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CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS OF THE YTTRIUM GROUP. I.

BY L. M. DENNIS AND BENTON DALES.

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HISTORICAL.

THE first of the rare earths was discovered by Gadolin,[1] in 1794, in a heavy black mineral which had been found at Ytterby some six years before by Arrhenius. Three years later the earth was named yttria by Ekeberg,[2] and the mineral "yttria-stone." The latter is the gadolinite of the present day mineralogists. Ekeberg[3] found yttria in a new mineral in which he had discovered tantalum and which he called yttrotantalite. The earth was further studied by Berzelius[4] and by Berlin,[5] both of whom considered it homogeneous.

Scheerer[6] observed that when yttria was heated strongly in an open vessel it took on a yellow color, which it lost on heating in the presence of reducing gases, and that it remained colorless if cooled quickly, whereas it became colored again if heated in contact with air. He thought this phenomenon due to the presence

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[1] Sv. Vet. Akad. Handl., p. 137 (1794); Crell's *Ann.*, (1796) 1, 313.

[2] Crell's *Ann.*, **2**, 63 (1799).

[3] Sv. Vet. Akad. Handl., p. 68 (1802); *Ann. de. Chim.*, **43**, 278.

[4] Schw. *J.*, **16**, 404.

[5] Sv. Vet. Akad. Handl., pp. 209, 212 (1835); *Ann. Chem.* (Liebig), **28**, 222.

[6] Pogg. *Ann.*, **56**, 482.

in the yttria of some other earth, perhaps new, perhaps lanthana. capable of forming easily a peroxide. His work was soon followed by the researches of Mosander,[1] who separated the old yttria into three new earths. He kept the name yttria for the most basic of these; the middle one he called terbia and the least basic one erbia. His yttria was white and gave colorless salts; terbia he thought to be white also. but it gave rose-colored salts, while erbia was orange-yellow and gave colorless salts. He used the methods of fractional precipitation of the oxalates by oxalic acid from acid solution, and of the hydroxides by dilute ammonia, in both of which his erbia was thrown out first, then terbia and lastly yttria. His results were confirmed by Berzelius[2]. by Svanberg, and by Scheerer.

The earths of old yttria were reexamined in 1860 by Berlin.[3] He was the first to use the classic method of fractional decomposition of the nitrates by heat. He obtained only two of Mosander's earths. the white yttria and the one giving rose-colored salts, terbia, which he and all subsequent investigators have called erbia. Mosander's yellow erbia. the present-day terbia, he could not obtain.

Popp[4] in 1864, and Delafontaine[5] in that year and the two following ones, working at this same problem, arrived at totally different conclusions. Popp, using both of Mosander's methods, could separate neither erbia nor terbia. He thought erbia a mixture of the cerite oxides, and terbia a mixture of erbia with yttria. Delafontaine maintained that these two earths existed. Mosander's erbia he obtained by fractional precipitation with primary potassium oxalate, the small amount of yttria and terbia being removed by treatment with potassium sulphate solution. To separate the terbia and yttria remaining, he fractioned again the least-colored oxalates, then dissolved out the yttria by repeated treatment with dilute acid.

Then Bahr and Bunsen[6] in 1866, using a modification of Berlin's method of fusion of the nitrates, corroborated Berlin's results. They obtained only the true or white yttria and the rose-colored

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[1] *Phil. Mag.*, **23**, 251; *Ann. Chem.* (Liebig), **48**, 219.

[2] "Lehrbuch," 2nd French Edition, **2**, 163.

[3] Scand. Naturf. 8 Möde Kjöbenhavn, p. 448 (1860).

[4] *Ann. Chem.* (Liebig). **131**, 179.

[5] *Arch. des Sci. phys. et nat.*, (2) **21**, 97; **22**, 30; **25**, 105; *Ann. Chem.* (Liebig), **134**, 99; **135**, 188.

[6] *Ann. Chem.* (Liebig), **137**, 1.

erbia of Berlin (Mosander's terbia). Cleve and Höglund[1] in 1872, using the same method, obtained the same result.

Until Mendeléeff's announcement of the periodicity of the elements,[2] yttria, ceria and the other rare earths had been generally assumed to have the formula RO. He, however, showed that their properties placed them in the third group of his arrangement, where their maximum valence would be three (oxide, R_2O_3). Lanthana he considered to be RO_2. In order to put them into this group, it was necessary to increase their accepted atomic weights by one-half. Cleve[3] in 1874, published new researches upon the salts of yttria and erbia, which tended to show the correctness of Mendeléeff's view of the triatomicity of these earths. Nilson,[4] working upon the selenites in 1875, and upon the chlorplatinum compounds in 1876, further strengthened the idea that the rare earths, lanthana included, were sesquioxides.

A great increase in activity in rare earth research occurred in 1878, when the mineral samarskite, found in large quantities in North America, became the source of the material.

Smith[5] in 1877 isolated an earth which he considered to be new, or perhaps the third earth of Mosander. He thought it new because of the insolubility of its double potassium sulphate in saturated potassium sulphate solution. Marignac[6] showed this property to be only a relative one, and he deemed Smith's mosandria to be identical with terbia. Neither could he agree to Smith's other claim that mosandria was identical with Soret's X. Delafontaine[7] considered mosandria to be terbia. Considerably later (1886), Lecoq de Boisbaudran,[8] having obtained a sample of Smith's impure mosandria, found that it contained, besides didymia and samaria, gadolinia and terbia.

Delafontaine[9] and Marignac[10] settled the question as to the existence of terbia by preparing it. Delafontaine treated his yttria earth mixture in solution with a saturated solution of sodium sulphate containing crystals of the salt, then fractioned the pre-

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[1] *Bull. Soc. Chim.*, (2), **18**, 193, 289.

[2] *Ann. Chem.* (Liebig), Suppl., **8**, 133, esp. p. 184 ff.

[3] *Bull. Soc. Chim.*, (2), **21**, 344.

[4] *Ber. d. chem. Ges.*, **8**, 655; **9**, 1056, 1142.

[5] *Proc. Acad. Nat. Sci.*, Phila., **29**, 194; *Compt. rend.*, **87**, 146, 148.

[6] *Arch. des Sci. phys. et nat.*, (2), **63**, 172; *Compt. rend.*, **87**, 281.

[7] *Compt. rend.*, **87**, 600.

[8] *Loc. cit.*, **102**, 647.

[9] *Arch. des Sci. phys. et nat.*, (2), **61**, 273; *Ann. chim. phys.*, (5), **14**, 238.

[10] *Arch. des Sci. phys. et nat.*, (2), **61**, 283; *Ann. chim. phys.*, (5), **14**, 247.

cipitated portion with oxalic acid from strong nitric acid solution, and finally treated the first of these precipitates with formic acid and concentrated. Terbia crystallized out as formate. There was also a yellow earth in the portion soluble in the sodium sulphate, but it was not so deeply colored as terbia and gave besides a base of lower atomic weight. He thought it a new element. Marignac obtained terbia as well as yttria and erbia by fusion of the nitrates. By making several hundred fractions and by properly combining them he obtained finally pure yttria at one end and erbia at the other. The intermediate products possessed a yellow color. These he combined and fractioned by oxalic acid in acid solution. Erbia and didymia he found to go with terbia. Didymia he removed by the potassium sulphate treatment, but he could not free his product from erbia. Hofmann and Krüss[1] in 1893 studied terbia, and by fractionation with aniline hydrochloride succeeded in breaking it up into two probable earths with metal atomic weights of 148 to 150 and 160. calculated as R^{III}. In 1895 Lecoq de Boisbaudran[2] called attention to an absorption band in his terbia material which could not belong to any known element. He called the one which gives it Z_δ. Its band was at $\lambda 487.7$.

The new earth which Delafontaine suspected in the saturated sodium sulphate solution mentioned above, was announced by him[3] as philippia. It was characterized by a magnificent absorption band in the violet at $\lambda 450$. Soret[4] stated that philippia was identical with the earth X, which Cleve[5] denied. Delafontaine[6] maintained that philippia. Soret's X. and Cleve's holmia were identical, which Cleve again denied. Delafontaine[7] then admitted that the absorption spectrum ascribed by him to philippia belonged to Soret's X, but maintained still the individuality of the former. Roscoe,[8] in 1882. by fractional precipitation of the double potassium sulphates with potassium sulphate, and by fractionation of the first portions of these by the varying solubilities of the formates, could obtain no product whose metal had

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[1] *Ztschr. anorg. Chem.*, **4**, 27.
[2] *Compt. rend.*, **121**, 709.
[3] *Loc. cit.*, **87**, 559.
[4] *Loc. cit.*, **89**, 521.
[5] *Loc. cit.*, **89**, 708.
[6] *Loc. cit.*, **90**, 221.
[7] *Arch. des Sci. phys. et nat.*, (3), **3**, 246.
[8] *Ber. d. chem. Ges.*, **15**, 1274.

a constant atomic weight of 121 to 123, and he concluded that philippia was a mixture of terbia and yttria. Crookes[1] agreed with Roscoe as to the non-existence of philippia. In 1897, Delafontaine[2] gave the methods by which philippia might be prepared; they were the standard ones of fractional precipitation of the nitrate solution of the rare earths with ammonia, or with primary potassium oxalate, or fractional decomposition of the nitrates by heat. Urbain.[3] in 1900, denied the existence of philippia.

In this year of 1878, while studying the impure didymia from samarskite, Delafontaine[4] discovered a new oxide which he called decipia. Its metal had a high atomic weight ($R^{III} = 159$), and it was characterized by the absorption bands $\lambda 416$ and $\lambda 478$. Lecoq de Boisbaudran[5] found, in a spectroscopic examination of a mixture of earths rich in didymia from samarskite, some new rays. In the spark spectrum there were four rays: in the absorption spectrum, two strong bands and three faint ones. The strong bands were in the blue and had their centers at $\lambda 480$ and $\lambda 463.5$. One of the other bands had a wave-length of $\lambda 416$, which had been ascribed by Delafontaine to one of the bands of decipia. Lecoq de Boisbaudran finally separated the earth giving these bands from didymia, and he called it samaria. Then Marignac.[6] by fusion of the nitrates and fractionation of the double potassium sulphates, isolated two earths which he called Y_α and Y_β. The double potassium sulphate of Y_α was comparatively soluble in potassium sulphate solution; solutions of the earth gave no absorption spectrum, and the equivalent weight of the metal was about 120.5 (RO). Y_β, on the other hand, gave a double potassium sulphate less soluble in potassium sulphate solution; solutions of the earth gave an absorption spectrum corresponding to that of decipia or better to that of samaria, and the metal had an equivalent weight of 115.6. Y_α has since been called gadolinium.[7] Delafontaine[8] again in 1881 showed that, by treating those earth sodium double sulphates most insoluble in a saturated solution of Glauber's salt with cold

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[1] *Phil. Trans. Roy. Soc.*, **174**, 910.

[2] *Chem. News*, **75**, 229.

[3] *Ann. chim. phys.*, (7), **19**, 192.

[4] *Compt rend.*, **87**, 632.

[5] *Compt. rend.*, **88**, 322; **89**, 212.

[6] *Arch. des Sci. phys. et nat.* (3), **3**, 413.

[7] *Compt. rend.*, **102**, 902.

[8] *Loc. cit.*, **93**, 63.

water, his decipia of two years before could be decomposed into two oxides, one with a metal equivalent of about 130 (RO) giving no absorption spectrum, the other with a base of much lower equivalent (not over 117) giving the absorption spectrum ascribed to the original decipia. He expressed the opinion that this second oxide and samaria were identical, as well as Marignac's Y_β. He also thought that the earth Y_α was a mixture of decipia and terbia, but Marignac pointed out that this could not be, because the oxide of Y_α was white. whereas that of terbium was colored. The oxide of Y_α and decipia were perhaps identical.

Cleve[1] has made an exhaustive study of samaria and its compounds. He isolated it by combining the methods of fractional precipitation with potassium sulphate solution. and with dilute ammonia. The atomic weight of samarium he found to be 150.02 (R^{III}). Its spark spectrum has been described by Thalén[2] and by Lecoq de Boisbaudran[3]. The latter also studied its fluorescence spectrum. The body giving the spark spectrum he called Z_ϵ, the one giving the fluorescence Z_ζ. Demarçay[4] found that samarium could be split into at least two simpler constituents. He used three methods, Welsbach's, fractional precipitation with ammonia, and another not given. He kept the name samarium for the element giving λ 407 and λ 400. and called the other provisionally S. Krüss and Nilson,[5] in an article on the rare earths giving absorption spectra. also observed the fact that solutions containing samarium did not always give the same absorption spectrum. They obtained some solutions showing only λ 417. and the body to which this band was due they called Sm_α. Crookes[6] in 1886, following the fractionation of samarium by examination of the phosphorescence spectra, concluded that the samarium of gadolinite enclosed three components, while the samarium from samarskite contained a fourth. He[7] also observed an anomalous ray in the phosphorescence spectrum of samarium. Its wavelength was 609, and the body to which it was due he called S_α.

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[1] *Compt. rend.*, **97**, 94; *Bull. Soc. Chim.*, (2), **43**, 162; *Chem News*, **53**.

[2] Sv. Vet. Akad. Handl., No. 7, p. 3 (1883) ; *J. de Phys.*, (2), **2**, 446; *Ber. d. chem. Ges.*, **16**, 2760.

[3] *Compt. rend.*, **114**, 575; **116**, 611, 674; **117**, 199.

[4] *Loc. cit.*, **102**, 1551.

[5] *Ber. d. chem. Ges.*, **20**, 2134.

[6] *Proc. Roy. Soc.*, **40**, 502.

[7] *Compt. rend.*, **102**, 1464.

In 1891 Bettendorff[1] obtained pure samaria by fractionation with ammonia, after the removal of ceria by fusion of the nitrates with potassium nitrate, the yttria group by treatment with potassium sulphate, and lanthana by decomposition of the nitrates by heat. He described the absorption spectrum, and denied that it had a phosphorescence one. He thought that samarium was a chemical individual. In 1893 Demarçay[2] decided that, as far as the absorption spectrum showed, there was no reason to suspect the complexity of samarium. He examined four different fractions of Lecoq de Boisbaudran's samarium material. In 1900 Demarçay[3] separated samaria from neodidymia by fractional crystallization of the magnesia double nitrates from nitric acid solution.

Crookes[4] questioned the individuality of gadolinium, stating that its phosphorescence spectrum was practically identical with that of a mixture of 61 parts of yttria and 39 of samaria. Lecoq de Boisbaudran[5] did not agree with him. Lecoq found, however, that Marignac's gadolinia contained about 10 per cent. of impurities, and he succeeded in removing all but about 0.02 or 0.03 per cent. of these. Crookes[6] described its phosphorescence spectrum, and Lecoq[7] its spark spectrum. Bettendorff[8] separated gadolinia from samaria and terbia by fractionation with ammonia. He could get no spark spectrum, nor could Thalén. In 1896 Demarçay[9] prepared gadolina by fractional crystallization of the earths rich in samaria from fuming nitric acid (sp. gr., 1.45), and gave the rays of its spark spectrum. Gadolinia was precipitated first, and samaria last. Between the two he discovered a new earth which he called Σ, characterized by its colorless salts with no absorption. The earth was colorless, which distinguished it from terbia; its spark spectrum was different from those of lanthana, ceria, gadolinia, ytterbia, terbia. It differed from gadolinia and samaria only in its spark spectrum. In 1899 Benedicks,[10] using Marignac's method partly, and partly by fusion of the ni-

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[1] *Ann. Chem.* (Liebig), **263**, 164.
[2] *Compt. rend.*, **117**, 163.
[3] *Loc. cit.*, **130**, 1185.
[4] *Chem. News*, **54**, 39, 115.
[5] *Compt. rend.*, **108**, 165 ; **111**, 393.
[6] *Ibid.*, **102**, 646.
[7] *Loc. cit.*, **111**, 472.
[8] *Ann. Chem.* (Liebig), **270**, 376.
[9] *Compt. rend.*, **122**, 728.
[10] *Ztschr. anorg. Chem.*, **22**, 393.

trates, then their fractionation from concentrated nitric acid, and lastly their precipitation by ammonia, prepared gadolinia and studied it. He could not obtain Demarçay's Σ. His gadolinia gave a spark spectrum, and the atomic weight of the metal was 156 (R^{III}). Demarçay,[1] in 1900, was unable to isolate Σ, even after 800 fractions with the magnesia double nitrates; but since then he[2] has isolated it sufficiently pure for characterization. He has named it europium.

Marignac,[3] in trying to isolate Delafontaine's philippia by partial decomposition of the nitrates by heat, discovered a new earth which he called ytterbia. It was colorless, and its metal had a high atomic weight ($R^{III} = 172.5$); further, it had no absorption spectrum. The method he used was a modification of Bahr and Bunsen's. He heated the nitrates till a portion was insoluble in hot water, whereas they heated only until the mass, which was entirely soluble in hot water, gave a crystalline precipitate of basic nitrates on cooling. In 1879 and 1880, Nilson[4], using Marignac's method, isolated more ytterbia, and studied it. He found the atomic weight of the metal ytterbium to be 173. Pure ytterbia was obtained only after 400 or 500 ignitions. While working with this material, he obtained a white oxide whose metal equivalent was lower than that of ytterbia. This caused him to suspect the presence of another oxide, the metal of which had a lower atomic weight. By following the same method of fractionation, he[5] succeeded in isolating this earth. Its base had an atomic weight of 44, and proved to be identical with Mendeléeff's ekaboron, both in its properties and its atomic weight. He called his earth scandia. Cleve[6] also prepared scandia. His atomic weight of scandium was a unit higher than Nilson's, probably because of ytterbium in the material. The spark spectrum of ytterbia has been studied by Thalén[7] and by Lecoq de Boisbaudran[8]: that of scandia by Thalén.[9]

Soret,[10] by a spectroscopic examination of Marignac's erbia and

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[1] *Compt. rend.*, **130**, 1019.

[2] *Loc. cit.*, **132**, 1484.

[3] *Arch des Sci. phys. et. nat.*, (2), **64**, 97; *Compt. rend.*, **87**, 578.

[4] *Ber. d. chem. Ges.*, **12**, 550; **13**, 1430.

[5] *Ber. d. chem. Ges.*, **12**, 554; **13**, 1439.

[6] *Bull. Soc. Chim.*, (2), **31**, 486.

[7] *Chem. News*, **47**, 217; *Compt. rend.*, **91**, 326.

[8] *Compt. rend.*, **88**, 1342.

[9] *Loc. cit.*, **88**, 646; **91**, 45; *Chem. News*, **47**, 217.

[10] *Compt. rend.*, **86**, 1062.

terbia materials, found a series of absorption bands which did not belong to erbia or to any other of the known elements. He called the earth giving them X. Cleve,[1] in 1897, showed that by fractional decomposition of the nitrates by heat, erbia free from ytterbia and scandia could be separated into three earths, each characterized by an absorption spectrum which was a portion of the one ascribed to old erbia. The metals in these earths were the true erbium. with an atomic weight of about 166 ;[2] holmium, and thulium with an atomic weight of about 170.7.[3] Soret[4] stated that holmia and his earth X were identical, and Cleve[5] admitted this to be true. Delafontaine maintained that his philippia was identical with both of these, but Cleve could not establish this fact. Delafontaine himself afterwards admitted that his philippia had no absorption spectrum. Lecoq de Boisbaudran[6] proved, by making many hundreds of fractions with ammonia and with potassium sulphate and alcohol, that the holmia spectrum could be divided into two portions, the bands characteristic of one being $\lambda 640.4$ and $\lambda 536.3$, and of the other $\lambda 451.5$ and $\lambda 753$. Since the first two bands were the ones by which Cleve and Soret originally characterized the element holmium, he kept this name for the one giving them ; the one to which the other bands were due he called dysprosium. Crookes,[7] soon after Lecoq's announcement, stated that he had isolated an earth in this group giving only the absorption band $\lambda 451$, and that therefore dysprosium was probably still a complex substance. Lecoq has expressed the same opinion. Krüss and Nilson[8] showed, by a spectroscopic examination of the absorption bands of the rare earths obtained from many different minerals, that the variations in intensities of the bands as found in these minerals, could be accounted for only upon the assumption that the bands belonged to different individuals. As a result of this, they considered what we now call erbia to be made up of two components, thulia of two, holmia of four, and dysprosia of three. Hofmann and Krüss[9] in 1893 concluded. as a result of their aniline hydro-

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[1] *Loc. cit.*, **89**, 478.
[2] *Compt. rend.*, **91**, 381.
[3] *Loc. cit.*, **91**, 328.
[4] *Loc. cit.*, **89**, 521.
[5] *Loc. cit.*, **89**, 708.
[6] *Loc. cit.*, **102**, 1003, 1005.
[7] *Proc. Roy. Soc.*, **40**, 502.
[8] *Ber. d. chem. Ges.*, **20**, 2134.
[9] *Ztschr. anorg. Chem.*, **3**, 407.

chloride fractionation, that holmium was a complex substance; Krüss[1] alone has thrown doubt upon the individuality of erbia. By fractionation of his material rich in erbia from alcoholic solution with an alcoholic solution of aniline, then of the middle portions of this series as earth chloride aniline hydrochloride by ammonia, he could not get an earth whose base had a constant atomic weight. The beautiful absorption spectrum of erbia was discovered by Bahr[2] in 1862. Crookes[3] mapped all of the spectra of erbia. The absorption, emission, and spark spectra of thulia have been studied by Thalén.[4]

In 1883 Crookes[5] discovered that the anhydrous sulphates of certain rare earths became phosphorescent when exposed to the electric discharge in a vacuum tube, and that this light gave characteristic spectra. He[6] had in 1881 observed that some of the earths themselves phosphoresced under the same conditions. In 1883 he discovered in these phosphorescence spectra the citron band which he decided to be due to yttria. In 1884, Lecoq de Boisbaudran[7] discovered that if the positive pole were immersed in a solution of some of the rare earths, and the negative one brought just above its surface, the light which was emitted on the passage of the spark gave an inversion spectrum which was nearly related to the phosphorescence spectrum of Crookes. Both were very delicate, and were greatly influenced by the presence of foreign oxides.

In 1886 and the year following Crookes[8] separated yttria by a large number of different fractionations into five portions, each of which had different phosphorescence spectra, but all of which showed the spark spectrum of yttria. The bodies responsible for these phosphorescence spectra he called "meta-elements," and he developed his theory of the genesis of the elements on the basis of this observation. In further support of the idea that yttria was a complex substance, he stated that Marignac's gadolinia gave him the same phosphorescence spectrum as yttria, except that the citron band was missing, and that the two green bands of samaria were present. Then a mixture of 61 parts of yttria

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[1] *Loc. cit.*, **3**, 353.

[2] Sv. Vet. Akad. Handl., p. 597 (1862); *Ann. Chem.* (Liebig), **131**, 256.

[3] *Chem. News.*, **53**, 75.

[4] *Chem. News.*, **47**, 217; *Compt. rend.*, **91**, 376.

[5] *Phil. Trans. Roy. Soc.*, **174**, 891; *Chem. News*, **47**, 261; **49**, 159, 169, 181, 194, 205.

[6] *Chem. News*, **44**, 23; *Proc. Roy. Soc.*, **32**, 209.

[7] *Compt. rend.*, **100**, 1437.

[8] *J. Chem. Soc.*, **55**, 250; *Chem. News*, **54**, 115; **55**, 83, 95.

with 39 of samaria gave the same phosphorescence as gadolinia, except for the presence of the citron band. He also found that the yttria from different minerals gave phosphorescence spectra with its rays of varying intensity, showing that a partial separation had taken place in nature.

This theory and all its conclusions were opposed by Lecoq de Boisbaudran.[1] He[2] showed that pure yttria gave no phosphorescence phenomena, either by his method or by that of Crookes. According to him, the fluorescence bands were attributable to impurities, to his substances Z_α and Z_β, in fact, and these it was almost impossible to remove completely from the yttria.[3] In connection with these substances giving fluorescence bands, he[4] has studied a considerable number of fluorescences with well-defined spectral rays, having for solid solvents alumina, gallium oxide, silica, zirconia, stannic and tantalic oxides, and for active matter samaria and the oxides of Z_α and Z_β. Demarçay[5] opposed Crookes' theory of "meta-elements," and stated that the radiant matter test of Crookes was far more delicate than the reversion spectra of Lecoq de Boisbaudran.

Duboin[6] made some compounds of yttria in the dry way. The accepted atomic weight of yttrium, 89.02 with $O = 16$ as the standard, is the one obtained by Cleve[7] in 1882. Rowland[8] published a method for the separation of yttria from other earths of its group by means of potassium ferrocyanide. His paper was severely criticized by Crookes.[9]

In 1896 Barrière[10] announced the existence, in the yttria earths from monazite, of a new metal which was separated from the other members of the group by precipitation with sodium thiosulphate in concentrated solution. This element, lucium, had an atomic weight of 104. Crookes.[11] by examination of its spark and absorption spectra, found that it was a mixture of yttrium and didymium, erbium and terbium, but was principally yttrium. Shapleigh[12]

[1] *Bull. Soc. Chim.*, (3), **3**, 53.

[2] *Compt. rend.*, **102**, 1536.

[3] *Compt. rend.*, **103**, 113.

[4] *Loc. cit.*, **105**, 258, 301, 343, 784; **110**, 24, 67.

[5] *Rev. gen. des Sci. pures et appliqués*, **1**, 396; *Chem. News*, **62**, 85.

[6] *Compt. rend.*, **107**, 99.

[7] *Loc. cit.*, **95**, 1225.

[8] *Chem. News*, **70**, 68.

[9] *Loc. cit.*, **70**, 81.

[10] *Chem. News*, **74**, 159. 212.

Loc. cit., **74**, 259.

[12] *J. Franklin Inst.*, **144**, 68; *Chem. News*, **76**, 41.

found by a quantitative analysis of a sample of lucia that it contained 93.98 per cent. of yttria earths, 3.74 per cent. of ceria earths, 1.07 per cent. of thoria, and 1.21 per cent. of other foreign oxides.

In 1896 and 1897 Schützenberger and Boudouard[1] worked on the yttric earths of monazite sands. They found by fractional fusion of the nitrates and by fractional crystallization of the sulphates that a lower limit of fractionation was reached, giving an earth whose metal-equivalent (R_2O_3) was about 95. They thought that they had found a new earth, whose metal had an atomic weight of about 102. Drossbach,[2] working also on monazite, thought he had a new earth similar to the others (the atomic weight of its base, 100). Further, Urbain and Budischovsky,[3] fractioning the yttria earths by means of the acetyl acetonates, found a similar lower limit. Urbain,[4] working with the ethyl sulphates, succeeded in showing that this hypothetical earth could be separated into terbia ($R^{III} = 151.4$) at one end of his fractionation series, and yttria ($R^{III} = 89$) at the other. In 1900 Urbain[5] again took up the question of this earth, and concluded that it was principally yttria, mixed with some erbia and terbia. This lower limit of various fractionation series, giving a base of nearly constant atomic weight, reminds one of the "oxide of gadolinium" of Nordenskjöld.[6] This was a rare earth mixture, obtained from different minerals, which he knew to contain at least three oxides, those of yttrium, erbium, and terbium, and yet its metal had a constant atomic weight of 107.

Crookes[7] in 1898 announced the existence of an element giving a group of phosphorescence bands in the ultraviolet only. He then called it monium. Its principal rays were λ 3120 and λ 3117, and its atomic weight about 118. In 1899, he[8] renamed it victorium, and told how it was isolated. The method was a long combination of the standard ones of fusion of the yttria group nitrates, fractional precipitation of the oxalates from concentrated nitric acid solution, fusion of the nitrates again, and finally fractional precipitation with potassium sulphate.

[1] *Compt. rend.*, **122**, 697; **123**, 782; **126**, 1648.

[2] *Ber. d. chem. Ges.*, **29**, 2452.

[3] *Compt. rend.*, **124**, 618.

[4] *Compt. rend.*, **126**, 835; **127**, 107.

[5] *Ann. chim. phys.*, (7), **19**, 184.

[6] *Compt. rend.*, **103**, 795.

[7] *Chem. News*, **78**, 134.

[8] *Proc. Roy. Soc.*, **65**, 237; *Chem. Centrbl.*, (1899) **II**, p. 748.

In addition to all of these earths, and. of course, ceria, lanthana. didymia and thoria. a few others have been announced. Their existence was generally short. Junonium was prepared in 1811 by Thomson[1] from allanite. Donarium was announced by Bergemann[2] in 1851. He prepared it by precipitating the silica-free acid solution of the mineral thorite with ammonia. Damour,[3] Berlin,[4] and finally Bergemann himself[5] thought that donaria was identical with thoria. Bahr[6] announced the discovery of wasium, which Nicklés[7] thought was a mixture of yttrium with didymium or terbium. Delafontaine[8] thought wasium was cerium, perhaps with some didymium. Popp[9] agreed with Delafontaine. Bahr[10] considered it probable that wasium and thorium were identical, and that both Nicklés and Delafontaine were mistaken in the matter.

Smith[11] announced the existence of two new elements in samarskite, which he called columbium and rogerium. This columbium is not, of course, to be confused with the well-known one. Chroustchoff[12] detected spectroscopically the existence of a new element, russium, in certain wash residues from rocks, in many alumina preparations, and in American monazite. He[13] prepared russium in much the same manner that Barrière prepared lucium. Linnemann[14] discovered austrium in the rare earth mixtures from orthite. Lecoq de Boisbaudran[15] considered it to be gallium. Pribram[16] decided that Linnemann's product was gallium, at the same time maintaining the probability of a new element in orthite.

EXPERIMENTAL.

In 1877 J. W. Mallett published an article on sipylite, a new niobate, from Amherst County, Virginia.[17] An analysis of the

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[1] Gilbert's *Ann.*, **42**, 115; **44**, 113.

[2] *J. prakt. Chem.*, **53**, 239.

[3] Pogg. *Ann.*, **85**, 555.

[4] *Loc. cit.*, p. 556 and **87**, 608.

[5] *Loc. cit.*, **85**, 558.

[6] Pogg. *Ann.*, **119**, 572; *J. prakt. Chem.*, **91**, 179.

[7] *Compt. rend.*, **57**, 740.

[8] *Ann. Chem.* (Liebig), **131**, 368.

[9] *Loc. cit.*, **131**. 364.

[10] *Loc. cit.*, **132**, 227.

[11] *Nature*, **21**, 146; *Chem. News*, **49**, 182.

[12] *Berg. u. huet. Ztg.*, **46**, 329; *Chem. Centrbl.*, p. 1277 (1887).

[13] *J. russ. phys. chem. Ges.*, **29**, 206; *Chem. Centrbl.*, **11**, 329 (1897).

[14] *Monatsh. Chem.*, **7**, 121.

[15] *Compt. rend.*, **102**, 1436.

[16] *Sitzungsber. d. k. Akad. d. Wiss.*, *Wien*, Div. 2b, **109**, 16; *Monatsh. Chem.*, **21**, 148.

[17] *Am. J. Sci.*, **14**, 397 (1877).

mineral made under his direction by W. G. Brown indicated the substance to be essentially a niobate of erbium containing some tantalic acid, about 1 per cent. of yttrum oxide and approximately 11.5 per cent. of the earths of the cerium group.

In the following year Delafontaine[1] examined this mineral and stated that it contained erbium, philippium, and ytterbium, the last-named element having been isolated but a short time before by Marignac.

A supply of sipylite which had been procured by one of us from Virginia and Texas was used as the source of the earths in this investigation. The mineral was finely powdered and was then mixed with a large excess of primary potassium sulphate, and this mixture was fused in deep iron dishes in a crucible furnace. When decomposition was complete, the mass was cooled, powdered, and thrown into ice-water, the water being stirred until complete solution of all soluble compounds had been effected. The clear supernatant liquid was then siphoned off, nearly neutralized with ammonia, and precipitated with oxalic acid. The oxalates were then washed, dried, ignited, dissolved in sulphuric acid, and precipitated with ammonium hydroxide. This precipitate, after thorough washing by decantation, was dissolved in nitric acid and to the neutral solution there was then added a saturated solution of potassium sulphate and crystals of the same salt. The mixture was violently stirred until the supernatant liquid failed to show the absorption bands of didymium. The resulting precipitate of the earths of the cerium group was removed by filtration, and was washed with a saturated solution of potassium sulphate. The filtrate was diluted with water and was precipitated by a solution of oxalic acid. These mixed oxalates which, of course, still contained traces of the earths of the cerium group, were dried and ignited. The resulting mixture of oxides weighed about 350 grams and was of a deep orange-yellow color.

The atomic weight of the oxide mixture, assuming that all the oxides present were of the R_2O_3 type, was determined by the oxalate method of Gibbs and the sulphate method of Krüss, and was found to be in the neighborhood of $R^{III} = 108$. Assuming that the average atomic weight of the elements other than yttrum lies in the neighborhood of 165, this result shows that the mixture consists largely of yttrium oxide, approximately 75 per cent.

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[1] *Compt. rend.*, **87**, 933.

The absorption spectrum when observed through a 10 cm. layer of the saturated solution of the nitrate of the mixture showed the bands tabulated below. The measurements in the table coincide with the maximum intensities of the absorption bands unless otherwise indicated.

Angle.	Wave-length λ.	Element.	Description of band.
12° 2′ 30″	6832.4	Erbium Thulium	Faint, rather broad, edges vague.
11° 45′ 10″	6670.7	Erbium	Slightly stronger than 6832.4
11° 29′ 00″	6519.9	Erbium	Moderately broad and strong with two maxima, one in center. the other at right edge.
11° 25′ 20″	6485.7		
11° 16′ 40″	6404.7	Holmium	Moderately strong, right edge sharp, maximum to right of center.
10° 11′ 50″	5797.9	Didymium	Edges of broad, very hazy band. Scarcely visible.
10° 4′ 00″	5725.5		
9° 39′ 50″	5497.7	Unknown (Crookes)	Faint.
9° 30′ 30″	5410.0	Erbium	Broad strong band. two maxima, one to left of center. the other at right edge.
9° 25′ 30″	5363.0	Holmium	
9° 11′ 10″	5228.2	Erbium	Strongest band in spectrum. two maxima, one at left edge, the other in center. Right edge indistinct.
9° 6′ 40″	5185.9		
8° 32′ 20″	4862.7	Samarium	Almost as strong as 5228.2. Extends from λ 4938.1 to λ 4825. Maximum to left of center.
8° 17′ 10″	4719.8	Samarium	Very faint.
8° 11′ 50″	4669.5	Samarium	Very faint.
7° 54′ 00″	4501.3	Dysprosium	Almost as strong as 5228.2. Extends from λ 4550.0 to λ 4449.4.
7° 43′ 40″	4403.8	Didymium (?)	Very faint.
7° 16′ 50″	4150.3	Samarium	Faint and hazy.

The measurement of the positions of the absorption bands was made with a small grating spectroscope manufactured for one of us by C. A. Steinheil Sons, of Munich. This instrument is so compact and convenient and the accuracy of the readings which can be made with it so far surpasses that attainable with a prism spectroscope as perhaps to justify the insertion here of a brief description of the instrument. The box of the apparatus carries the plate *EFGH* (Fig. 2) as a cover, and upon this a divided quadrant *LMN*, a vernier and a microscope. Inside the box are the grating *D*, the prism *P* and the mirror *K*. The grating is turned about the axis *a* by the vernier-arm *Q*. A is the collimator tube with slit *J*. *B* the telescope, and *C* the scale tube. The parallel rays from the collimator-objective are reflected by the prism in the direction *Pa* upon the grating *D* and from there are reflected in the direction *aO*. When the grating is so placed that the perpendicular to its plane bisects the angle *PaO*, one sees through the telescope the image of the slit reflected from the grating. The zero point of the instrument is obtained by placing the cross hairs of the eye-piece over the image of the slit. Both the quadrant and the vernier are so divided that the grating may be turned either way, the readings for the same line on either side of the zero being thus the same. The quadrant is divided into intervals of 10′: the vernier may be read to 10″. The scale tube *C* may be turned on an arm so that it may be used for spectra of the second and third orders. The wave-length of the line measured is a function of the angle through which the grating must be turned to bring the line into the position occupied by the image of the slit at the zero point. It is obtained by the formula $\lambda = \frac{K \sin \omega}{n}$, *K* being the constant of the instrument, and *n* the order

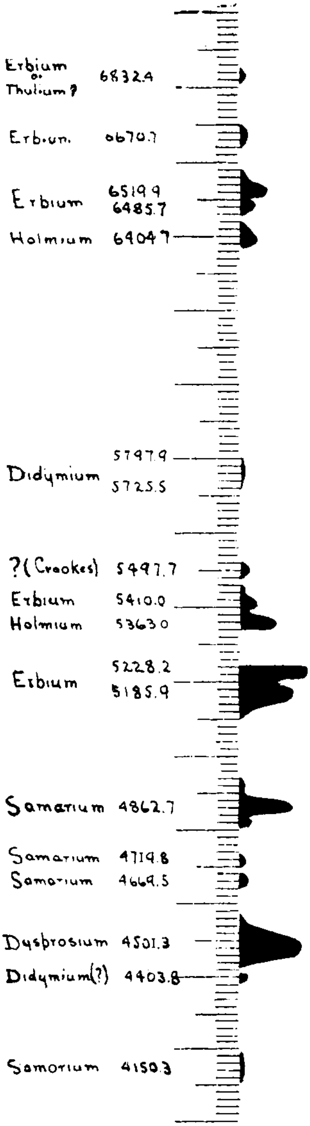

FIG. 1.

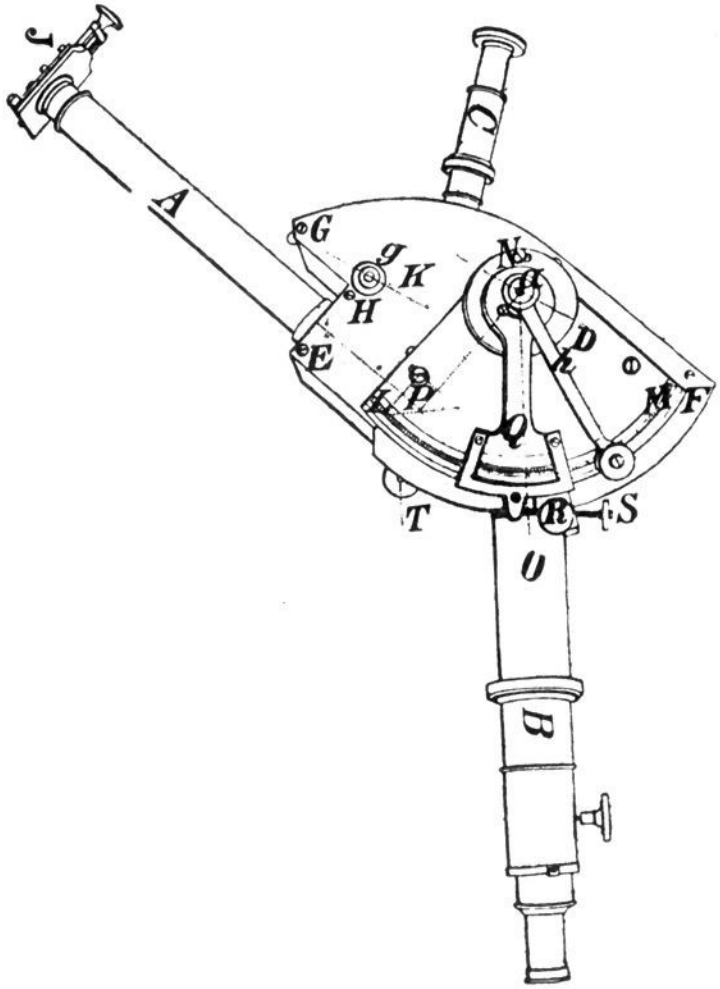

FIG. 2.

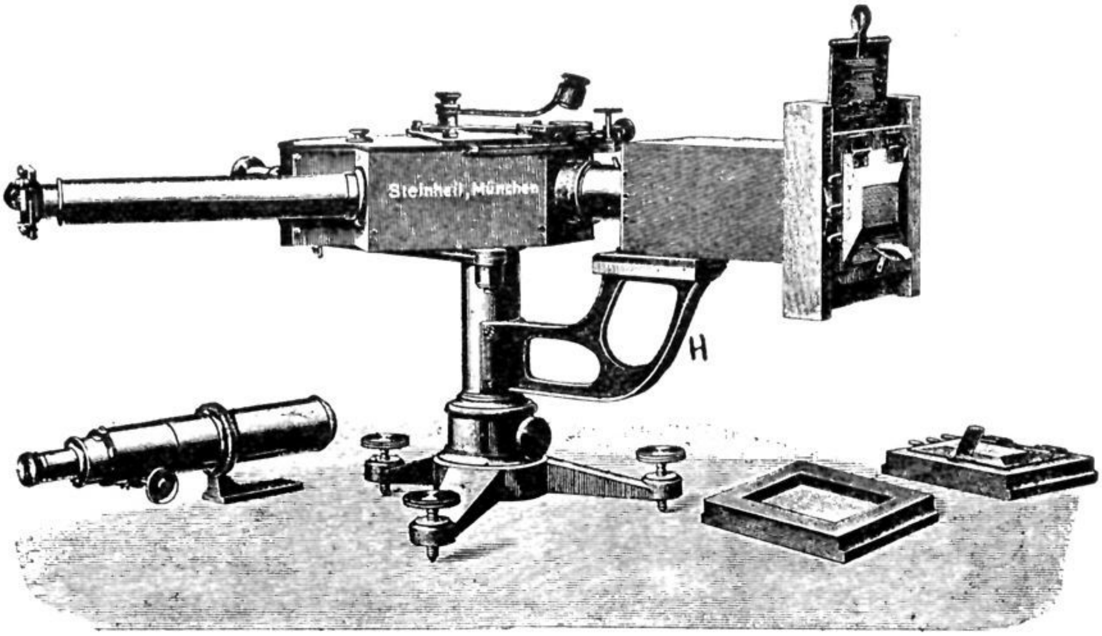

Fig. 3.

of the spectrum. Fig. 3 shows the instrument with a camera attachment substituted for the telescope tube. As the source of light a zirconia disk and a Linnemann oxyhydrogen blowpipe were used.

THE DETERMINATION OF THE ATOMIC WEIGHTS OF THE ELEMENTS.

The method described by Gibbs[1] was used when only an approximate result was desired. The procedure was as follows: A neutral or only very slightly acid solution of the earths whose atomic weight is to be determined is diluted with water. brought nearly to the boiling-point, and is then precipitated with a hot dilute solution of pure oxalic acid. The precipitate is washed by decantation and on the filter with hot water to remove the excess of oxalic acid and is then dried at a temperature of 125°. A weighed portion of the oxalate precipitate is then converted to the oxide by ignition and this oxide is weighed. Another weighed portion of the oxalate is dissolved in dilute sulphuric acid (1 : 8) and the oxalic acid is determined by titration with potassium permanganate. The atomic weight of the earths in the mixture of the rare earths is then easily calculated from the ratio of $R_2O_3 : C_2O_3$. This method of determining the atomic weights gives results that are sufficiently accurate to enable one to judge of the progress of a method of separation or fractionation, but which are far from being exact, and comparison of the method with the sulphate method showed that the Gibbs procedure gave results differing by as much as four units from the sulphate method of Krüss. To ascertain the effect of changes in the conditions prevailing at the time of precipitation the following experiments were made.

A solution of the earths was carefully freed from other elements by precipitating it with hydrogen sulphide. filtering off a very slight precipitate which formed, boiling the filtrate to remove the hydrogen sulphide and precipitating it with ammonia, dissolving the washed precipitate in hydrochloric acid, and after nearly neutralizing with ammonia. precipitating this solution with oxalic acid. The oxalates thus obtained were washed with very dilute hydrochloric acid (0.1 per cent.) to remove iron, then with water, and were then dried, ignited, and the resulting oxides were dissolved in hydrochloric acid. This chloride solution was divided

[1] *Am. Chem. J.*, **15**, 547.

into two parts. One was precipitated with a hot and dilute solution of oxalic acid, while the other was precipitated in the cold and in more concentrated condition with a cold concentrated solution of oxalic acid. Another portion of the same original material was purified and treated in exactly the manner described above, and was divided and precipitated in the same way. The results of the atomic weight determinations of these various portions by the oxalate method were as follows :

	Hot.	Cold.
1	111.28	108.26
2	105.06	104.70

The variations in these results show that they are greatly influenced by changes in the conditions, and that they by no means agree even when the same conditions pertain.

The other method employed for the determination of the atomic weights was that described by Krüss.[1] In this procedure the oxalate of the earth is placed in a porcelain crucible and ignited over a blast-lamp to constant weight. The crucible containing the oxide is placed on a water-bath, covered with a funnel, and the heating of the water-bath is continued until the water vapor has slowly and completely slaked the oxide. The substance is then dissolved in the crucible with dilute hydrochloric acid. A moderate excess of dilute sulphuric acid is added and the solution is concentrated as far as possible on the water-bath. The excess of sulphuric acid is removed by placing the crucible on an iron plate 5 mm. thick and heating the plate with a small Bunsen flame. This is continued until constant weight is obtained, and from the ratio of the oxide to the anhydrous sulphate. the atomic mass of the earth or earths present is calculated. Considerable difficulty was experienced in making duplicate analyses agree satisfactorily. The probable explanation of this trouble is to be found in the article by Brauner and Pavlicek,[2] in which those authors call attention to the fact that the sulphate which is finally weighed is liable to contain some acid sulphate. This acid sulphate is so stable that some of it remains undecomposed even at a temperature above 500°, while in other parts of the crucible it may have partially been broken down into a basic sulphate. They state that the error is greatest in the case of lanthanum and that it decreases as the basicity of the earth decreases. They deter-

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[1] *Ztschr. anorg. Chem.*, **3**, 46.

[2] *Proc. Chem. Soc.*, London, **17**, No. 235, p. 63.

mine the amount of sulphuric acid which is present in excess over the amount necessary to form the normal sulphate by dissolving the dry sulphates in water and titrating the free sulphuric acid with a twentieth normal solution of sodium hydroxide using ethyl orange as an indicator. The normal sulphate obtained by repeated crystallization was found by them to be neutral to ethyl orange.

These statements concerning the sulphates of the earths of the cerium group hold true for those of the yttrium group, but the error is less because the basicity of the earths of this group is less. For example, two weighed portions of a sulphate which had given $R^{III} = 115.90$ and 116.42, were dissolved in water and the excess of free acid titrated as above. using methyl orange as an indicator. The corrected results for these two samples were $R^{III} = 116.19$ and 116.47. Another set which had given $R^{III} = 141.22$ and 141.53 gave after correction 141.51 and 141.73. A third set giving $R^{III} = 107.31$ and 106.75 gave after correction 107.37 and 106.92. There seems to be no regularity in the amounts of acid sulphate which are formed. The maximum error caused by its presence seems to be about 0.3 of a unit. All of the solutions which were tested showed an acid reaction, but in some cases a drop or two of the solution of sodium hydroxide was sufficient to neutralize the free acid. The results of duplicate determinations were usually brought to closer agreement by the introduction of the correction. In only one case was the opposite effect noted.

EXPERIMENTS UPON METHODS FOR SEPARATING YTTRIUM GROUP EARTHS.

The aim which the authors had in view in this work was not so much the isolation of one or another constituent of the mixture of the rare earths, but rather the study of various methods of separation to ascertain along what lines different treatments will cause the earths to separate. A complete systematic study of the different methods of separation was also not undertaken, for those procedures which give slow results and in which the successive treatments are of but slight effect upon the rare earth mixture, can not be successfully employed, because of the time which is consumed and of the incompleteness of the separation which they bring about. Therefore, in the trials of the different methods to be described below it will be seen that the procedure was abandoned as soon as it became apparent that only slow separation was being effected.

FUSION OF THE YTTRIUM GROUP NITRATES WITH ALKALI NITRATES.

The method first tried was that of fusion of the rare earth nitrates with alkali nitrates, proposed by Debray, and which, as modified by Dennis and Magee,[1] gives such satisfactory results in separating cerium from the other members of the group. It was hoped that the decomposition points of some of the yttria group double nitrates might be found sufficiently far apart to admit of a sharp separation, but such was not the case.

The dry yttrium group nitrates were mixed with six times their weight of a molecular mixture of potassium and sodium nitrates, placed in a deep porcelain evaporator, and fused in a large double air-bath, the space between the walls of the bath being filled with infusorial earth to prevent radiation. Three fusions were made and after each the substance was extracted with hot water, yielding an insoluble and a soluble portion. Fusions were made at three temperatures, 280°, 320°, and 360°, using different mixtures each time. These temperatures were measured by means of a Le Chatelier pyrometer manufactured by Keiser and Schmidt, of Berlin. Each portion was fused for about three hours. The results were irregular and gave no indication of a sharp separation by this method, as the following atomic weights show.

Atomic weight of the initial metal mixture, 108.19.

Insoluble.	Temperature.	Soluble.
114.70	280°	108.31
127.55	320°	108.14
112.24	360°	102.43

A comparison of the absorption spectra of solutions of these portions and of the original material with a direct-vision spectroscope showed no appreciable differences.

PARTIAL PRECIPITATION WITH HYDROCHLORIC ACID GAS.

Partial precipitation of the anhydrous chlorides by hydrochloric acid gas from a cooled solution was next tried. A concentrated solution of the chlorides ($R^{III} = 107.94$) was placed in a gas wash-bottle surrounded by a freezing-mixture of ice and salt; hydro-

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[1] This Journal, **16**, 653.

chloric acid gas from a Norblad generator was then passed through the liquid for about five hours. Quite a heavy white crystalline precipitate was obtained. This was thrown on to a porous plate and drained. It is very deliquescent. The concentrated solution of the crystals had a yellow color. The mother-liquor changed color from rose to orange while saturated with hydrochloric acid, due probably to the forcing back of the dissociation of the chloride by hydrochloric acid.

The mother-liquor was precipitated with ammonia and washed to remove chlorides, the precipitate dissolved in hydrochloric acid, concentrated and again treated for two hours with hydrochloric acid gas in the freezing-mixture. Another heavy white crystalline precipitate was obtained, which gave a slightly yellow solution.

The spectra of the original solution and of saturated solutions of these two precipitates were compared by means of the small comparison spectroscope manufactured by Zeiss of Jena and described by Dr. Pulfrich in the *Zeitschrift für Instrumentenkunde*, October, 1900. No changes in the relative intensities of the various bands were visible.

PARTIAL DECOMPOSITION OF THE CHROMATES.

Pattison and Clarke[1] separated cerium from lanthanum and didymium by heating the normal chromates to 230° F. for some hours. The method when tried on this material gave no separation whatever. About 3 grams of the oxides ($R^{III} = 103.75$) were dissolved in concentrated chromic acid and the solution evaporated to dryness. The dry mass was heated for six hours at a temperature of about 200° but decomposition merely on the surface was the only result. as could be told by the change in color from the red of the chromate to the green of the chromic oxide. This same substance was then pulverized and heated for six hours to 250° with practically the same result. The substance was extracted with hot water. yielding a red solution and a greenish black residue. The solution was evaporated to dryness and was then heated to 300° for eight hours. but only very slight decomposition resulted. The insoluble greenish black residue was again obtained from this portion. These two residues were treated with hot hydrochloric acid, and the green solution which was obtained was neutralized with ammonia and precipitated with

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[1] *Chem. News*, **16**, 259.

oxalic acid. Only a faint trace of the rare earth oxalates were thrown down.

FRACTIONAL PRECIPITATION WITH POTASSIUM CHROMATE.

The first to use this method in the separation of the rare earths was Gerhard Krüss.[1] This has since been modified by Moissan[2] and in this form was employed by the authors on the material which gave $R^{III} = 107.94$. Krüss added a neutral solution of potassium chromate to a neutral nitrate solution of the earths, while Moissan used a sulphate solution of the earths, neutralizing the liquid with ammonium hydroxide before each fractional precipitation with potassium chromate. The authors followed Moissan's directions carefully, but used a solution of the nitrates of the rare earths instead of the sulphates. This nitrate solution, amounting to 15 liters and containing about 140 grams of the oxides was first neutralized with ammonium hydroxide and 1 liter of the solution of potassium chromate containing 97 grams to the liter was added with continual stirring. The precipitation was carried on in tall glass cylinders of about 10 liters' capacity. The flocculent precipitate was allowed to settle and the red supernatant liquid was removed by means of a siphon. The precipitate was washed with water until the wash-water gave no precipitate with ammonium hydroxide. The earths in the wash-water were recovered by precipitation with ammonium hydroxide and this precipitate was dissolved in nitric acid to a neutral solution and was added to the mother-liquor. This liquid was then again carefully neutralized with ammonium hydroxide and was then treated with the same amount of potassium chromate solution as was used for the first fraction. This procedure was repeated four times, giving in all five fractions. The mother-liquor and wash-water from the last fraction were precipitated by ammonium hydroxide yielding fraction 6. With each succeeding precipitation the dilution of the solution was increased by about 1 liter.

Precipitate 1 was so small in amount as to render its separate treatment inadvisable; it was therefore united to precipitate 2 and the two were treated as one fraction. Each precipitate was dissolved in dilute hydrochloric acid, the chromic acid was reduced by adding alcohol and heating on the water-bath, and the resulting green solution was then nearly neutralized with ammonia,

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[1] *Ztschr. anorg. Chem.*, **3**, 92.

[2] *Compt. rend.*, **122**, 573.

heated to boiling. and precipitated with a boiling solution of oxalic acid. In each case the precipitated oxalates were washed with a 1 per cent. solution of hydrochloric acid and were then dried and ignited. The resulting oxide was dissolved in hydrochloric acid. For the atomic weight determinations by the Gibbs method a portion of each of these solutions was precipitated with oxalic acid and the oxalate was washed and dried.

Fraction 1 gave a pink oxalate, a deep orange oxide, and its saturated solution of a brownish-yellow color showed the same absorption bands as the original solution, but the bands were slightly stronger.

Fraction 2 was practically identical with fraction 1.

Fraction 3 gave a pink oxalate and an orange-yellow oxide somewhat lighter in tint than the oxide from fraction 2. Its saturated solution showed all of the absorption bands strongly.

Fraction 4 yielded an oxide somewhat lighter in color than that from fraction 3. and its solution showed the bands plainly but not as plainly as the preceding fractions.

Fraction 5 gave an oxalate of a pale pink color and a very light yellow oxide. The saturated solution of its oxide was much paler in color than the solutions of the preceding fractions, and while it showed all of the absorption bands they were much less distinct than in fraction 4.

Fraction 6 gave a perfectly white oxalate and the oxide showed only the faintest tinge of buff color. and its solution had a pale greenish-yellow tint. The absorption bands of this last solution were quite weak.

The atomic weights of the original material and the six fractions with fractions 1 and 2 united are as follows :

Original. 107.94.

1 and 2	3	4	5	6
133.54	126.13	114.04	97.83	94.01

Fractions 1, 2, 3. and 4 were then united and were again fractionally precipitated by the chromate method. The atomic weights of the three fractions thus obtained were 145.34. 127.38 and 103.75. The middle fraction was then split up into two parts. one showing an atomic weight of 150.03 and the other 124.53.

Fractions 5 and 6 contain yttria with about 10 per cent. of oxides having high atomic weights as terbia, erbia. and ytterbia.

These two fractions comprised nearly half the material used in the fractionation. After 7 grams of oxides with metal atomic weight of 107.07 had been extracted from them by this same process, the rest was set aside as yttria material. The two highest fractions $R^{III} = 145.34$ and 150.03 were also set aside for future use.

It is thus seen that fractionation with potassium chromate separates the earths of this group with considerable rapidity. It is especially serviceable as a means of obtaining yttria free from the other earths, this substance being separated in quite pure form at the end of a comparatively short series of fractions. The mixture of oxides in the first fractions is still a very complicated one and further application of the chromate method does not appear to affect it appreciably.

FRACTIONAL PRECIPITATION WITH PRIMARY POTASSIUM OXALATE.

The separation of the earths with this method proceeds but slowly as is shown by the atomic weights given below. The method is a modification of the one used by Delafontaine for the separation of terbia from yttria and erbia. He added the solution of primary potassium oxalate to a solution of the rare earths until a point was reached at which another drop of the reagent caused a permanent precipitate. The liquid was then allowed to stand until the oxalates crystallized out. The solid substance was then removed and crystallization was repeated after the addition of more of the oxalate.

The authors used very dilute solutions in carrying on this method of fractionation, that of the primary potassium oxalate being about one-twelfth molecular. while the solution of the rare earths was diluted until the absorption bands were just visible with distinctness. The solution of primary potassium oxalate was made by dissolving in water molecular proportions of potassium oxalate and oxalic acid.

In order to be able to judge of the effect of fractional precipitation by this method upon the absorption bands of the solution, the precipitation was carried on before the spectroscope. The solution of the rare earths was transferred to a large crystallizing dish about 20 cm. in diameter and this dish was placed directly before the slit of a Steinheil grating spectroscope. Light was furnished by a Linnemann zircon-disk lamp. The solution was kept in constant motion by means of a stirrer run by a Porter electric motor, and the solution of the primary potassium oxalate was added drop by drop from a burette. Before beginning the fractionation it is necessary to add a concentrated solution of the oxalate until a permanent precipitate just forms.

The first effect of the precipitation was to weaken the holmium bands. while all the bands decreased in intensity, the most persistent being the erbium band in the green. About 5 grams of the oxides were obtained from fraction 1. Half of the mother-liquor from this fraction was then precipitated and 6 grams were obtained. This halving of the solution was made necessary because of the limited size of the dish, and concentration was undesirable because of the possible disturbing action of the more concentrated oxalate solution upon the earths. The mother-liquor from fraction 2 was again divided and about 5 grams of oxides were obtained in fraction 3. At the end of this third fraction all of the absorption bands had disappeared with the exception of the erbium band in the green which was just visible. The mother-liquor from the last fraction amounting to one-fourth of the original solution was completely precipitated by the addition of the concentrated solution of primary potassium oxalate. Each of the precipitates was washed. dried, ignited, and dissolved in nitric acid. The oxalates of the first three fractions were pink while that of the last one was white. The oxides of the first three fractions were orange-yellow in color while that of the last fraction had a pinkish tinge. All the solutions showed the rose-pink color of erbium salts. In determining the atomic weights, a portion of each nitric acid solution was precipitated with ammonium hydroxide and this precipitate was thoroughly washed with water to remove potassium salts. It was then dissolved in nitric acid to a barely acid solution and precipitated with oxalic acid.

Original, 112.16

1	2	3	4
118.80	116.71	111.08	102.53

The precipitates which are thrown down by these oxalate reagents are finely crystalline and are consequently easily freed from the mother-liquor. Fractionation could probably be carried on with a fair degree of rapidity and interesting results might be obtained. The separation was, however, too slow for the authors' purposes and therefore no further trials have yet been made of it.

FRACTIONAL DECOMPOSITION OF A SOLUTION OF THE MIXED NITRATES BY MEANS OF AN ELECTRIC CURRENT.

About 120 cc. of a solution of the nitrates ($R^{III} = 107.94$) were carefully neutralized with ammonium hydroxide. This solution was placed in a Classen platinum electrolysis dish and was connected with the negative terminals of two cells of a storage battery. A platinum disk about 3 cm. in diameter was used as the positive electrode. A low current of $N. D._{100} = 0.17$ to 0.42 ampere at a potential difference between electrodes of 2.2 to 2.7 volts was passed into the solution for about twenty hours, the solution being kept neutral and at room temperature (about 21° C.). A white precipitate of the hydroxides was obtained at the cathode. A brownish deposit collected on the anode, but this was found to be lead dioxide due to a trace of lead present in the solution. The solution was poured off from the precipitate, the latter adhering to the dish sufficiently to make it possible to wash it without loss. The solution was evaporated to its original volume and was again submitted to electrolysis, with a current of $N. D._{100} = 0.18$ to 0.20 ampere at 1.8 to 1.9 volts for seven hours at 21° C. Again there was a small amount of precipitate formed. This being non-adherent, it was removed by filtration and the wash-water and solution were again evaporated to the original volume and electrolyzed. A current of $N. D._{100} = 0.17$ ampere failed to produce any further precipitation after six hours, so the current was raised to $N. D._{100} = 0.33$ to 0.42 ampere with a potential difference of 2.45 to 2.55 volts and allowed to run for twenty-three hours. A further white precipitate was obtained. These two precipitates were united for the second fraction; the atomic weight of the fraction was then determined as was that of the first fraction and that of the residual solution. These three values compared with the original are as follows:

Original. 107.94.

1	2	Residual solution.
120.22	116.61	106.20

If the decomposition voltages of the rare earths of this group were far enough apart to permit of a separation by means of electrolysis, the two fractions here should have atomic weights which differ more than do these. For if the earth or earth mixture which is thrown out of solution by a current of $N.D._{100} = 0.17$ ampere at a potential difference between electrodes of about 2.5

volts was different from that which is precipitated by a current of about twice the density, the difference should show itself in the atomic weights. It is evident therefore that, under the conditions here prevailing, the separation of the rare earths can only slowly be effected.

FRACTIONAL PRECIPITATION WITH MAGNESIA USTA.

Muthmann and Rölig[1] separate cerium in the quadrivalent condition from lanthanum and didymium by precipitation with powdered zinc oxide, and then separate lanthanum from didymium by partially precipitating the hot concentrated solution with magnesia usta until the absorption bands of didymium have disappeared.

The effect of magnesium oxide as a precipitant was tried with a nearly saturated neutral solution of the chlorides of these yttrium earths ($R^{III} = 104.4$). Muthmann states that he stopped the precipitation when the didymium absorption bands had just disappeared. The authors found, however, that while a precipitate formed easily it would not settle sufficiently to enable the absorption bands to be observed.

The solution of the chlorides was heated to boiling, and while in vigorous ebullition, powdered magnesia was added in small quantities, with constant stirring. The precipitate which soon separated was first washed by decantation and was then washed upon a filter with hot water. The mother-liquor and the four wash-waters were evaporated nearly to saturation and the precipitation was repeated. A second repetition of this procedure gave a third fraction and the mother-liquor and wash-waters from this were then precipitated with oxalic acid for the fourth and final fraction.

Each of the precipitates was dissolved in hydrochloric acid and the solution was concentrated. These four solutions showed practically no variations in absorption bands when examined with a direct vision spectroscope. The solution from the first precipitate was treated with ammonium chloride and ammonium oxalate as Muthmann recommends, and the resulting precipitate was washed by decantation with hot water containing 0.1 per cent. hydrochloric acid and was then washed with water alone. The precipitate was free from magnesia but contained iron. The oxalates were at first non-crystalline and settled very slowly, but the

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[1] *Ber. d. chem. Ges.*, **31**, 1719.

addition of the dilute acid caused them to separate in crystalline condition. It was found that, by adding oxalic acid to the neutral chloride solution of these precipitates. complete precipitation of the rare earths could be obtained and this precipitate was free from magnesia, provided ammonium chloride was present. This method of purification was therefore used with the other fractions. The oxalates from all four of the fractions were ignited and dissolved in hydrochloric acid. Since the resulting solution contained traces of iron, portions of each fraction were freed from iron by reprecipitation with oxalic acid, and the atomic weight determinations were made with this purified material. The atomic weights and absorption spectra showed that very little change had been caused in the earth mixture by fractional precipitation with magnesium oxide.

TREATMENT WITH POTASSIUM TRINITRIDE, KN_3.

The method proposed by Dennis and Kortright[1] for the separation of thorium from members of the cerium and yttrium groups, by means of potassium trinitride, was tried to see if perhaps some reaction similar to the one for thorium could be found. The results were entirely negative. Partial precipitation by potassium trinitride was found to fraction the rare earths of this group rather slowly. The precipitate in the case of thorium was thorium hydroxide. In this case it seemed rather to be a basic nitrate. It was white, very finely divided, and adhered to the beaker, and had also a tendency to go through the filter.

A dilute solution of the nitrate ($R^{III} = 112.16$) was treated with a dilute solution of potassium trinitride containing free hydronitric acid and boiled. A precipitate was obtained on boiling for two or three minutes. It was filtered. washed with hot water, dissolved in nitric acid and converted into oxalates. The atomic weight was 118.96. The nitric acid solution was pink, and the absorption bands were practically the same as in the original solution.

FRACTIONAL PRECIPITATION WITH AMMONIA.

The work of many chemists who have investigated the earths of the yttrium group has shown that these elements can unquestionably be partially separated by a long series of fractions with dilute ammonium hydroxide, but the work is so extremely tedious

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[1] *Ztschr. anorg. Chem.*, **6**. 35.

and the separations are so very slow that it is questionable whether this procedure can be considered to be of material value. As an illustration of the slight effect of fractionation by this reagent one experiment will suffice.

A very dilute solution of the neutral chlorides containing about 57 grams of the oxides in 12 liters was treated with an amount of dilute ammonia sufficient to precipitate only one-tenth of the earths present. During the addition of the ammonia the solution was vigorously stirred by blowing through it a blast of air and this stirring was continued for about an hour. A precipitate formed very slowly. The hydroxides were then washed by decantation until the wash-water gave no precipitation with ammonia. The mother-liquor and wash-waters were evaporated to the original volume and precipitated again with the same amount of ammonia. The atomic weights of the earths precipitated in these two treatments were 103.9 and 104.0, while that of the original material was 96.

FRACTIONATION WITH AMMONIUM CARBONATE AND DILUTE ACETIC ACID.

Mosander[1] in 1843 mentioned that the hydroxides of the rare earths of this group are soluble in a concentrated solution of ammonium carbonate and that they could be fractioned in this way. Krüss[2] also mentioned this solubility.

This treatment alone was first tried here. The results were much better than was expected. The rare earth hydroxides were precipitated by ammonia (the latter need not be washed out). By a single treatment of these hydroxides with a quantity of a saturated solution of ammonium carbonate sufficient to dissolve one-fourth of the whole, an earth mixture was dissolved whose metal atomic weight was 121.41. The bases in the undissolved portion had an atomic weight of 107.94, while the original solution contained a metal mixture of atomic weight 108.08.

Quantities of saturated ammonium carbonate solution sufficient to dissolve other amounts of the precipitated hydroxides than one-fourth were then tried on different portions of this earth-mixture. An amount of carbonate solution sufficient to dissolve one-tenth of the hydroxides precipitated was added to one portion, while to others were added amounts of the carbonate solu-

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[1] *Phil. Mag.*, **23**, 251; *Ann. Chem.* (Liebig), **48**, 219.

[2] *Ann. Chem.* (Liebig), **265**, 1.

tion sufficient to dissolve nine-tenths, one-fifth, one-third, and one-half. On the whole, however, the addition of one-fourth or perhaps one-fifth the amount of carbonate solution necessary to dissolve all the hydroxides seems to be most suitable for this method of fractionation. The total precipitation of the earths by a solution of ammonium carbonate with partial solution of the precipitate in an excess of that reagent was also tried, but this is no better than precipitation with ammonia and partial solution in ammonium carbonate. A second extraction of the hydroxides from the undissolved portion ($R^{III} = 107.94$) from the first treatment was made, and the atomic weight of the metal mixture which dissolved was 125.91. Evidently the material could be thus extracted at least twice with profit.

To the dissolved portion mentioned above ($R^{III} = 121.41$) there was then added very dilute acetic acid (1 : 30) slowly and with constant stirring, first adding concentrated acetic acid just to turbidity. This treatment had a most marked effect. The granular precipitate thrown out was of a pink color and when dissolved showed all the absorption bands very strongly, while the bands in the remaining solution were much weakened.

When the dilute acetic acid had been added as above, a point was reached at which the addition of more acid would produce no further precipitate. This is due to the fact that the rare earth hydroxides of this group are nearly as soluble in ammonium acetate as in ammonium carbonate, and a state of equilibrium is soon reached between the three. after which dilute acetic acid has no effect upon the double ammonium salts of the rare earths. It was necessary, when this point was reached, to filter, decompose the ammonium carbonate solution with hydrochloric acid, dissolve the precipitate which was formed by further addition of the acid, and then to precipitate the whole with ammonia, wash, redissolve in hydrochloric acid and reprecipitate with ammonia. The hydroxides were then dissolved in saturated ammonium carbonate solution and the precipitation by dilute acetic acid repeated.

This particular material after having been treated three times with ammonium carbonate and dilute acetic acid in the manner above described. gave a very small amount (less than 1 gram) of an earth which yielded a white oxalate and a white oxide. A determination, not in duplicate, of its metal atomic weight gave the interesting result of 170. In the dry oxide only, the green absorption band of erbium was visible by reflected light. In saturated solution this earth mixture did not show the absorption bands of holmium, thulium, nor dysprosium, but those of erbium and samarium were visible. They were, however, much weaker than in the original solution. The spark spectrum of this solution was also examined, and the following lines of ytterbium as given by Thalén[1] were found :

Angle.	Wave-length.	Thalén's measurements.
10° 57′ 00″	6220.9	6221.0 (1)
9° 46′ 00″	5555.6	5555.5 (1)
9° 37′ 30″	5475.7	5476.0 (1)
9° 24′ 30″	5353.5	5352.0 (1)
9° 22′ 30″	5334.8	5334.0 (1)
9° 18′ 50″	5300.3	5300.0 (4)
8° 24′ 10″	4785.7	4785.5 (2)
8° 17′ 40″	4724.5	4725.0 (2)

The spark spectra of erbium and samarium were very weak. None of the characteristic gadolinium lines were found. The mixture was, therefore, ytterbium and erbium with some samarium, but no holmium, thulium, or dysprosium, no yttrium, gadolinium, or terbium.

To show further the effectiveness of this method of fractionation, it was tried on nearly all of the material in hand. The material was divided into two parts, in one of which the bases had an atomic weight of 117.37 and in the other of 107.15. Each of these portions was carefully purified by treating the boiling, slightly acid chloride solution with hydrogen sulphide, filtering, boiling to expel hydrogen sulphide, then precipitating with ammonia and washing, dissolving the precipitate in dilute hydrochloric acid, neutralizing and precipitating with oxalic acid solution, stirring the while by blowing air through the solution. The oxalate precipitate was washed with 0.1 per cent. hydrochloric acid to remove iron. then with water, dried, ignited, and dissolved in hydrochloric acid. The atomic weights given above were obtained from the material thus purified by precipitating this chloride solution again with oxalic acid, both solutions being boiling hot.

The details of the treatment for the solution ($R^{III} = 117.37$) were as follows : The chloride solution was divided and placed in three tall cylinders, diluted and precipitated with ammonia.

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[1] *J. de Phys.*, (2), **2**, 37.

The hydroxides were washed, then dissolved completely in saturated ammonium carbonate solution, and concentrated acetic acid added just to turbidity. Then to each of the three cylinders was added 1000 cc. of dilute acetic acid (1 part acid diluted to 30 with water) in small quantities at a time and with constant stirring by a current of air. The flocculent precipitate soon became granular and could easily be separated from the mother-liquor by decantation. The last of the mother-liquor was removed from this fraction 1 by suction. Dilution with water caused the earths to precipitate from the ammonium carbonate solution: therefore the mother-liquor could not be washed out. The mother-liquors were treated with concentrated hydrochloric acid till the ammonium carbonate was destroyed and the resulting hydroxides dissolved, then precipitated with ammonia, dissolved in hydrochloric acid and reprecipitated with ammonia; then these hydroxides were treated again with saturated ammonium carbonate solution. This time the carbonate solution was placed in two cylinders, the excess of ammonium carbonate neutralized by concentrated acetic acid and 700 cc. of dilute acetic acid added to each one slowly and with constant stirring. The precipitate was fraction 2.

The mother-liquors here were removed and decomposed exactly as before, and the ammonium carbonate solution of the hydroxides neutralized with concentrated acetic acid and treated in one cylinder with about 600 cc. of dilute acetic acid (fraction 3). The mother-liquor from this fraction still showing a trace of the erbium band in the green after its conversion by the usual decomposition into chloride solution and concentration, it was diluted, precipitated with ammonia, dissolved in saturated ammonium carbonate solution as before and precipitated this time after neutralization by about 30 cc. of dilute acetic acid. The precipitate (fraction 4) was, of course, slight. The mother-liquor from it was dissolved in hydrochloric acid, nearly neutralized with ammonia and precipitated with oxalic acid to remove most of the iron. The oxalates were washed, dried, ignited, and dissolved in hydrochloric acid. This solution concentrated to saturation gave three absorption bands, the red and the green of erbium, and the samarium band between the blue and the green, none of them strongly. The atomic weights of the bases for the series were:

Original. 117.37.

1	2	3	4	Residual mother-liquor.
115.25	116.33	141.62	159.78	165.48

The other material (R = 107.15) treated in the same manner yielded the following series of atomic weights :

1	2	3	4	Residual mother-liquor.
105.33	102.4	110.6	119.45	146.53

It is worthy of note here that the metal atomic weights of the first two of the fractions in each of these series are quite close together, while those of the other fractions show a marked divergence from one another. In the second series the curve of atomic weights even goes through a minimum. There are two reasons for the apparent non-fractionation in these first two fractions. One is that the larger portion of the material used was precipitated in these first two fractions. The other and more important one is that the erbium ($R^{111} = 166$). terbium ($R^{III} = 159$), and yttrium ($R^{111} = 89$) have so distributed themselves in the first and second fractions, more terbium in the first, more erbium in the second, that the atomic weights of the metal mixtures are about the same.

The changes in color of the ignited oxides from these series were very marked. In the first series the original earth was a deep orange-yellow color. No. 1 gave a more deeply colored earth, No. 2 was chamois-colored, No. 3 pink. No. 4 white with a pinkish cast. and the earth from the mother-liquor almost white. In the second series the earth from the original solution had a deeper orange-yellow color than that from the other original solution. No. 1 was more deeply colored yet than this original solution, No. 2 lighter, No. 3 chamois-colored, No. 4 the same, and that from the mother-liquor white with a pinkish cast.

This color change evidences a marked change in the terbium content of the various fractions. Terbium concentrates very markedly in the first fractions. It is true that much the larger portion of the earths was thrown out in the first fraction in these two series, but by a short systematic fractionation, erbium material can unquestionably be obtained terbium-free.

This method seems then to offer a method for the comparatively rapid concentration of terbium with yttrium at one end of the series, and of erbium and ytterbium at the other. Holmium, thulium, and dysprosium concentrate in the middle fractions.

The results thus far obtained in this investigation may be briefly summarized as follows :

The Gibbs method of determining the equivalent weight does not give exact results even when the conditions prevailing in different series of determinations are identical.

There is a slight error in the sulphate method of determining the equivalent weights, due to the formation of some acid sulphate.

Of the many methods of partial precipitation which were investigated the following seem to be the most rapid : primary potassium oxalate, potassium trinitride, partial decomposition by fusion of the nitrates with alkali nitrates, and electrolysis of neutral solutions. Magnesia usta causes fractionation of this material, but the progress of the separation can not be easily controlled with the spectroscope as was done by Muthmann in his work on didymium.

One of the best methods for the separation of yttria from the other members of this group is that of fractional precipitation of a neutral solution by potassium chromate. Quite pure yttria may be obtained in this manner at the end of a comparatively short series of fractions.

Unusually rapid separation of the earths of this group is effected by ammonium carbonate and acetic acid. Fractional solution of the hydroxides by means of a saturated ammonium carbonate solution causes quite rapid separation, and if this ammonium carbonate solution be fractionally precipitated by addition of acetic acid, the results are most striking. Ytterbium is the last of the earths to be precipitated by this treatment. Erbium and terbium concentrate in the first fraction.

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ELECTROLYTIC DEPOSITION OF LEAD FROM A PHOSPHORIC ACID SOLUTION.

BY A. F. LINN.

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LEAD has been successfully deposited as metal, by the electric current, from a solution of the double oxalate, the acetate, the oxide in sodium hydroxide, and also the phosphate dissolved in the latter reagent.[1] From each of these solutions the separa-

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[1] Smith's "Electrochemical Analysis," p. 62.