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## SOME OBSERVATIONS ON COLUMBIUM.

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THE starting-out material in this study was columbite from Lawrence County, South Dakota. Its specific gravity equaled 5.86. It contained 81 per cent. of the mixed oxides of columbium and tantalum. The total quantity of substance decomposed by fusion with acid potassium sulphate (58.5 kilograms) was 21.3 kilograms. Each fusion was made in a platinum dish, using 100 grams of mineral and 275 grams of acid potassium sulphate. While still liquid the mass was poured into a porcelain dish. When cold the fusion separated readily from the dish and was broken into small pieces, which were boiled with water in large No. 11 evaporating dishes until thoroughly disintegrated, when they were transferred to precipitating jars and the hydroxides washed by decantation until the wash-water gave no precipitate or only a slight precipitate with ammonium hydroxide. The solution and the washings were evaporated to dryness. The residue was designated part I. The moist hydroxides of columbium and tantalum were covered with ammonium sulphide and allowed to stand for several days. This ammonium sulphide solution was decanted and designated part II. The remaining oxides were finally treated with very dilute sulphuric acid and then thoroughly washed with water. The washings and the diluted sulphuric acid solution were also evaporated to dryness and marked part III. The

residue labeled part I contained potassium and the bases from the mineral in the form of sulphates. It was dissolved in water, poured into five-gallon jars and there precipitated with a slight excess of ammonium hydroxide. Having decanted the supernatant liquid the precipitate was washed once with water, after which the hydroxides were covered with a solution of ammonium carbonate and allowed to stand for several days. The ammonium carbonate solution was then siphoned off, acidulated with dilute hydrochloric acid, and any metal present precipitated with a slight excess of ammonium hydroxide. The hydroxide obtained in this way was dissolved in dilute hydrochloric acid, and an excess of ammonium carbonate, together with ammonium sulphide, added to its solution. The iron separated in the form of sulphide and with it there was a small amount of titanium. The filtrate from this precipitate was boiled with hydrochloric acid and ammonium hydroxide added. The hydroxide which was precipitated was ignited and tested as to its photographic power. It gave a picture after an exposure of five days. It contained uranium. It showed the greenish color characteristic of  $U_3O_8$ . After this it was fused with acid potassium sulphate, taken up in water and the solution boiled. A precipitate formed on cooling but disappeared on warming, thus indicating the presence of members of the cerium group or of zirconium. On the addition of ammonium hydroxide there separated a hydroxide which, after filtration and washing, dissolved completely in a solution of oxalic acid. This pointed to the presence of zirconium. The hydroxides were again precipitated, dissolved in sulphuric acid, and the solution neutralized with potassium carbonate and saturated in the cold with potassium sulphate. By this precipitation the zirconium was obtained in the form of insoluble double sulphate, while the uranium remained in solution. After filtering out the zirconium potassium sulphate it was dissolved in hydrochloric acid and zirconium hydroxide precipitated with ammonium hydroxide. It was well washed with water and dissolved in hydrofluoric acid. An equivalent amount of potassium carbonate was added and, on evaporation, potassium zirconium fluoride crystallized out. Three grams of this salt were obtained.

*Analysis.*—0.5043 gram of the salt ignited with sulphuric acid gave 0.5272 gram of  $K_2SO_4 + ZrO_2$ , and contained 0.2212 gram of  $ZrO_2$ , leaving 0.3060 gram of  $K_2SO_4$ .

	Calculated for $K_2ZrF_6$	Found.
2KF .....	41.05	40.47
ZrF <sub>4</sub> .....	58.95	59.52
	<hr/> 100.00	<hr/> 99.99

The uranium in the filtrate from the zirconium was precipitated with ammonium hydroxide, dissolved in hydrochloric acid, and an excess of sodium hydroxide added to this to obtain any glucinum. This was not found. The uranium was changed to nitrate and the solution allowed to evaporate, when large characteristic crystals of uranium nitrate separated. The solution decanted from the original ammonium hydroxide precipitate, which contained manganese and allied elements, was treated with an excess of sodium carbonate. The precipitate produced was allowed to settle, the supernatant liquid decanted into other jars, and hydrogen sulphide passed through it. A small amount of a black sulphide was obtained. It consisted of zinc, iron, copper and nickel (from the crucible tongs). The precipitate produced by sodium carbonate contained manganese, zinc and iron. Ten grams of it were dissolved in hydrochloric acid and the iron removed by the basic acetate method. The zinc was then precipitated as sulphide. The latter was changed to chloride and tested for gallium. Not a trace of the latter was found. Zinc lines alone were shown in the spectrum.

Tin and tungsten were contained in part II. Part III was not further examined. It may be concluded, therefore, that the columbite from South Dakota contains as acids: tantalum, columbium, titanium, silicon, zirconium, tin and tungsten; as bases: iron, manganese, zinc, uranium, copper (?) and nickel (?).

The moist metallic acids, after having been washed with dilute sulphuric acid, were brought into a large platinum dish and dissolved in fairly concentrated hydrofluoric acid. This solution was then filtered, through a hot water funnel, from undecomposed mineral and from potassium silicofluoride (due to the presence of some potassium sulphate in the moist oxides). The hydrofluoric acid solutions were collected in large rubber dishes and sufficient potassium hydroxide was introduced to convert the tantalum into potassium tantalum fluoride, most of which separated out and was removed by filtration. This precipitate was dried as far as possible by suction. It was washed once and then allowed to dry in the air. It weighed 11 kilograms. The mother-liquor from the

potassium tantalum fluoride was evaporated in stages, potassium hydroxide being added. The columbium separated usually in hexagonal, hard, short crystals, such as separate from a strongly acid solution containing an insufficient amount of potassium fluoride. The total residue obtained in this way amounted to about 8 to 10 kilograms. These residues were decomposed by treating them with twice their own weight of sulphuric acid, heating gently until the bulk of the hydrofluoric acid was expelled, and then evaporating until the mass fumed strongly and maintaining the temperature until the excess of sulphuric acid had been almost completely driven out. Several hours were required for this. It is necessary in order to get rid of the hydrofluoric acid. The residual mass was boiled with water to extract the bases which dissolved as sulphates. The insoluble hydroxides were thoroughly washed and dissolved in hydrofluoric acid. The first crop of crystals, obtained by evaporation with potassium hydroxide, was removed and the mother-liquor then evaporated to dryness with sufficient potassium hydroxide to change all of the metallic acids into double fluorides. A portion of these crystals (first crop) was dissolved in water and the tantalum removed by adding dilute potassium hydroxide to the solution, which, after the formation of a permanent precipitate, was boiled for some time. The precipitate consisted mainly of potassium tantalum oxyfluoride. It was filtered out and the filtrate evaporated to dryness. The residue was baked for some time at 200°. By this procedure some hydrofluoric acid was expelled and, on taking up the residue with water and boiling, more potassium tantalum oxyfluoride separated. By repetition of this process all of the tantalum was removed from the solution. The only test relied upon for the detection of tantalum was the solution of this precipitate in a drop of hydrofluoric acid and evaporation to crystallization. If needles separated, their solubility in water was used to ascertain whether they were potassium tantalum fluoride or potassium columbium oxyfluoride. It is true that this test consumes considerable time, yet it is the only satisfactory means of determining with which of the metals the chemist is dealing. The formation of a precipitate by protracted boiling of a dilute solution of potassium tantalum fluoride is not conclusive, for Krüss and Nilson<sup>1</sup> have shown that potassium colum-

<sup>1</sup> *Ber.*, 1881, p. 1676

bium oxyfluoride deposits under like conditions a small amount of a salt containing less fluorine. Further, the double fluoride must be recrystallized several times, so that it will be sufficiently free from acid that tantalum, if it is present in small amounts, may be precipitated by boiling.

Having freed the double fluoride from tantalum it was dissolved in water and hydrogen sulphide conducted through its solution. A slight precipitate of platinum sulphide was obtained. The filtrate from it was evaporated to dryness and the residue baked. On dissolving in water more platinum sulphide was found, but when hydrogen sulphide was conducted through the filtrate no further precipitation took place. The first crop of crystals obtained by the evaporation of this solution showed the usual form of potassium columbium oxyfluoride. They were allowed to dry in the air and labeled crystals No. 1 (A). The filtrate from them was reduced to a small bulk. Strong hydrofluoric acid was added when the needles of potassium columbium fluoride ( $K_2CbF_7$ ) separated. These were dried between bibulous paper and labeled crystals No. 2 (B). Samples from these two crops of crystals were analyzed.

*Analysis of No. 1 (A):*

0.53 gram of salt gave 0.2346 gram of oxide and 0.3161 gram of potassium sulphate.

$$0.2346 : 0.3161 :: x/2 : 174 \quad x = R_2O_5 = 258.2.$$

	Calculated for $K_2CbOF_5 \cdot H_2O$ .	Found.
$K_2SO_4$ .....	57.81	59.64
Oxide.....	44.52	44.26

The crucible in which the ignition of oxide occurred was stained. This was undoubtedly due to the presence of tin, which had not been removed, although hydrogen sulphide had been conducted through the solution of the double fluoride.

*Analysis of No. 2 (B):*

0.8428 gram of salt gave 0.3635 gram of oxide and 0.4803 gram of potassium sulphate.

0.4811 gram of salt gave 0.2082 gram of oxide and 0.2775<sup>1</sup> gram of potassium sulphate.

$$0.3635 : 0.4803 :: x/2 : 174 \quad x = 263.4.$$

$$0.2082 : 0.2775 :: x/2 : 174 \quad x = 250.1.$$

<sup>1</sup> Probably too high because it was not heated enough to expel all of the sulphuric acid.

	Calculated for $K_2CbF_7$	Found.	
$K_2SO_4$ .....	57.05	56.99	57.68
Oxide.....	43.93	43.13	43.28

Specific gravity of oxide (B):

18.5924 pycnometer + water,	$t = 18^\circ$	
0.2346 gram of oxide taken		
<hr/>		
18.8270		
18.7760 pycnometer + water + oxide	0.2346	
<hr/>		
0.0510 gram water displaced	0.0510	4.60 sp. gr.

To determine the titanium content of the columbium oxide re-course was had to a comparison of the color tint produced by hydrogen peroxide in an oxalate solution against known amounts of titanium hydroxide dissolved in oxalic acid. Thus, 0.2262 gram of columbium oxide was fused with acid potassium sulphate and the fusion dissolved in oxalic acid and diluted to 50 cc. It gave a color equivalent to 0.4 cc. of the standard titanium solution (1 cc. contained 0.00106 gram of titanium dioxide). In other words, by this test the columbium oxide was thought to contain 0.000424 gram of titanium dioxide, or 0.18 per cent.

#### SOLUBILITY OF CRYSTALS A.

One part of the salt was found to be soluble in a little over 12 parts of water. This is the solubility of potassium columbium oxyfluoride.

One hundred grams of the residues obtained by the evaporation of mother-liquors (page 1372) to dryness were dissolved in water and fractionally crystallized. After having removed as much of the tantalum as possible by introducing dilute potassium hydroxide into the boiling solution until a rather considerable and permanent precipitate was obtained, the solution was boiled for some time. The first fraction of crystals (2) and the third fraction of crystals (3) were removed, after which hydrofluoric acid was added to the mother-liquor, from which there separated a crop of needles, which we shall designate crystals 4. These last were recrystallized from hydrofluoric acid. They probably contained silicon and tantalum. The acid mother-liquors from these different crops of crystals were treated as described by Hermann.<sup>1</sup> That is, they were treated with 20 parts or two liters of water and

<sup>1</sup> *J. pr. Chem.* [2], 15, 105 (1877).

150 grams of sodium hydroxide. A clear solution resulted, from which a fine crystalline precipitate separated. The filtrate from this precipitate gave no reduction test when treated with acid and zinc, nor was anything obtained from it after having added dilute sulphuric acid and a slight excess of ammonium hydroxide. It was free from earthy bases and metallic acids.

The crystals of the sodium salt (2.5 grams), obtained as outlined in the last paragraph, dissolved almost completely in 20 parts of boiling water and separated in well-defined forms from the cold solution. A portion of this salt heated in a salt of phosphorus bead imparted a blue color to the latter in the reducing flame.

The next step was to decompose the solution of this crystalline sodium salt with dilute sulphuric acid. The solution was hot. The precipitate which separated was thrown upon a filter and washed, after which it was dissolved in hydrofluoric acid and an equivalent amount of potassium carbonate added in order to form potassium columbium oxyfluoride. The solution was evaporated to dryness upon a water-bath, the residue repeatedly moistened, and evaporation to dryness repeated until the odor of hydrofluoric acid could not be detected by the smell; then the salt was baked, taken up in water, and the solution boiled for some time. A trace of tantalum oxyfluoride separated. It was filtered out. On evaporation to crystallization the leafy, characteristic crystals of potassium columbium oxyfluoride appeared. They were dried between bibulous paper and then analyzed.

*Analysis:*

0.5502 gram of salt gave 0.2452 gram of oxide and 0.3224 gram of potassium sulphate.

$0.2452 : 0.3224 :: x/2 : 174 \quad x = 264.6.$		
	Calculated for $K_2CbOF_5 \cdot H_2O.$	Found.
Oxide.....	44.52	44.56
$K_2SO_4$ .....	57.81	58.60

A portion of crystals No. 4 (page 1374) was recrystallized and analyzed.

0.5588 gram of sample gave 0.2407 gram of oxide and 0.3232 gram of potassium sulphate.

$0.2407 : 0.3232 :: x/2 : 174 \quad x = 259.2.$		
	Calculated for $K_2CbF_7.$	Found.
Oxide.....	43.93	43.08
$K_2SO_4$ .....	57.05	57.84

Analysis of recrystallized portion of crystals (4), page 1374.

0.5588 gram of sample gave 0.2407 gram of oxide and 0.3232 gram of potassium sulphate.

$$0.2407 : 3232 :: x/2 : 174 \quad x = 259.2.$$

	Calculated for $K_2CbF_7$ .	Found.
Oxide.....	43.93	43.08
$K_2SO_4$ .....	57.05	57.84

The results of analysis as well as the behavior point to the fact that the oxide contained in these residues is mainly columbium oxide,  $Cb_2O_6$ , with a small portion of another oxide causing the equivalent weights obtained to be too low. These results may in part be due to the presence of some potassium silicofluoride, but more likely to potassium titanium fluoride. Yet these last fractions of double fluoride in which the titanium should be concentrated show only very small amounts. Starting with so much material the last fractions should show more titanium, if it is present in the mineral in appreciable amounts.

The only tests for small amounts of titanium which we have are the hydrogen peroxide test of Schönn,<sup>1</sup> and the chromotropic acid test used by Geisow.<sup>2</sup> Of these the former is the only one relied on, and it offers the only direct evidence which we have for the presence of titanium in the potassium columbium oxyfluoride obtained from columbite.

The methods applicable in the preparation of columbium oxide relatively free from titanium are as follows:

1. Crystallization of potassium columbium fluoride ( $K_2CbF_7$ ) which is not isomorphous with potassium titanium fluoride. The difficulty in this case is that the hydrofluoric acid increases the solubility of the columbium body and decreases that of the titanium double fluoride so that the titanium would have less tendency to concentrate in the mother-liquors.

2. Fractional precipitation with dilute ammonium hydroxide. The columbium hydroxide is precipitated first and the titanium concentrated in the last fractions. No fraction consists entirely of titanium hydroxide; even the last fraction is largely columbium hydroxide.

3. The formation of the chloride or oxychloride of columbium and the chloride of titanium and separating these by distillation.

<sup>1</sup> *Jsb.*, 1893, p. 901.

<sup>2</sup> Dissertation, 1902.

4. Treatment of the hydroxide with cold, fairly concentrated sulphuric acid, in which the titanium hydroxide should dissolve and leave the columbium.

All of these methods were tried in the endeavor to obtain sufficient titanium from the columbium to identify it and prepare some of its derivatives, *e. g.*, the potassium double fluoride. In order to try our method "1" the remainder of the residues (page 1372)—2 to 3 kilos—was crystallized twice from hydrofluoric acid, thus getting potassium columbium fluoride ( $K_2CbF_7$ ). The mother-liquors were united. They equaled 600 cc. They were neutralized with dilute ammonium hydroxide; the precipitated hydroxide filtered out and the filtrate made alkaline with a large excess of ammonium hydroxide, which gave a further precipitate. This last hydroxide was filtered out and dissolved in hydrofluoric acid. Potassium carbonate was added and the solution evaporated to dryness on a water-bath, the residue taken up in water and crystallized. The crystals obtained were short, stubby needles. They were evidently not potassium columbium oxyfluoride ( $K_2CbOF_5$ ). Their quantity was too small to recrystallize, but they were analyzed:

0.4672 gram of sample gave 0.1740 gram of oxide = 37.6 per cent.

0.4672 gram of sample gave 0.3050 gram of  $K_2SO_4$  = 65.3 per cent.

The specific gravity of the oxide was found to be 5.2, although too little of it was at hand for accurate work. The determination of the titanium in the oxide colorimetrically gave 0.0106 gram of  $TiO_2$  = 6.1 per cent.

The salt originally taken showed 0.62 per cent. of its oxide to be titanium dioxide by the colorimetric determination, while the double fluoride of potassium and columbium obtained showed a titanium dioxide content equal to 0.25 per cent. of its oxide. Hence it would seem that by method "1" the titanium or oxide with lower specific gravity and molecular weight did concentrate in the mother-liquors.

Crystals 2 and 3 (page 1374) were combined. Their total weight was about 1 kilo. This, in portions of 100 grams at a time, was dissolved in about 2 liters of water and fractionally precipitated with ammonium hydroxide, using dilute alkali and working in the cold with constant stirring. The alkali was added until the solu-

tion was barely acid to litmus, the precipitate formed was filtered off and the filtrate made alkaline with an excess of the precipitant. This second fraction contained about 3-4 grams of oxide from each 100 grams of double fluoride taken. These ten last fractions were combined and dissolved in hydrofluoric acid, 15 grams of potassium hydroxide added, then dilute ammonium hydroxide until slightly acid, and the precipitate filtered out. It was marked *A*. Ammonium hydroxide was then added to the filtrate until litmus showed the reaction to be just neutral. The precipitate was designated *B*. *C* was obtained in the filtrate from *B* by adding a large excess of ammonium hydroxide. It, *C* presumably, should contain most of the titanium from the 1,000 grams of double fluoride taken. The oxide actually present in it was changed to double fluoride by dissolving in hydrofluoric acid and adding potassium carbonate. The first crop of crystals was obtained from strong hydrofluoric acid. It recrystallized from the same in needles. These were analyzed:

0.6954 gram of sample gave 0.3018 gram oxide and 0.3900 gram potassium sulphate.

$$0.3018 : 0.3900 :: x/2 : 174 \quad x = 269.3.$$

	Calculated for $K_2Cbf_7$ .	Found.
Oxide.....	57.05	56.09
$K_2SO_4$ .....	43.93	43.40

The specific gravity of the oxide equaled 4.45. 0.3 gram of it showed the presence of the equivalent of 0.0025 gram of  $TiO_2$ , or 0.83 per cent.

The needles from *C*, not taken for analysis, and the mother-liquor were combined and evaporated to dryness on a water-bath to expel the excess of hydrofluoric acid. This was repeated once. The solution of the salt was then fractionally precipitated with ammonium hydroxide, the fractions up to the point where litmus showed a slightly alkaline reaction being discarded, when the filtrate from them was made strongly alkaline with ammonium hydroxide. The precipitate obtained was changed to its potassium double fluoride. About 2.5 grams of the double salt were obtained.

#### *Analysis:*

0.7248 gram of sample gave 0.3014 gram of oxide and 0.4205 gram of  $K_2SO_4$ .

$$0.3014 : 0.4205 :: x/2 : 174 \quad x = 249.4.$$

	Calculated for $K_2CbOF_6 \cdot H_2O$ .	Found.
Oxide.....	57.81	58.02
$K_2SO_4$ .....	44.52	41.58

The specific gravity of the oxide was found to be 4.667. 0.2930 gram of oxide gave a color with hydrogen peroxide equivalent to 0.0322 gram of  $TiO_2 = 11$  per cent.

The crucible in which the oxide was ignited was deeply stained. The analysis and the color test showed the presence of titanium, while the stain on the crucible and the high specific gravity of the oxide could be due to tin in considerable amount, which is precipitated in the last fractions on fractional precipitation with ammonium hydroxide.

The crystals and the mother-liquor remaining from this salt were dissolved in boiling water and an excess of sodium hydroxide added, when a heavy flocculent precipitate separated. This was filtered, boiled with water and the insoluble portion changed to double fluoride. It was again taken up in boiling water and an excess of sodium hydroxide added. The precipitation was not complete. The portion precipitated was treated with boiling water, filtered, and the filtrate found to contain a large amount of titanium. That portion of the precipitate insoluble in water was changed to double fluoride.

*Analysis:*

0.5570 gram of sample gave 0.2248 gram of oxide and 0.3468 gram of  $K_2SO_4$ .

$$0.2248 : 0.3468 :: x/2 : 174 \quad x = 225.6.$$

The specific gravity of the oxide was found to be 4.2. The oxide gave a color with hydrogen peroxide showing the presence of about 21 per cent. titanium dioxide.

Crystals A (page 1373) were changed to double fluoride and recrystallized.

*Analysis:*

0.7184 gram of sample gave 0.3188 gram of oxide and 0.4176 gram of potassium sulphate.

$$0.3188 : 0.4176 :: x/2 : 174 \quad x = 265.7.$$

	Calculated for $K_2CbOF_6 \cdot H_2O$ .	Found.
Oxide.....	44.52	44.38
$K_2SO_4$ .....	57.81	58.13

The specific gravity of the oxide was found to be 4.481.

0.3160 gram of oxide gave a color with hydrogen peroxide equivalent to 0.0022 gram  $\text{TiO}_2 = 0.7$  per cent.

Crystals *B* (page 1373) analyzed as follows:

0.8098 gram of sample gave 0.3614 gram of oxide and 0.4708 gram of  $\text{K}_2\text{SO}_4$ .

$$0.3614 : 0.4708 :: x/2 : 174 \quad x = 267.0.$$

	Calculated for $\text{K}_2\text{C}_2\text{bOF}_5 \cdot \text{H}_2\text{O}$ .	Found.
Oxide.....	44.52	44.63
$\text{K}_2\text{SO}_4$ .....	57.81	58.14

The specific gravity of the oxide was found to be 4.864. 0.3600 gram of oxide gave with hydrogen peroxide a color equivalent to 0.0013 gram of  $\text{TiO}_2 = 0.36$  per cent.

Having failed to get any evidence of the existence of neptunium in the last fractions of the double fluoride from the South Dakota mineral, it was decided to test some of the mineral from Haddam, Conn., the source of the material used by Hermann in his investigation. The last fractions of the potassium double fluoride from 5.87 kilos of columbite from Haddam, Conn., amounting to 100 grams, were dissolved in boiling water and an excess of sodium hydroxide added. The precipitate obtained was partly crystalline and partly flocculent, as described by Hermann. It was filtered out, dried on a porous plate, and boiled with 25 parts of water. The crystals dissolved, leaving a yellowish residue evidently containing much iron. This residue gave a yellow bead in the reducing flame containing so much iron that it was impossible with a small blowpipe to keep it all reduced. Is it not probable that this is what Hermann supposed was neptunium?

This salt was fused with acid potassium sulphate to remove the iron; the oxide remaining after extracting the fusion with boiling water was changed to double fluoride, dissolved in boiling water, and an excess of sodium hydroxide added. The precipitate obtained was crystalline and perfectly soluble in water, leaving an inappreciable residue, from all of which it may be inferred that the material from the Haddam locality showed no more evidence of neptunium than did that from South Dakota.

Ten kilograms of the main bulk of the potassium columbium oxyfluoride were crystallized from strong hydrofluoric acid. Five hundred grams were taken at one time and the mother-liquors from the two fractions combined, evaporated one-half, and another crop of crystals removed. The mother-liquors from

these were united and evaporated, the crystals obtained were recrystallized, the mother-liquors from the recrystallization combined and evaporated to dryness with sulphuric acid. The oxide obtained from that portion evaporated to dryness was 5 grams. The fraction of crystals immediately preceding, 60 grams in weight, was decomposed with sulphuric acid and the oxide obtained from it. The 5 grams of oxide and about one-half of the oxide from the 60 grams of double fluoride were heated in carbon tetrachloride vapors, taking about 2 grams of oxide at a time. The more volatile portion, which should contain the most of the  $\text{TiCl}_4$ , was distilled away from the  $\text{CbOCl}_3$ . The portions of this liquid were combined, the oxides—3 grams—obtained from it, and these oxides again heated in carbon tetrachloride. Again only the liquid portion and that of the solid which was carried over mechanically was taken. The oxide from this portion was changed to double fluoride.

*Analysis:*

0.5678 gram of sample contained 0.2196 gram of oxide and 0.3390 gram of  $\text{K}_2\text{SO}_4$ .

$$0.2196 : 0.3390 :: x/2 : 174 \quad x = 225.4.$$

	Calculated for $\text{K}_2\text{CbOF}_5 \cdot \text{H}_2\text{O}$ .	Found.
Oxide.....	44.52	38.6
$\text{K}_2\text{SO}_4$ .....	57.81	59.7

Amount of  $\text{TiO}_2$  in the oxide 0.0594 gram = 29.7 per cent.

The oxide from the salt taken for analysis was combined with the oxide from the double fluoride not taken for analysis, and this, with the remaining half of the oxide from the 60 grams of double fluoride mentioned above, was mixed with the oxide from all the previous double fluorides which had been tested for titanium and had shown its presence in a fair degree. This mixture of oxides was heated in a current of sulphur monochloride, the chloride formed collected in a receiver, and this was then heated until all of the sulphur monochloride was distilled out. This sulphur monochloride and any other chlorides which it might contain was again distilled to remove the last of the columbium chloride which might have been carried over mechanically. It was then treated with water and oxalic acid, the sulphur filtered off, and any oxide dissolved in the oxalic acid precipitated with ammonium hydroxide. This hydroxide was changed to potassium double fluoride.

*Analysis:*

0.5444 gram of sample gave 0.1952 gram of oxide and 0.3850 gram of potassium sulphate.

$$0.1952 : 0.3850 :: x/2 : 174 \quad x = 175.9.$$

	Calculated for $K_2CbOF_5 \cdot H_2O$ .	Calculated for $K_2TiF_6$ .	Found.
Oxide.....	44.52	33.33	35.85
$K_2SO_4$ .....	57.81	72.50	70.72

0.0310 gram of the oxide was found to contain 0.244 gram  $TiO_2$ , or 78.7 per cent.

A solution of the oxide in hydrochloric acid reduced with zinc to an amethyst or violet color; the oxide also gave a violet titanium bead in the reducing flame with salt of phosphorus.

It would seem that about 80 per cent. of the oxide from this double fluoride was titanium dioxide.

The remainder of the double fluoride, about 0.5 gram, was dissolved in the mother-liquor from which it came by heating, and an excess of sodium hydroxide added. A flocculent precipitate formed. After cooling, this was filtered off and the filtrate acidified with hydrochloric acid and tested for metallic acids with ammonium hydroxide. A precipitate was obtained, which was filtered out and, after washing thoroughly, dissolved in hydrochloric acid.

Upon passing hydrogen sulphide through this solution a heavy precipitate of yellow stannic sulphide was obtained, showing that tin had been carried over with the titanium by the sulphur monochloride.

The precipitate formed by the excess of sodium hydroxide was drained thoroughly and boiled up with water. Nothing went into solution, as would have happened had there been any sodium columbate in the precipitate. This well-washed precipitate was dissolved in hydrofluoric acid and potassium carbonate added to change it to the potassium double fluoride.

*Analysis of the crystals obtained:*

0.1893 gram of sample gave 0.0642 gram of  $TiO_2$  and 0.1366 gram of  $K_2SO_4$ .

	Calculated.	Found.
Oxide.....	33.33	33.91
$K_2SO_4$ .....	72.50	72.16

The determination of the titanium dioxide colorimetrically gave 0.0636 gram. The salt was undoubtedly potassium tita-

nium fluoride, proving conclusively the presence of titanium in columbite.

BEHAVIOR OF SOLUTIONS OF THE DOUBLE FLUORIDES OF COLUMBIUM AND OF TITANIUM WITH A VARIETY OF BASES.

Excess of sodium hydroxide was found to precipitate titanium completely from a solution of potassium titanium fluoride, while with potassium columbium oxyfluoride it gave a precipitate soluble in slight excess but again insoluble and separating in a crystalline form from a large excess of the sodium hydroxide. The precipitate formed in the case of the titanium was insoluble in water, while in the case of columbium the crystalline deposit was completely soluble in hot water. It was hoped that this difference of behavior might afford a means of separating these two elements. To test this, experiments were tried as follows:

(1) 0.9600 gram of  $K_2CbOF_5 + H_2O$ , containing 0.4272 gram of  $Cb_2O_5$ , and 1.1600 grams  $K_2TiF_6$ , containing 0.3753 gram of  $TiO_2$ , were dissolved in 200 cc. water, brought to boiling and an excess of sodium hydroxide added. The precipitate which formed was partly crystalline and partly flocculent. The solution was allowed to stand over night. The precipitate was filtered out, drained, and washed back into a platinum dish. It was covered with 200 cc. of water, brought to boiling, filtered hot, and washed with hot water. The filtrate which should contain most of the columbium and none of the titanium was brought to boiling and sulphuric acid and ammonium hydroxide added. The hydroxide obtained was ignited to oxide and weighed 0.1640 gram. It was found to contain 0.0117 gram of  $TiO_2$ . The titanium content was determined colorimetrically by fusing with potassium acid sulphate, dissolving the fusion in oxalic acid and comparing the color developed with hydrogen peroxide with that of a titanium solution, of known strength, in oxalic acid.

Part insoluble—0.2749  $Cb_2O_5$ , 0.3636  $TiO_2$ .

$TiO_2 \cdot 4Cb_2O_5$  soluble portion;  $Cb_2O_5 \cdot 4TiO_2$  insoluble portion.

(2) A mixture containing 0.1270 gram  $K_2TiF_6$ , or 0.0423 gram  $TiO_2$  and 2.5280 grams  $K_2CbOF_5 \cdot H_2O$ , or 1.1376 grams  $Cb_2O_5$ , was treated as above. The precipitate was nearly all crystalline. That part of it insoluble in water weighed 0.0470 gram and contained 0.0074 gram of  $TiO_2$ , leaving 0.0349 gram of  $TiO_2$  in solution (by far the greater quantity).

(3) 0.2830 gram  $K_2TiF_6$ , containing 0.0943 gram  $TiO_2$ , and 2.7040 grams  $K_2CbOF_5 \cdot H_2O$ , containing 1.2168 grams  $Cb_2O_5$ , were treated as before. The precipitate was chiefly crystalline. A small part of it was flocculent. The part insoluble in water weighed 0.0740 gram and contained 0.0148 gram  $TiO_2$ , showing that 0.0795 gram  $TiO_2$  went into solution and would be found with the bulk of the columbium.

(4) 0.6790 gram  $K_2TiF_6$ , containing 0.2263 gram  $TiO_2$ , and 2.2530 grams  $K_2CbOF_5 \cdot H_2O$ , containing 1.0139 grams  $Cb_2O_5$ , were treated as before. The precipitate contained a considerable amount of flocculent material. The part insoluble in water weighed 0.1720 gram and contained 0.0710 gram  $TiO_2$ , leaving 0.1553 gram of  $TiO_2$  in solution.

The action of potassium hydroxide was also tried. It gave a precipitate with columbium, soluble in an excess, and reprecipitated by greater excess. When the solution was evaporated pearly plates of potassium columbate separated out. With a solution of  $K_2TiF_6$  a heavy precipitate was obtained, but the filtrate gave a slight test for titanium.

1.3130 grams  $K_2TiF_6$ , containing 0.4377 gram of  $TiO_2$ , and 1.0060 grams  $K_2CbOF_5 \cdot H_2O$ , containing 0.4467 gram  $Cb_2O_5$ , were dissolved in 200 cc. of water and the solution brought to boiling, when an excess of potassium hydroxide was added. The precipitate obtained weighed 0.5900 gram after ignition. The filtrate gave a very pronounced test for titanium.

Solutions of  $K_2TiF_6$  and  $K_2CbOF_5$  were studied with various organic bases in the hope that differences of behavior might present themselves which would lead to a quantitative separation of these two elements.

Reagent.	Solution of $K_2TiF_6$ .		Solution of $K_2CbOF_5$ .		
	Precipit. complete,		Precipit. soluble excess.		
1. Monomethylamine,	"	"	"	"	"
2. Dimethylamine,	"	"	"	"	"
3. Trimethylamine,	"	"	"	"	"
4. Tetramethylamine,	"	"	"	"	"
5. Monoethylamine,	"	"	"	"	"
6. Diethylamine,	"	"	"	"	"
7. Triethylamine,	"	"	"	by large excess. insoluble excess. dif. soluble in water.	
8. Dipropylamine,	"	"	"	soluble excess.	
9. Amylamine,	"	"	"	"	"

Reagent.	Solution of $K_2TiF_6$ .	Solution of $K_2C_2O_7$ .
10. Isobutylamine,	Precipit. complete,	Precipit. soluble excess.
11. Allylamine,	" "	" " "
12. Ethylenediamine,	" "	" " "
13. Propylenediamine,	" "	" " "
14. Butylenediamine (secondary),	" "	" " "
15. Butylenediamine (normal),	" "	" " "
16. Hexylamine,	" "	" " "
17. Benzylamine,	" "	" " "
18. Benzylmethylaniline,	" "	" " "
19. Piperidine,	" "	" " "
20. Camphylamine,	" "	slightly soluble excess.
21. Dibenzylamine,	" "	Precipit. complete.
22. Pyridine,	" "	" "
23. Diisobutylamine,	" "	" "
24. Tripropylamine,	" "	" "
25. Diamylamine,	" "	" "
26. Heptylamine,	" "	" "
27. Toluylenediamine (meta),	Partial precipitation,	" "
28. Picoline,	" "	" "
29. Triisobutylamine,	Slight precipitation,	" nearly but not quite complete.
30. Bornylamine,	" "	" not complete.
31. Aniline,	Precipit. not complete,	" heavy but not complete.
32. Toluidine ( <i>m</i> ),	Slight precipitation,	" " "
33. Monomethylaniline,	" " after 24 hours,	" " "
34. Monoethylaniline,	Slight prec. on standing,	" slow—incomplete.
35. Isoquinoline,	" " "	" heavy—incomplete.
36. Quinoline,	" " "	" nearly complete.
37. Hexylmethylenetetramine,	" " "	" heavy—incomplete.
38. Bromaniline ( <i>m</i> ),	No precipitation,	Slight prec. on standing.
39. Chloraniline ( <i>o</i> ),	" "	" " "
40. Dichloraniline,	" "	" " "
41. Diethylaniline,	" "	" " "
42. Chloraniline ( <i>p</i> ),	" "	" " "
43. Dimethylaniline,	" "	" " "
44. Xylidine ( <i>p</i> ),	" "	Precipit. slow—incomplete.
45. Xylidine ( <i>o</i> ),	" "	" " "
46. Xylidine ( <i>m</i> ),	" "	" " "
47. Tetrahydroquinoline,	" "	Slight prec. on standing.
48. Benzylaniline,	" "	No precipitation.

Reagent.	Solution of $K_2TiF_6$ .	Solution of $K_2C_2O_7$ .
49. Diphenylamine,	No precipitation.	No precipitation.
50. Tribenzylamine,	" "	" "
51. Naphthylamine ( $\beta$ ),	" "	" "
52. Naphthylamine ( $\alpha$ ),	" "	" "
53. Nitronaphthalene,	" "	" "
54. Bromphenylhydrazine,	" "	" "
55. Nitrophenylhydrazine,	" "	" "
56. Benzidine,	" "	" "
57. Nitraniline ( <i>o</i> ),	" "	" "
58. Nitraniline ( <i>p</i> ),	" "	" "
59. Nitraniline ( <i>m</i> ),	" "	" "
60. Diphenyl,	" "	" "
61. Diphenyl carbonate,	" "	" "
62. Methyl carbonate,	" "	" "
63. Ethyl carbonate,	" "	" "
64. Piperine,	" "	" "
65. Monochlorhydrin,	" "	" "
66. Trichlorhydrin,	" "	" "
67. Dibromhydrin ( $\beta$ ),	" "	" "
68. Nitrosodipropylin,	" "	" "
69. Nitrosodiethylene,	" "	" "
70. Nitrosodimethylene,	" "	" "
71. Succinimide,	" "	" "
72. Methyl diphenylamine.	" "	" "
73. Tetranitromethylaniline,	" "	" "
74. Bromaniline,	" "	" "

The behavior of the bases which react with the above solutions of titanium and columbium may be divided into the following classes:

(1) Those which precipitate the titanium completely, and while they precipitate the columbium dissolve it upon the addition of an excess of the reagent to form columbates. This class, while showing pronounced difference of behavior, is useless as a means of separation, for upon treating a solution containing both titanium and columbium with one of these reagents the titanium was found both in the soluble and in the insoluble portion. Columbium was also found in the titanium precipitate. The probable explanation for this is that a columbate was formed which dissolved the freshly precipitated titanium hydroxide to a salt of a complex titanoso-columbic acid, which was soluble, and also a small amount of an acid salt or a free acid containing an excess of titanium, which was insoluble.

(2) To the second class of reagents belong those which precipi-

tate the hydroxides of the two elements and are not sufficiently basic to dissolve the columbium hydroxide and form columbates. Those reagents which are sufficiently basic to completely precipitate the columbium are strong enough to partially precipitate the titanium. Quinoline seemed the most promising of all the reagents which were tried.

(3) Those reagents which gave only a partial precipitation with columbium and no precipitation with titanium solutions did not precipitate columbium hydroxide free from titanium, from a solution containing both titanium and columbium. The hydroxide precipitated always gave a strong test for titanium after dissolving it in oxalic acid. This may have been due in part to the extreme difficulty encountered in washing the precipitate free from mother-liquor.

(4) The remaining reagents precipitated neither titanium nor columbium.

*Reactions of the Double Fluorides of Columbium, Titanium, Tantalum, Tin and Tungsten with Various Reagents in Concentrated Sulphuric Acid.*

A small amount of the reagent was dissolved in eight to ten drops of concentrated sulphuric acid on a glazed porcelain surface and the crystalline double fluoride introduced into this acid solution. In most cases the color was destroyed upon diluting with water. No color was imparted to tin solutions by any of the reagents which appear below.

Reagent.	Ta.	Cb.	W.	Ti.
Codeine,	No color,	No color,	Faint pink; may be due to morphine,	Light brown; on standing trace purple.
Morphine,	Faint yellow,		Red to brown; very delicate,	Gray brown, becoming purple, H <sub>2</sub> O ppt.
Resorcinol,	No color,	No color,	Red-brown; fairly delicate,	No color.
Naphthol ( $\beta$ ),	"	Faint yellow, brown,	Coffee-brown; very delicate,	Brown, becoming dark blue.
Naphthol ( $\alpha$ ),	"	Faint brown,	Green to dark greenish brown,	Deep blue; very delicate.
Pyrogallol,	"	Yellow to light brown,	Dull dark red,	Deep red to brown to dirty blue.

Reagent.	Ta.	Cb.	W.	Ti.
Salicylic acid,	No color,	Very faint yel- low,	Deep red,	Reddish yellow.
Cinchonidine,	"	No color,	No color,	On standing a slight purple.
Apomorphine,	"	Yellow brown,	Light red-brown,	Purple to brown to green and blue.
Narceine,	"	Brownish yel- low,	Brown,	Dirty dark green.
Bebeerine,	"	No color,	Clear brown,	Dark brown to green.
Narcotine,	"	Yellow,	Brown,	Light brown to green.

Strychnine, quinidine, cinchonidine and atropine gave no color with any of the elements tested. Narceine and bebeerine alone in sulphuric acid gave a considerable color, and with them the amount of reagent used must be very small or it will obscure any change produced by the addition of the double fluoride. In this connection it is of interest to note that Levy<sup>1</sup> studied the colors produced by the phenol-like bodies, dissolved in concentrated sulphuric acid, when brought in contact with the oxides of titanium, tin, tantalum, columbium and other elements, with the following results. Columbium could be tested for in the presence of all the others by using codeine, as it gave a pink color, while titanium yielded no color and tantalum but a faint green. Titanium could be tested for by using morphine, with which it gave a carmine color, columbium no color and tantalum a yellow color passing into brown. Tantalum with resorcinol gave a dirty green color, changing to amethyst and rose, while titanium yielded a flesh-red color going to chocolate-brown, and columbium a yellowish tint. None of the results were duplicated save the morphine test for titanium, which proved exceedingly delicate, yet to have the color show definitely in columbium the latter must contain 0.5 per cent. of titanium dioxide. Codeine gave no color with columbium, nor did resorcinol with tantalum, therefore Levy could not have had pure material for his tests.

In our use of these reagents we failed to find satisfactory tests except in the case of morphine for titanium. None answered for columbium in the presence of titanium or for tantalum in the presence of columbium. Resorcinol proved to be a fairly delicate test

<sup>1</sup> C. R., 103, 1074 and 1195.

for titanium. It gave no color with columbium, tantalum or tungsten.

*Action of Hydrochloric Acid Gas on Ignited Columbic Oxide.*

0.25 gram of ignited columbic oxide was completely volatilized in three hours in a current of dry hydrochloric acid gas. It volatilized as a white powder with no indication of reduction by change of color. The compound formed adhered to the walls of the glass tube, was insoluble in oxalic acid, and only very slowly soluble in concentrated sulphuric acid, requiring long boiling to dissolve a thin layer. It contained hydrochloric acid, as was shown by washing with ammonium hydroxide and testing the washings with silver nitrate and nitric acid. It would be very difficult to collect in a form convenient for analysis, yet this should be done, as the body evidently contains no water, as is given in the formula of a similar body obtained by Smith and Maas<sup>1</sup> by passing moist hydrochloric acid gas over the hydrated oxide. It is undoubtedly analogous to the body obtained on heating molybdic acid in hydrochloric acid gas, namely,  $\text{MoO}_3 \cdot 2\text{HCl}$ . It is likely  $\text{Cb}_2\text{O}_3 \cdot x\text{HCl}$ .

*Action of Sulphuric Acid on the Hydroxides of Columbium and Titanium after Precipitation by Ammonium Hydroxide from Solutions of Their Double Fluorides.*

The method used was to precipitate the hydroxides from a weighed amount of the double fluorides, filter and wash as thoroughly as possible, then transfer to a weighed platinum dish, reweigh, the difference being water, after which a weighed amount of sulphuric acid of definite specific gravity was added and allowed to stand in contact with the hydroxides for a definite time. The portion insoluble was filtered off, and the amount of oxide going into solution determined by precipitation with ammonium hydroxide, igniting and weighing. The amount of titanium in the oxide which went into solution was determined colorimetrically.

In making these trials columbium oxyfluoride was used in which the titanium oxide as compared with the columbium oxide was 0.00095 gram  $\text{TiO}_2$ , or 0.41 per cent. The specific gravity of the sulphuric acid used was 1.145.

*Experiments.*

(1) One gram of  $\text{K}_2\text{TiF}_6$ , containing 0.3330 gram of  $\text{TiO}_2$ , was

<sup>1</sup> *Z. anorg. Chem.*, 7, 96.

used to obtain the hydroxide. The latter was treated with 40 cc. of water and 70 grams of sulphuric acid. It dissolved completely in fifteen minutes.

(2) 0.4450 gram of columbic oxide, in the form of hydroxide, was treated with 40 grams of water and 108 grams of sulphuric acid for one hour. Only a slight precipitate was obtained with ammonium hydroxide in the filtrate. It was not weighed but contained 0.00032 gram of  $\text{TiO}_2$ , or 0.07 per cent. of the total oxide taken, or one-sixth of the total  $\text{TiO}_2$  present.

(3) Columbic hydroxide, containing 0.4450 gram of oxide, was treated with 60 grams of water and 123 grams of sulphuric acid for four hours. The portion which dissolved equaled 0.0060 gram = 1.33 per cent., and contained 0.000424 gram of  $\text{TiO}_2$ , or 7 per cent. of the oxide dissolved and about one-fourth of the total titanium present.

(4) The hydroxide from 3 grams of columbium oxyfluoride, equivalent to 1.35 grams of oxide, was allowed to stand in contact with 50 grams of water and 100 grams of sulphuric acid for seventeen hours. The acid solution showed 0.0236 gram of oxide = 1.75 per cent., containing 0.000954 gram  $\text{TiO}_2$  = 4 per cent. of oxide dissolved or 17 per cent. of the total  $\text{TiO}_2$  present.

(5) A hydroxide containing 0.445 gram of oxide when treated with 57 grams of water and 85 grams of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.435) for forty-five hours showed in solution 0.0500 gram = 11.1 per cent., containing 0.0008 gram  $\text{TiO}_2$  = 1.6 per cent. of the oxide dissolved or 43 per cent. of the total  $\text{TiO}_2$  present.

Known amounts of the two hydroxides were next treated together as in the following experiments.

(6) 0.2816 gram of  $\text{K}_2\text{TiF}_6$ , containing 0.0939 gram of  $\text{TiO}_2$ , and 0.5078 gram of  $\text{K}_2\text{CbOF}_5 \cdot \text{H}_2\text{O}$ , containing 0.2255 gram  $\text{Cb}_2\text{O}_5$ , were treated with 50 grams of water and 15 grams of sulphuric acid (sp. gr. 1.435) for four hours. The amount of oxide remaining insoluble was only 0.07 gram. It was not examined as to its titanium content.

(7) The hydroxide from 0.2420 gram  $\text{K}_2\text{TiF}_6$ , containing 0.0807 gram  $\text{TiO}_2$ , and that from 0.3454 gram of  $\text{K}_2\text{CbOF}_5 \cdot \text{H}_2\text{O}$ , containing 0.1537 gram of  $\text{Cb}_2\text{O}_5$ , were covered with 70 grams of water and 5 grams of sulphuric acid (sp. gr. 1.435). The amount of oxide in solution after four hours was 0.0800 gram, corresponding well with the weight of the oxide of titanium present, but the insoluble

portion was found to contain 0.0350 gram of titanium dioxide, determined colorimetrically, so that only about one-half of the titanium hydroxide had been dissolved out while nearly as much columbium hydroxide had gone into solution. The acid used would not have dissolved any columbium hydroxide had it been free from titanium hydroxide: further it would have dissolved out all of the titanium hydroxide had it not been mixed with the columbium hydroxide. It may, therefore, be concluded that this method of separation is worthless. It remains to be seen how haloid acids would act.

*The Chromotropic Acid Test for Titanium.*

Geisow<sup>1</sup> observed that the color developed by chromotropic acid with titanium solutions offered a very delicate test for that element. In concentrated solution it gives a deep red, in dilute solutions, a pink color. The color-giving compound was isolated by Geisow and found to have the following composition: one molecule of chromotropic acid to 4 of  $\text{TiO}_2$  and 9 of  $\text{H}_2\text{O}$ .

As it was most important to find some means of estimating the amount of titanium in columbium we were induced to study this reaction of Geisow, using solutions of titanate hydroxide in oxalic, sulphuric and hydrochloric acids.

Solutions used:

(A) 0.53 gram of  $\text{TiO}_2$  dissolved in 3.42 grams of oxalic acid and diluted to 500 cc. 1 cc. = 0.00106 gram of  $\text{TiO}_2$  and contained 0.00684 gram of oxalic acid.

(B) Ten cc. of (A) diluted to 100 cc. 1 cc. = 0.000106  $\text{TiO}_2$ .

(C) Ten cc. of (B) diluted to 100 cc. 1 cc. = 0.0000106  $\text{TiO}_2$ .

(D) Ten grams of oxalic acid in 100 cc. 1 cc. = 0.1 gram of oxalic acid.

(E) One gram chromotropic acid in 100 cc.

Fifty cc. Nessler tubes, one inch in diameter, were used for all of the tests.

0.5 cc. of (E) in 50 cc. of water gave a mere trace of color, for which reason the solution to be tested was always compared with another tube containing the same amount of chromotropic acid, thus making allowance for the slight color given by the solution of that reagent.

0.15 cc. of (C) gave a faint pink color when added to 50 cc. of water containing 0.5 cc. of (E); 0.00000159 gram of  $\text{TiO}_2$  in 50

<sup>1</sup> Dissertation, (1902).

cc. of water gave a change of color; 0.3 cc. of the same solution gave a very distinct coloration, or 0.00000318 gram of  $\text{TiO}_2$  in 50 cc. More than 1 cc. of the chromotropic acid gave so much color as to interfere with the delicacy of the test.

*Effect of Oxalic Acid.*

One cc. of (E).

One cc. of (D), or 1 gram of oxalic acid in 50 cc., required 2.6 cc. of titanium solution (C) to show the characteristic pink color, or 0.0000275 gram of  $\text{TiO}_2$ .

One cc. of reagent was adopted as the amount best suited to use and was the amount taken in all of the following cases unless otherwise stated.

With 0.2 gram of oxalic acid, 0.0000339 gram of  $\text{TiO}_2$  in 50 cc. gave a pink color.

With 0.5 gram of oxalic acid, 0.0000275 gram of  $\text{TiO}_2$  was required to give the test for titanium.

1.0 gram of oxalic acid required 0.0000244 gram of  $\text{TiO}_2$  to give the test.

In the presence of 2.0 grams of oxalic acid, 0.0000244 gram of  $\text{TiO}_2$  gave a distinct pink color in 50 cc., while with 5.0 grams of oxalic acid, 0.0000265 gram of  $\text{TiO}_2$  gave a color.

The amount of oxalic acid seems to have little effect although the presence of the acid diminishes the delicacy of the test, but this is independent of the amount of the acid present when more than 0.1 gram is used.

*Effect of the Presence of Hydrochloric Acid.*

The solution of hydrochloric acid used was one part of concentrated acid to five parts of water.

With 1 cc. of hydrochloric acid (1:5) and 1 cc. of chromotropic acid in 50 cc., 0.0000795 gram of  $\text{TiO}_2$  gave a distinct pink color.

With 2 cc. of hydrochloric acid (1:5) 0.00017 gram of  $\text{TiO}_2$  was required to give the color.

When 5 cc. of hydrochloric acid (1:5) was used 0.000424 gram of  $\text{TiO}_2$  gave a pink color to 50 cc.

Ten cc. of hydrochloric acid (1:5) required 0.000848 gram of  $\text{TiO}_2$  for the color.

Twenty cc. of hydrochloric acid (1:5) required 0.00169 gram of  $\text{TiO}_2$  in 50 cc. to give a definite test for titanium.

It may, therefore, be concluded that the destruction of the color

given by chromotropic acid is in proportion to the amount of acid present, so if this test is used hydrochloric acid should be absent.

*Effect of Sulphuric Acid.*

With 1 cc. of sulphuric acid (sp. gr. 1.435), 0.000318 gram of  $\text{TiO}_2$  was required to give a pink color in 50 cc. of solution.

With 2 cc. of sulphuric acid, 0.000742 gram of  $\text{TiO}_2$  was required to give the titanium test.

While more dilute solutions of sulphuric acid were not tried it is evident that the effect of the sulphuric acid is roughly proportional to the amount of acid present, and that any appreciable amount of this acid seriously interferes with the delicacy of the test. The same is true of hydrofluoric acid.

In the presence of oxalic acid in any appreciable amount chromotropic acid will show 0.000025 gram of  $\text{TiO}_2$  in 50 cc. very distinctly. Half that amount could be detected but the color is very faint and its similarity to the color possessed by the solution of chromotropic acid itself renders the detection of this amount uncertain. In making the test it is best to avoid the presence of free mineral acids, as they interfere and generally in direct proportion to the amount of acid present. The neutral chlorides and sulphates are without effect, as Geisow has stated. It is probable that the color developed in oxalate solution could be used to determine the amount of titanium present by comparison with the color developed by known amounts of titanous acid, but this method would offer no special advantage over the hydrogen peroxide method.

*The Action of Carbon Tetrachloride on the Oxides of Titanium, Columbium and Tantalum.*

According to Demarçay<sup>1</sup> carbon tetrachloride vapor passed over the ignited oxides of columbium, titanium and tantalum changes them to chlorides—in the case of titanium with the formation of an intermediate oxychloride.

Lothar Meyer<sup>2</sup> found no action on oxide of titanium. He did not try the other two.

Delafontaine and Linebarger<sup>3</sup> found that oxide of columbium was changed to oxychloride,  $\text{CbOCl}_3$ , with the formation of a

<sup>1</sup> *C. R.*, 104, 111.

<sup>2</sup> *Ber.*, 20, 681.

<sup>3</sup> *This Journal*, 18, 532.

small amount of the chloride. In the case of tantalum the oxide was not driven from the boat but remained behind as a pasty mass, suffering no change to chloride. They suggest this as a possible separation of the two elements columbium and tantalum.

The vapor of carbon tetrachloride was found to act slowly on ignited titanic oxide at a low red heat, some chloride of titanium being continuously formed. In time all of the oxide was converted into chloride.

The oxide of columbium is readily acted upon by carbon tetrachloride even at a low red heat. The principal product is the white oxychloride. Some of the yellow chloride is simultaneously produced. It continues to be formed in small amounts as the oxychloride is sublimed in the vapors of carbon tetrachloride. Columbium oxide heated in a sealed tube with carbon tetrachloride, is completely changed to chloride after several hours at 200–225°. The chloride dissolves in carbon tetrachloride and separates from it in large, well-formed, needle-like crystals.

The action of the vapors of carbon tetrachloride on ignited oxide of tantalum is rapid, contrary to Delafontaine and Linebarger, converting it into chloride, which can be readily freed from the carbon tetrachloride and thus obtained pure. If the carbon tetrachloride used contains traces of moisture, oxide will be produced by the decomposition of the chloride. This oxide dissolves in the fused chloride and remains as a glassy mass upon sublimation of the chloride. Therefore, care should be taken in the dehydration of the tetrachloride used; otherwise the product will be contaminated with oxide. This seems to be the best method for the preparation of tantalum chloride in large quantities and in a high state of purity. The chloride is an excellent starting-out material for a re-determination of the atomic weight of tantalum, a number none too definite, as a study of the series of results obtained by Marignac<sup>1</sup> by the analysis of potassium tantalum fluoride and ammonium tantalum fluoride will show.

The action of carbon tetrachloride on the oxide of columbium also affords an excellent method for the preparation of the oxychloride of that element. It is produced, however, in a very voluminous state, and mats together to a tough felt, completely stopping up any tube used in its preparation. When heated in a sealed tube it condenses on a warm surface to very compact lus-

<sup>1</sup> *Z. anal. Chem.*, **8**, 478.

trous silky needles. It is very difficult to remove the last traces of columbium pentachloride from this body. This may be done, however, by subliming it in a current of chlorine over ignited oxide, but as long as any carbon tetrachloride is present the columbium chloride will continue to be formed. To make the chloride of columbium it is necessary to have recourse to the action of sulphur monochloride on the oxide or to act on the oxide with carbon tetrachloride in a sealed tube.

*Properties of Columbium Chloride.*

As already mentioned, columbium chloride is soluble in carbon tetrachloride, forming a yellow solution. It is much more soluble when hot than when cold and crystallizes out on cooling in well-defined crystals. It is also soluble in sulphur monochloride, the hot, saturated solution being red in color and depositing yellow crystals of the chloride on cooling. It dissolves in ether with a yellow color. On evaporating this solution on a water-bath a thick liquid remains, and an acid vapor is given off, but no crystals separate. Upon ignition the mass chars, then burns and leaves a residue of oxide. On passing dry ammonia gas into the ethereal solution of the chloride a heavy precipitate is formed. This is ammonium chloride and columbium nitride. On washing with water the ammonium chloride is dissolved out, leaving a white residue which reverts on ignition to oxide of columbium, and when boiled with sodium hydroxide gives off ammoniacal vapors, thus pointing to nitride of columbium, likely  $\text{Cb}_3\text{N}_5$ .

Columbium chloride containing some sulphur monochloride was treated with benzene. The sulphur monochloride dissolved out, while the columbium chloride was decomposed, leaving an insoluble gummy mass. Chloroform dissolved the chloride readily, but the solution seemed to undergo decomposition on warming and evaporating, as the liquid became brown and a brown powder separated. No crystalline product could be procured.

The chloride is also soluble in alcohol. In the cold there is no decomposition. On warming and concentrating the solution, acid vapors were given off, due perhaps, as H. Rose has suggested, to the formation of ethyl columbate. That there is no decomposition in dilute solution is shown by the formation of the compound  $\text{CbCl}_5(\text{C}_8\text{H}_{17}\text{N})_8$ , which was obtained on adding piperidine to the alcoholic solution.<sup>1</sup> Other bases, such as aniline, pyridine, etc.,

<sup>1</sup> *Z. anorg. Chem.*, **36**, 100.

gave addition products which were insoluble in the solvent.

The best solvent for columbium chloride is carbon tetrachloride. In this solution reactions should take place, as they do with other chlorides in aqueous solution; also double chlorides, analogous to the double fluorides, should be formed by bringing together solutions of the chlorides in carbon tetrachloride.

*Potassium Fluoxypercolumbate.*

When potassium columbium oxyfluoride is dissolved in 3 per cent. hydrogen peroxide the solution acquires a yellow color. When a saturated solution cools, a pasty mass of crystals separates. These are very hard to free from mother-liquor. When dry they have only a faint yellow tint. On dissolving in water, containing hydrogen peroxide, the solution again becomes yellow in color. The salt obtained in this way is potassium fluoxypercolumbate of the following composition— $K_2CbO_2F_5 \cdot H_2O$ .

*Method of Analysis.*

The potassium was determined as sulphate and the columbium as oxide in the usual way, that is, expelling the fluorine with sulphuric acid, boiling with water, filtering out the insoluble columbium hydroxide and evaporating the filtrate to dryness and weighing the potassium sulphate after ignition.

The oxygen and water were determined in another sample by weighing a portion of the substance in a tube sealed at one end, covering it with a plug of ignited asbestos, connecting with a gas burette and igniting. The oxygen was collected and measured, the tube was reweighed, the loss being water and oxygen. The water was obtained by difference.

*Analysis:*

0.4004 gram of the salt gave 0.1672 gram of oxide and 0.2196 gram of  $K_2SO_4$ .

0.4432 gram of the salt lost 0.0470 gram, which contained 17.9 cc. of oxygen at  $24^\circ$  and under 742 mm. pressure, or 0.0229 gram, the difference—0.0241 gram—being water.

	Calculated.	Found.
$K_2SO_4$ .....	54.89	54.84
Oxide .....	42.28	41.84
O (active).....	5.05	5.16
$H_2O$ .....	5.68	5.44

This salt was obtained and the above composition ascribed to it by Piccini.<sup>1</sup> He regarded it as a derivative of percolumnic acid

<sup>1</sup> *Z. anorg. Chem.*, 2, 21.

and not an addition product of potassium columbium fluoride and hydrogen peroxide, because the water was lost on heating at  $100^{\circ}$ , while the oxygen did not escape until the temperature reached  $150^{\circ}$ .

On crystallizing this salt from concentrated hydrofluoric acid and hydrogen peroxide in the hope of getting a perfluoride, large plates were obtained, which were quite yellow in color with a green tint when dry. They did not seem to differ if little or much hydrofluoric acid was used. The crystals taken for analysis were obtained from a solution consisting of one-half hydrofluoric acid, 48 per cent., and one-half hydrogen peroxide, 3 per cent. They were dried between filter-paper and promptly weighed out for analysis.

*Analysis:*

0.7260 gram of salt gave 0.3274 gram of oxide and 0.3982 gram of potassium sulphate.

0.7482 gram of salt lost 0.0784 gram of ignition, *i. e.*, 29.1 cc. of oxygen at  $24^{\circ}$  and under 742 mm. pressure, or 0.0374 gram, the difference—0.0410 gram—being water.

	Calculated.	Found.
K <sub>2</sub> SO <sub>4</sub> .....	54.89	54.85
Oxide .....	42.28	42.34
O (active).....	5.05	5.00
H <sub>2</sub> O.....	5.68	5.48

Hence it may be concluded that the salt obtained from strong hydrofluoric acid is the same as that obtained when hydrofluoric acid is not used.

It would seem impossible to obtain a derivative of percolumnbic acid which does not contain oxygen.

The salt separates from solutions containing hydrofluoric acid in large well-formed plates, which may be easily measured. They are much easier to handle than when crystallized from a solution free from acid. The crystals are always greenish yellow in color.

Piccini states that the salt obtained by him had a slight yellow tint, but that this color was completely removed by two recrystallizations from hydrogen peroxide. The salt obtained above was recrystallized six times from hydrogen peroxide containing hydrofluoric acid. The crystals from the last crystallization were fully as highly colored as those which had not been recrystallized. They were then recrystallized twice from hydrogen peroxide containing

no acid. The resulting salt was practically colorless, but it dissolved in water and hydrogen peroxide with a yellow color, which was intensified by the addition of hydrofluoric acid, and on evaporating again to crystallization the crystals were as highly colored as any obtained previously.

The oxide from the double fluoride, originally used, gave a color equivalent to 0.4 per cent.  $\text{TiO}_2$ . It was supposed that this color was due entirely to titanium and that the yellow color of the solution and of the crystals of potassium fluoxypercolumbate was also due to this element. To test this supposition 100 grams of the purest potassium columbium oxyfluoride were crystallized twice from strong hydrofluoric acid. The crystals obtained were decomposed with concentrated sulphuric acid, and the hydroxide after extraction with water ignited to oxide. The color which this oxide developed in oxalic acid solution with hydrogen peroxide was equivalent to 0.24 per cent. of its weight of titanous acid. It was now heated in sulphur monochloride and converted into chloride. The latter, together with the excess of monochloride, was collected in a receiver and the sulphur monochloride distilled out in the hope that any titanium tetrachloride present would be expelled with it. The chloride remaining after removing the sulphur monochloride was converted into oxide. It contained titanous oxide equivalent to 0.16 per cent. The oxide was again heated in sulphur monochloride and treated as before. After the second treatment the titanous oxide equivalent was 0.12 per cent. and the color now developed was different. It was greenish yellow instead of yellow inclining towards red, which is characteristic of titanium. About 5 grams of the oxide which had passed through this treatment were changed to double fluoride and crystallized from hydrogen peroxide and hydrofluoric acid. Its solution, in hydrogen peroxide, was yellow and its color increased in intensity on adding hydrofluoric acid. The crystals from it were canary-yellow with a tint of green, differing in no respect from those previously obtained.

About 10 grams of this yellow salt were next dissolved in water and hydrogen peroxide. This solution was distinctly yellow in color. It was divided into two portions. To one portion 0.5 gram of potassium titanium fluoride was added. The color in this portion became considerably deeper, but the excess of color was completely discharged upon adding hydrofluoric acid, the two solutions becoming again identical in color.

Potassium titanium fluoride dissolved in hydrogen peroxide to a deep yellow solution. On cooling crystals were deposited, which were not yellow but colorless when completely free from mother-liquor. The addition of hydrofluoric acid to the colored solution completely destroys the color, and in the presence of hydrofluoric acid the salt formed is white, resembling potassium titanium fluoride. When air-dried it gives off neither water nor oxygen on ignition.

The only elements which give a distinctive color in acid solution with hydrogen peroxide and which might occur here are titanium, vanadium and molybdenum. Of these the first has been excluded and the second also by reason of the color which it gives (red to rose-red). There still remains molybdenum. Its color in an oxalic acid solution with hydrogen peroxide is identical with that observed in the case of the columbium as free from titanium as it could be obtained. Although the columbium oxide used for these tests had passed through several manipulations which should remove molybdenum, such as, fusion with sodium carbonate and sulphur, changing to chloride with sulphur monochloride and distilling off the more volatile portion, it was thought best to determine how much molybdenum would be required to give a test equal to that obtained from the purest oxide of columbium at hand. To this end weighed amounts of molybdenum were dissolved in oxalic and sulphuric acids, and the color, developed with hydrogen peroxide, compared with that obtained with a standard titanium solution of hydrogen peroxide.

(1) 0.2780 gram of molybdic acid developed a color equivalent to 0.0048 gram  $\text{TiO}_2$ , or 0.0058 gram of molybdic acid will give a color equal to that given under similar conditions by 0.0001 gram  $\text{TiO}_2$ .

(2) 0.0660 gram of molybdic acid gave a color equal to 0.0015 gram  $\text{TiO}_2$ , or 0.0044 gram of molybdic acid is equal to 0.0001 gram  $\text{TiO}_2$ .

The variation in these results is due to the difficulty in matching the different shades as to intensity of color. The average is about right, or 0.0050 gram of molybdic acid is equivalent to 0.0001 gram  $\text{TiO}_2$ . Calculating on this basis, the best oxide of columbium obtained, which gave a color equivalent to 0.12 per cent.  $\text{TiO}_2$ , would contain 6 per cent. of  $\text{MoO}_3$  if the color was due to the presence of molybdenum, which would be impossible after the

treatments through which the oxide has passed. It had been crystallized twice as potassium oxyfluoride, fused with sodium carbonate and sulphur, the tantalum removed, again crystallized as the oxyfluoride of potassium and twice from hydrofluoric acid as potassium columbium fluoride, then changed to chloride in sulphur monochloride, the sulphur monochloride and the more volatile portions distilled off and rejected, again changed to oxide and this treatment with sulphur monochloride repeated. The final oxide was converted into potassium fluoxypercolumbate and crystallized once from hydrogen peroxide and hydrofluoric acid. This salt was yellow in color, and 0.3540 gram of oxide from it, dissolved in oxalic acid, gave with hydrogen peroxide a color equivalent to 0.000424 gram  $\text{TiO}_2$  or 0.12 per cent. At the most it could not have contained more than a bare trace of oxide of molybdenum.

0.3470 gram of the oxide from the yellow fluoxypercolumbate was dissolved in oxalic acid and chromotropic acid and diluted to 50 cc. It gave a very slight pink color, about equal in intensity to the color developed in 50 cc. by 0.000025 gram  $\text{TiO}_2$  in the same amount of oxalic acid on treating with chromotropic acid. This would correspond to less than 0.01 per cent. of  $\text{TiO}_2$  and is likely not very far wrong.

From these experiments it may safely be concluded that the color produced in hydrofluoric acid solution of columbium with hydrogen peroxide is not due to the presence of titanium. Also it is likely that columbium itself gives a distinctive color with hydrogen peroxide, equivalent to from 0.10 per cent. to 0.15 per cent. of its weight of titanium dioxide, yet yellow-green instead of straw-yellow, as is given by titanium in dilute solutions. Possibly there may still be present some other element. For this, careful search will be made.

#### *Preparation and Analysis of the Yellow Oxide of Columbium.*

Hydroxide of columbium, containing 10 grams of oxide, was prepared by decomposing the double fluoride with sulphuric acid, evaporating off the excess of acid and extracting with boiling water. This hydroxide was washed repeatedly with boiling water and air-dried. It was covered with about 20 cc. of concentrated hydrochloric acid and brought to boiling for several minutes, until all of the lumps had thoroughly disintegrated, when it was diluted to about three times its original volume with water. All but a few particles were dissolved. This solution was filtered and an equ

volume of 13 per cent. hydrogen peroxide added. It became yellow and after a few minutes a yellow precipitate appeared. The solution was allowed to stand over night. The precipitate was then filtered out, washed with cold water, in which it was insoluble, and air-dried.

Under the above conditions about one-quarter of the oxide in solution was precipitated by the hydrogen peroxide. If the remainder of the oxide in solution were recovered and dissolved in hydrochloric acid, as before, a fresh portion of it could be precipitated on adding hydrogen peroxide. The air-dried precipitate lost oxygen and water on ignition and regained its white color.

As the precipitation of the columbium was only partial it was best to be certain of the identity of the portion precipitated. To this end 2.5 grams of the yellow oxide were obtained, ignited to remove the excess of oxygen, and changed to the potassium double fluoride. This analyzed as follows:

0.6822 gram of the salt gave 0.3026 gram of oxide and 0.3966 gram of  $K_2SO_4$ .

	Calculated.	Found.
Oxide .....	44.52	44.36
$K_2SO_4$ .....	57.81	58.14

Hence the compound obtained is a derivative of columbium.

Columbium is not precipitated from the solution remaining after the yellow precipitate has been filtered out, by an excess of ammonium hydroxide, until the hydrogen peroxide in the solution has been destroyed.

*Analysis of the yellow precipitate:*

0.1917 gram of sample gave 0.1298 gram of  $Cb_2O_5$ .

0.2556 gram of sample gave 7.8 cc. of oxygen at  $22^\circ$  and under 741 mm. pressure, equal to 0.0101 gram.

	Percentage.	Ratio.
$Cb_2O_5$ .....	67.71	1.000
O (active).....	3.95	0.984
$H_2O$ (difference).....	28.34	6.240
	<hr/> 100.00	

This corresponds to  $Cb(OH)_8$ , or to  $Cb_2O_5 \cdot H_2O_2 \cdot 5H_2O$ .

Melikoff and Pissarjewsky<sup>1</sup> obtained a percolumbic acid of the formula  $HCbO_4 + nH_2O$  by heating columbium hydroxide with 30 per cent. hydrogen peroxide on a water-bath. They also obtained it by adding sulphuric acid to a solution of sodium per-

<sup>1</sup> *Z. anorg. Chem.*, **20**, 340.

columbate, dialyzing out the excess of sulphuric acid and the potassium sulphate, then evaporating the clear yellow solution to dryness on a water-bath. They describe it as a yellow amorphous powder, insoluble in water.

The color of these higher oxides seems characteristic of columbium and is certainly not due to the presence of titanium. The hydroxide obtained by Melikoff and Pissarjewsky contained twice as much active oxygen, in proportion to the columbium, as did the hydroxide obtained during this investigation.

*Difference in Solubility of Double Fluorides.*

It is of interest to note that the solubility of potassium titanium fluoride is increased upon the addition of hydrogen peroxide, while that of the potassium columbium oxyfluoride is decreased. In hydrofluoric acid this order is reversed the columbium salt becoming more soluble and the titanium salt less soluble. This suggests alternating these solvents in the crystallization of columbium and potassium double fluorides as one of the best means for removing titanium.

Recrystallization from hydrofluoric acid in the form of  $K_2CbF_6$  will remove tin and probably also tungsten from impure potassium columbium oxyfluoride. Two recrystallizations from that solvent are sufficient to give an oxide, the ignition of which in a platinum crucible gave no stain on the crucible. If partially dried oxide wrapped in the filter-paper be ignited directly in a platinum crucible the presence of a stain on the crucible after removing the oxide will be a very delicate test for tin. It is likely that when tin is removed by crystallization tungsten is also, if they are present in about equal amounts and in such cases where the total amount is very small. The procedure would remove the necessity for the tedious sodium carbonate and sulphur fusions used in this work.

*Behavior with Precipitants.*

Pennington<sup>1</sup> noted that disodium hydrogen phosphate gave no precipitate in a solution of potassium columbium oxyfluoride, while it completely precipitated titanium from a solution of its double fluoride. This was studied briefly in order to determine if it might not serve as a quantitative separation of columbium from titanium. It was found that when the reagent was added to a solution containing a large excess of columbium and only a

<sup>1</sup> This Journal, 18, 38.

little titanium no precipitate was produced even on prolonged boiling. If the amount of titanium was increased slightly both the titanium and the columbium were completely precipitated by the disodium hydrogen phosphate. This reagent, therefore, does not separate the two elements.

Geisow found that an alkaline formoxime solution precipitated zirconium and titanium, but did not precipitate columbium.

Formoxime, or its polymerization product, was prepared by bringing together solutions of the calculated quantities of formaldehyde, sodium carbonate, and hydroxylamine hydrochloride. The resulting solution gave no precipitate when added to a solution of titanium as double fluoride, zirconium as double fluoride, or to a solution of columbium double fluoride. Further, after the addition of the formoxime solution, ammonium hydroxide failed to give a precipitate with any of the solutions noted above. It did, however, give a precipitate with tantalum double fluoride, but this was only partial.

The statement of Geisow that titanium and zirconium can be separated from columbium by means of an alkaline formoxime solution was not verified. The precipitation with tantalum is only partial, and not complete as stated by him.

It was noted<sup>1</sup> that potassium iodate gave a complete precipitation in a solution of potassium titanium fluoride, and no precipitate with a solution of columbium double fluoride. Potassium iodate, free from periodate, was prepared, and it was found to give no precipitate with either columbium or titanium, except in acid solution, when both were precipitated. A solution of a periodate was not tried.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 97.]

## ELECTROLYTIC CALCIUM.

BY JOSEPH H. GOODWIN.

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METALLIC calcium can be easily made in large quantities as shown by the following experiments which required only a short time and simple and easily constructed apparatus. The method

<sup>1</sup> This Journal, 26, 1248.