

Calcium Sodium Pertantalate, $\text{CaNaTaO}_8 \cdot 4\frac{1}{2}\text{H}_2\text{O}$.—The composition of this salt was perfectly analogous with the corresponding potassium salt described by Melikoff and Pissarjewsky. It gave the following analytical results:

Calculated: CaO , 12.31; $0.5\text{Na}_2\text{O}$, 6.81; $0.5\text{Ta}_2\text{O}_5$, 49.01; 4O , 14.07; $4.5\text{H}_2\text{O}$, 17.80.
 Found: CaO , 12.81; $0.5\text{Na}_2\text{O}$, 6.69 (diff.); $0.5\text{Ta}_2\text{O}_5$, 48.85; 4O , 14.03; $4.5\text{H}_2\text{O}$, 17.62.

UNIVERSITY OF PENNSYLVANIA,
 PHILADELPHIA, PA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

A STUDY OF THE SPECTRUM AND THE BROMIDES OF COLUMBIUM.¹

BY WILLIAM M. BARR.

Received August 21, 1908.

The results presented in this communication constitute a short chapter in the larger research upon columbium and tantalum begun years ago in this laboratory and still in progress.

Hall and Smith² proved that the hydrogen peroxide test for titanium in a hydrofluoric acid solution of columbium was not reliable, so that it seemed as if the only means remaining for the identification of titanium in the presence of columbium was the spectroscopic examination.

Balke and Smith³ obtained large quantities of potassium oxyfluocolumbate, K_2CbOF_3 , from American columbites. This was freed from all other metals usually accompanying it. From titanium it was separated by recrystallizing the salt five times from concentrated hydrofluoric acid. The oxide from this salt was submitted to a spectroscopic examination by Hildebrand⁴ who found by comparing the spectrum with that published by Exner and Haschek that nearly all the titanium lines given by these investigators were absent from the oxide of Balke and Smith. However, there were some lines common to both spectra and to the spectrum of titanium.

As the pure oxide of Balke and Smith had been prepared from columbite from Lawrence County, South Dakota, it seemed desirable to obtain columbium oxide from minerals of widely different character and locality. The thought was of course to purify such an oxide by the methods used with the Dakota material and then examine it spectroscopically, comparing the results with those previously obtained by Hildebrand. It was further hoped to determine whether the lines that appeared to be common to the spectra of titanium and columbium were really coincident lines or whether they belonged to some other element.

¹ From author's thesis for the Ph.D. degree.

² *Proc. Am. Phil. Soc.*, **44**, 209 (1905).

³ THIS JOURNAL, preceding article.

⁴ THIS JOURNAL, following article.

The following minerals were employed in this study:

1. Tantalite (mangano-tantalite) from Pilbarra Dist., Australia, sp. gr. = 7.04.
2. Euxenite from Arendal, Norway, sp. gr. = 4.92.
3. Aeschynite from Hitterö, Norway, sp. gr. = 5.08.

At first an effort was made to decompose the finely divided tantalite by fusion with acid potassium sulphate but, this proving unsatisfactory, recourse was had to the method of Wolcott Gibbs.¹ The white oxides of tantalum and columbium obtained in this way were converted into their potassium double fluorides, which were separated in the manner generally pursued in this laboratory.

The columbium oxide, from the pure potassium oxyfluocolumbate, was next subjected to a spectroscopic examination.

The euxenite and aeschynite were similarly decomposed. The columbic oxide from them was practically obtained in the same way, bearing in mind that there was here an excess of titanitic oxide and that the quantity of tantalum was slight. Absolute purity in these oxides was not expected. They had not been subjected to the rigorous purification treatment bestowed on the oxide of Balke and Smith. Photographs of the spectra of the following oxides were made:

1. Columbium oxide prepared by Balke and Smith.
2. Columbium oxide from Australian tantalite, potassium acid sulphate fusion.
3. Columbium oxide from Australian tantalite, potassium acid fluoride fusion.
4. Columbium oxide from euxenite, potassium acid fluoride fusion.
5. Columbium oxide from aeschynite, potassium acid fluoride fusion.
6. Columbium oxide (prepared by Balke and Smith), to which 0.01 per cent. of titanium oxide had been added.

All the lines found in No. 1 were present in the spectra of all the other oxides. The only impurity found in any of the specimens was titanium, except in No. 3, which showed tin lines.

In 2, 3, 4 and 5, titanium was present in small quantities and the more prominent titanium lines appeared, while in No. 1 a few lines apparently due to titanium were scarcely discernible but most titanium lines were entirely absent, though the lines common to titanium and columbium appeared as intense as in the other specimens.

In No. 6 the titanium lines were barely visible, showing that No. 1 must contain considerably less than 0.01 per cent. of titanium oxide.

These results would seem to indicate that the methods of purification used by Balke and Smith were effective, that the spectra of columbium, from whatever sources, are identical when sufficient purification is ap-

¹ *Am. J. Sci. and Arts*, 37, 357 (1864).

plied, and that the lines found in the spectrum of No. 1 which also appeared in the titanium spectrum, were not due to the presence of titanium and probably not to any other element (since they appeared in all columbium spectra), but that they were merely coincident lines.

Bromides of Columbium.—In 1858 H. Rose¹ attempted the preparation of the bromides of columbium by passing a mixture of bromine vapor and carbon dioxide over heated columbium oxide and carbon. A voluminous yellow-colored product resulted. This Rose called "niobunterbromid" from its analogy to his "niobunter chlorid." It was further observed that a dark red mass was formed simultaneously and that it could be sublimed in vapor of bromine at a gentle heat, but that if the latter became too intense the substance became yellow in color. No analysis of these compounds was given by Rose.

No further study having, apparently, been made upon these products it was concluded to prepare them with the view of determining their real composition. To this end 15 grams of pure columbic oxide, intimately mixed with carbon (1 part Cb_2O_3 and 2 parts carbon), were placed in a combustion tube of Jena glass and after the air had been swept out by the prolonged passage of pure nitrogen, heat was applied and when all moisture had been expelled bromine was turned into the tube and carried over the hot mixture of oxide and carbon. Several grams of the voluminous, light yellow "niobunterbromid" were obtained. It was resublimed in an atmosphere of bromine and nitrogen (or carbon dioxide), then transferred to weighed tubes as quickly as possible and analyzed.

The tubes were opened under water containing a little ammonia. Decomposition of the yellow product proceeded rapidly with the formation of columbium hydroxide. As its precipitation by the ammonia was incomplete, the liquid was acidulated with nitric acid. The columbium hydroxide was collected, washed, dried and ignited over a blast lamp to constant weight.

The bromine in the filtrate from the columbium hydroxide was weighed as silver bromide on a Gooch crucible.

The results of the analyses made indicate the voluminous, yellow substance—the "niobunterbromid" of Rose—to be columbium oxybromide, $CbOBr_3$.

	Wt. sample. Grams.	Cb_2O_3 . Grams.	AgBr. Grams.	Cb found. Per cent.	Br found. Per cent.
1.....	0.4513	0.1751	0.7281	27.22	68.66
2.....	0.4636	0.1787	0.7477	27.04	68.63
3.....	0.5234	0.2020	0.8426	27.09	68.65
4.....	0.4685	0.1796	0.7558	26.89	68.65
5.....	0.8459	0.3249	1.3684	26.94	68.84

¹ *Pogg. Ann.*, 104, 441.

The theoretical requirements of columbium oxybromide, CbOBr_3 , are 26.87% of columbium and 68.56% of bromine.

Columbium oxybromide is bright yellow, very voluminous, fumes in the air, and on standing in moist air is soon converted into white columbic oxide. It sublimes at the heat of the Bunsen flame without melting, and may be sublimed in an atmosphere of nitrogen or carbon dioxide containing bromine, but even in this atmosphere there is a partial breaking down into columbic oxide and a small amount of the dark red compound, which proved to be columbium pentabromide. Columbium oxybromide dissolves in anhydrous ethyl bromide or alcohol with a considerable evolution of heat.

The dark red compound, it will soon be shown, is undoubtedly a pentabromide. This was evidently the opinion of Rose, though he gave no analytical proof of the same. Since its formation never occurs in great quantities by the method pursued when the oxybromide resulted, search was made to get it in other ways. Knowing that the most satisfactory course to follow in preparing columbium pentachloride was to heat the oxide in the vapor of sulphur monochloride an analogous course was adopted here, but all experiments tried with sulphur monobromide and oxide were fruitless. It was then decided to brominate the metal. The latter was prepared by the Goldschmidt method. In only two out of a number of trials were globules of metal obtained. The product was usually an amorphous powder. However, the globules were cleaned by treatment with acid, then dried, crushed to a coarse powder and exposed in a combustion tube to the action of bromine vapor. In the cold there was no visible sign of action, but on applying a gentle heat dark red vapors appeared over the boat and about twelve inches beyond the latter condensed to a dark red powder, while near the boat were dark, garnet red crystals. The latter and powder were collected in weighed bottles filled with nitrogen. The analysis showed powder and crystals to be identical—both were columbium pentabromide, CbBr_5 .

ANALYSES.

Wt. taken.	Cb_2O_5 found.	AgBr found.	Per cent. Cb.	Per cent. Br.
0.5611	0.1544	1.0602	19.30	80.41
0.4297	0.1169	0.8103	19.08	80.25

The theoretical requirements for the pentabromide are 19.04% of columbium and 80.96% of bromine.

Columbium pentabromide is either a fine crystalline powder resembling red phosphorus in color, or when crystallized from the melted condition it forms dark garnet-red prisms which melt on heating the tube with a low Bunsen flame (about 150°) and distil at a higher temperature (about 270°) without decomposition. It is stable in carbon dioxide or nitrogen, and can be distilled in either. It fumes strongly in air, passing to the

yellow oxybromide, then to the oxide. It is decomposed by water with hissing and the evolution of heat. It is very hygroscopic and if allowed to stand in moist air absorbs considerable water before decomposition is complete. It dissolves readily in anhydrous ethyl bromide or alcohol with the liberation of heat.

An impure columbium iodide was prepared from the bromide. Further work is being done upon it. It is quite stable but is freed from bromide with difficulty.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ARC SPECTRUM OF COLUMBIUM.

BY JOEL H. HILDEBRAND.

Received August 15, 1908.

Part I.—Measurement of the Spectrum.

The arc spectrum of columbium has been measured between λ 2376 and λ 4700 by Exner and Haschek¹ who used for the purpose the ammonium columbium oxyfluoride upon gas-carbon electrodes. The spectrum they obtained was contaminated strongly by titanium, and also, the authors declare, by an unknown element common to columbium and titanium which they designated Ω . This state of affairs invited a further investigation of the spectrum of this element, and the abundance of very pure columbic oxide which has been obtained in this laboratory offered an exceptional opportunity. Moreover, it was desired to test spectroscopically the efficacy of the method of Smith and Balke² for obtaining columbium free from titanium, a most difficult analytical problem which it was thought had been finally solved.

The spectroscope used in this study is the property of the University of Pennsylvania, and was kindly put at my disposal by Prof. A. W. Goodspeed, to whom I here express my sincere thanks. The grating was ruled by a Rowland engine and is two inches long, seven-eighth inches high and contains 14,438 lines to the inch. The focal length is six feet. The mounting was made by Brashear, of Allegheny City, Pennsylvania, and is the usual type for a concave grating. The usual adjustments were made.

Inasmuch as the purity of the material was to be investigated, carbon electrodes, with their many impurities, were replaced by copper rods one-quarter inch in diameter. These were placed in an enclosed hand-feed lantern. The lower rod which was made the positive electrode was reamed out, making a cavity to receive the oxide. After a little practice it was found quite easy to start the arc, using a third rod held in the hand.

¹ Wellenlängentabellen-Bogenspektra-Franztz Deuticke, Leipzig, 1904.

² THIS JOURNAL, 30 (1908).