the solution remained clear. A comparison of the absorption spectrum of the nitrate solution of this sample, with a nitrate solution containing a known amount of holmium from a holmium-yttrium mixture, indicated the presence of approximately 1.5% of holmium. Assuming the correct atomic weight of holmium as 163.5, the value given in the International Table, this amount would affect the atomic weight of the sample approximately 0.01 unit. The oxides of Samples 1, 2 and 3 had a light cream color, almost white.

Sample 4 was obtained from the three most soluble fractions in the first ethyl sulfate series after it had undergone about forty series of crystallizations. There was only a very slight trace of holmium in this material. The color of the oxide was darker than that of the other samples. This indicated the presence of a slight amount of terbium, which seemed to lower the atomic weight.

Sample 5 was obtained from near the insoluble end of the second ethyl sulfate series after about seventy series of crystallizations. The oxide was cream colored.

All weighings were made by the method of substitution, the tare flask being of quartz and similar in size, shape and weight to the reaction flask. The weighings were made on a Ruprecht balance, which is used exclusively for atomic weight work. The weights were carefully standard-

[1] Urbain, *Compt. rend.*, 143, 598 (1906).

[2] *Loc. cit.*

ized to 0.01 mg. All weights were corrected to vacuum standard. The specific gravity of the weights was taken as 8.4, that of the chloride as 3.67,[1] and that of the oxide as 7.81, which was determined. The atomic weight of oxygen was taken as 16, and that of chlorine as 35.46. The following values were obtained:

Sample.	Weight oxide.	Weight chloride.	Oxide: chloride.	Atomic wt.
1.....	0.50996 g.	0.73300 g.	1 : 1.437367	164.354
2.....	1.05741	1.51988	1 : 1.437361	164.357
3.....	0.65617	0.94352	1 : 1.437920	164.116
4.....	1.22603	1.76297	1 : 1.437950	164.104
5.....	1.96935	2.83135	1 : 1.437707	164.207
				Mean, 164.228

X. Specific Gravity of Dysprosium Oxide.—In order to change the weight of dysprosium oxide in air to vacuum standard it was necessary to know the specific gravity of this substance. A single determination was made, using oxide from Analyses numbers 1 and 2 of the atomic weight determinations. A Gay-Lussac specific gravity bottle of about six cubic centimeters capacity was used, with water as the liquid. For the weighings in which there was water in the specific gravity bottle this was put inside a weighing bottle to guard against evaporation. Tare vessels similar in size and shape to the containing bottles were used in weighing. Weights were corrected to vacuum standard. Data and results were as follows:

Weight of oxide	1.4645 g.
Weight of water displaced	0.1869 g.
Volume of water displaced	0.1875 cc.
Temperature	27°
Specific gravity of dysprosium oxide, Dy_2O_3	7.81 27°/4°

XI. Summary of Results.

1. The bromate method of separating the rare earths of the yttrium group has been studied. It has been found efficient for concentrating erbium, yttrium and dysprosium material.

2. A comparative study has been made of the permanganate and sulfuric acid volumetric methods for control analyses. They have been found to give practically the same results in earth mixtures whose bromates have a solubility near that of yttrium bromate.

3. Dysprosium material of very high purity has been obtained by fractional crystallization of the rare earth bromates, followed by fractional crystallization of the ethyl sulfates.

4. The ratio of dysprosium oxide to dysprosium chloride has been studied, and as a means of five consecutive determinations the value 164.228

[1] Bourion, *Loc. cit.*

obtained for the atomic weight of dysprosium. This value is considerably higher than the one now in the International Table.

5. Some properties of dysprosium chloride are given.

6. The specific gravity of dysprosium oxide was found to be 7.81.

[CONTRIBUTION FROM THE DEPARTMENT OF PEDIATRICS, THE JOHNS HOPKINS HOSPITAL.]

A COLORIMETRIC METHOD FOR THE DETERMINATION OF THE CO_2 PERCENTAGE IN AIR.

BY H. L. HIGGINS AND W. McKIM MARRIOTT.

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An analysis for CO_2 in the air is the simplest and probably the most used method of determining the condition of the ventilation in halls, school-rooms, factories, mines, submarines, etc. This method would doubtless be still more extensively used if it were not that a more or less expensive apparatus and a fairly skilful analyst are required. One of us has recently described a simple method for determining the carbon dioxide tension in the alveolar air.[1] With some slight modification this same method may be applied for the determination of CO_2 of any percentage in air.

Principle of the Method of Analysis.—If a current of air containing CO_2 is passed through a solution of sodium bicarbonate until the solution is saturated with CO_2, the final solution will contain sodium bicarbonate and dissolved CO_2. The reaction (hydrogen-ion concentration) of such a solution will depend on the relative amounts of the alkaline bicarbonate and the carbonic acid present. This, in turn, will depend on the pressure of the carbon dioxide in the air with which the mixture has been saturated and *will be independent of the volume of air blown through, provided saturation has once* been attained. High pressures of carbon dioxide change the reaction of the solution toward the acid side. Low pressures have the reverse effect; hence the reaction of such a solution is a measure of the pressure of CO_2 in the air with which it has been saturated.

The reaction of such a solution may be determined by adding to it an indicator such as phenolsulfonephthalein[2] which shows over a considerable range of reaction definite color changes, and by comparing the resulting color with solutions of a known reaction containing the same amount of indicator.

Solutions of a given reaction may be prepared by mixing acid and alkaline phosphates in definite proportions. Such solutions, owing to

[1] Marriott, *J. Am. Med. Assoc.*, **66**, 1594 (1916).

[2] Levy, R. L., Rowntree, L. G. and Marriott, W. M., "A Simple Method for Determining Variations in the Hydrogen-Ion Concentration of the Blood," *Arch. Int. Med.*, 16, 389 (1915).