

of Standards prove that this method of reduction is quick, accurate and most convenient.

3. Some of the advantages of the method over those most commonly employed have been outlined.

4. Mention is made of a number of other substances whose solutions are reduced by mercury.

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THE SEPARATION OF COLUMBIUM AND TANTALUM BY MEANS OF SELENIUM OXYCHLORIDE.¹

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It was found by Lenher² that columbium oxide is soluble in a mixture of sulfuric acid and selenium oxychloride, while tantalum oxide is insoluble, or very much less soluble, in the same reagent. This appeared to afford a means of separating the two elements. The purpose of the present investigation was to work out the best experimental conditions for accomplishing the separation.

Previous Methods.—The separation of columbium and tantalum has hitherto been one of the most difficult tasks with which the chemist is confronted. In their chemical properties, the corresponding compounds of the two elements show hardly any points of divergence which are sharp enough to be used for methods of separation. Of the various methods which have been proposed, only one—the double fluoride method of Marignac³—merits any consideration. The Marignac method consists of the crystallization of the normal potassium fluotantalate, K_2TaF_7 , under such conditions of acidity and concentration of potassium fluoride that the columbium will form the more soluble oxyfluoride, K_2CbOF_5 . The chief advantage of the Marignac method is that the two double fluorides are not isomorphous, and hence no mixed crystals should be obtained. The difference in crystal form affords a convenient means of following the course of the separation. The disadvantages of the method are many and serious. The ratio of the solubility of the columbium compound to that of the tantalum is only about 10 to 1, potassium columbium oxyfluoride being soluble in 12 parts of hot water, and potassium fluotantalate requiring about 120 parts. This necessitates many recrystallizations before an approximately complete separation is accomplished, and in no case can all of either constituent be obtained in a state of purity, since some of each will inevitably remain in the various mother liquors. From the analytical standpoint, this means that the Marignac method cannot be made other than a very rough one. Its limit of error is probably at least 10%. In addition to this inherent error, the method is liable to grave inaccuracies, due to the difficulty in maintaining the concentration of hydro-

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² Lenher, *This Journal*, **43**, 29 (1921).

³ Marignac, *Ann. chim. phys.*, [4] **3**, 5, 49, 68 (1866). Simpson, *Chem. News*, **99**, 243 (1909).

fluoric acid and of potassium fluoride constant within very narrow specified limits. If the acidity is too great, the columbium forms a normal fluoride; if too low, the tantalum may form an oxyfluoride; in either case, the whole basis of the separation is destroyed. If too much or too little potassium fluoride is present, double fluorides are formed in which the ratio of potassium fluoride to columbium or tantalum pentafluoride is more or less than 2 : 1. Finally, the Marignac method is extremely laborious and time-consuming, and requires the use of platinum vessels throughout.

The Problem.—In the ordinary course of analysis, columbium, tantalum and titanium are separated from the other elements as oxides. Titanium accompanies columbium in the Marignac separation, and no separation of columbium and titanium is known. Titanium dioxide and columbium pentoxide (Cb_2O_5) are both soluble in selenium oxychloride and sulfuric acid. The problem, therefore, is to extract these two oxides completely from a mixture with tantalum pentoxide (Ta_2O_5), under such conditions that the minimum amount of the last is dissolved. To ascertain these conditions, the effect of various factors upon the solubility of each oxide was first determined separately. From the data thus obtained, a tentative method of separation was formulated, and tested upon synthetic mixtures of the oxides.

Reagents.—The columbium and tantalum oxides employed were obtained from various commercial sources, and from stocks previously prepared in this laboratory. These oxides were further purified by the Marignac method.

Selenium oxychloride was prepared by the interaction of selenium dioxide and tetrachloride and was purified by vacuum distillation.⁴ The purity of the other reagents employed was ascertained by the usual tests.

Manipulation.

To determine the effect of various factors upon the solubility of each oxide, the oxide in question was boiled with the solution of selenium oxychloride and sulfuric acid in an Erlenmeyer flask, using a sand-bath. The mouth of the flask was covered with a small watch glass, the upper part of the flask acting as an air condenser, so that with proper regulation of the heat very little of the solvent was lost, and little or no hydrolysis of the oxychloride took place. The solution was filtered with suction, through an asbestos mat, in a Gooch crucible. In some cases, an excess of the oxide was employed, and the amount dissolved was determined in a known amount of the filtrate. In most instances a weighed sample of the oxide was employed, and the undissolved portion was transferred to the crucible, ignited, and weighed.

By this procedure, the effect of the following factors upon the solubility was determined: (1) composition of the reagent; (2) condition of the oxide, *i. e.*, hydration; (3) size of sample; (4) time of digestion; (5) amount of solvent employed. The temperature was in all cases the boiling point of the solvent.

⁴ Lenher, *THIS JOURNAL*, 42, 2498 (1920).

The rate of solution of both oxides is slow, so that results obtained do not represent the true solubility, but rather the amount dissolved under definite experimental conditions in a short time (minutes or hours).

Composition of the Reagent.—Neither columbium oxide nor tantalum oxide is acted upon by selenium oxychloride alone. Columbium oxide is readily soluble in conc. sulfuric acid, even when the oxide is ignited. Tantalum oxide is soluble in sulfuric acid to a much less extent. The effect of adding selenium oxychloride to sulfuric acid is to decrease the solubility of both oxides. Experiments have shown that a mixture of equal parts by volume of the reagent constituents is best suited for the separation of columbium and tantalum pentoxides. When an excess of the oxide is boiled for 30 minutes with 50 cc. of this reagent, the approximate amounts of pentoxides dissolved are 0.35 g. and 0.005 g., respectively. In conc. sulfuric acid, the amounts dissolved are 0.9 g. and 0.08 g. The effect of increasing the ratio of the oxychloride to the acid beyond 1 : 1 is to decrease the solubility of columbium pentoxide much more than that of tantalum pentoxide.

Free sulfur trioxide as contrasted with sulfuric acid, has practically no solvent action upon either oxide. Solutions of fuming sulfuric acid in selenium oxychloride, such as were employed in Lenher's experiments, have about the same action as solutions of conc. sulfuric acid.

It is probable that the sulfuric acid attacks the oxide in the first instance, forming a loose addition compound which is soluble in selenium oxychloride. This is evidenced by the fact that, once the oxide has been dissolved, the solution may be diluted with selenium oxychloride to any extent without the formation of a precipitate.

Hydration of the Oxides.—The freshly precipitated hydrated oxides are much more readily soluble than are the ignited oxides. While the solubility decreases with increasing temperature of ignition, the solubility of hydrated tantalum peroxide is too great to permit the separation to be applied to the hydrated oxides, and good results can be obtained only when the oxides have been ignited at bright red heat.

Effects of Size of Sample, Amount of Solvent and Time of Digestion.—The effects of these factors are not the same upon the solubilities of both oxides. Tantalum pentoxide is so slowly soluble that equilibrium is not even approached in actual practice. Hence the amount dissolved is independent of the amount of solvent employed, and is directly proportional to the amount of solid oxide present, *i. e.*, to the surface exposed, and to the time of contact between solvent and solid. With columbium pentoxide, the process of solution is fairly rapid, so long as the amount of surface exposed is large. If the oxide is present in large excess, the amount dissolved is approximately proportional to the amount of solvent, and is independent of the amount of oxide taken and of the time, showing that equilibrium is at least approached. When, however, the amount of solid

columbium pentoxide is small, the rate of solution is very slow. If a large sample is treated with an excess of the reagent, the larger portion of the oxide is quickly dissolved, but the rate of solution becomes slower and slower as the area of contact between the phases diminishes. The solution of the last traces of columbium pentoxide takes place very slowly indeed. This means that *complete* solution of a given sample requires a considerable period of digestion, and furthermore that this period will be about the same whether the actual quantity of oxide originally taken is large or small.

Experiments have shown that an hour's boiling with the 1:1 reagent is required for the complete solution of a given sample of columbium pentoxide. So long as the solvent is present in excess, increasing the amount of solvent has little influence upon the time. Fifty cc. of solvent per 0.25 g. of columbium pentoxide has been found sufficient. The amount of tantalum pentoxide dissolved in this amount of reagent in an hour depends entirely upon the amount of this oxide which is present. It is obvious that from the analytical standpoint, the direction and magnitude of the errors are dependent upon the relative proportions of the two oxides which are present in a mixture. In all cases, there is some danger that traces of columbium pentoxide will not be dissolved. If the percentage of tantalum is low, very little tantalum pentoxide will be dissolved, and hence the results found will tend to be high for tantalum and low for columbium. If the percentage of tantalum is high, considerable amounts of tantalum pentoxide may be dissolved, in which case the results found will be low for tantalum and high for columbium. When the two oxides are present in approximately equal amounts, the two errors will be roughly compensatory.

The size of the sample employed must be kept as small as is consistent with percentage accuracy of weighing, in order to keep the amount of tantalum oxide present as small as possible. Samples of from 0.2 to 0.3 g. have been found to give the best results.

Procedure for the Analysis of Mixed Oxides of Columbium and Tantalum.

In accordance with the results of the experiments described above, the following method for the analytical separation of the two oxides is suggested.

1. The oxides are separated, together with titanium dioxide if the latter is present, from the other elements by the usual methods and the total percentage of tantalum and columbium pentoxides (plus titanium dioxide) is determined.

2. A weighed sample (0.2 to 0.3 g.) of the ignited oxides is boiled with 50 cc. of a 1:1 mixture of selenium oxychloride and conc. sulfuric acid in an Erlenmeyer flask on a sand-bath for half an hour, care being taken

that the boiling is not so vigorous that clouds of vapor are given off. The contents of the flask, after cooling, are decanted with suction through a weighed Gooch crucible. The filtrate is poured into a large volume of water, and the resulting solution is brought to a boil. A voluminous white precipitate of hydrated columbium pentoxide indicates the presence of columbium in the mixture. The residue in the flask is boiled with 20 cc. of the reagent for 15 minutes, the solution decanted through the crucible, and the filtrate poured into water. This process is repeated until the filtrate, upon hydrolysis, gives only a faint precipitate, due to traces of dissolved tantalum pentoxide. Care should be taken that as little as possible of the solid oxide is carried onto the filter in the first decantations, since this portion escapes treatment in the subsequent extractions. By this procedure, the course of the solution of the columbium oxide can be followed. Three or four treatments of the oxide with the reagent are usually enough to remove all the columbium pentoxide.

3. The undissolved tantalum pentoxide is transferred to the crucible with the jet from a wash-bottle. Complete washing of the oxide is not necessary, since all the decomposition products of the reagent are volatile. The crucible is ignited and weighed, the gain in weight representing the pentoxide. Columbium (plus titanium) is determined by difference. The titanium is best determined colorimetrically in a separate sample, and deducted from the columbium.

The method outlined above was applied to synthetic mixtures of tantalum and columbium pentoxides. In a number of experiments, the mixed oxides were fused with potassium hydrogen sulfate, and precipitated by hydrolysis, in order to simulate actual working conditions. The results obtained with these intimate mixtures were no different from those obtained with mechanical mixtures.

TABLE I.

SEPARATION OF MIXTURES OF TANTALUM AND COLUMBIUM PENTOXIDES.								
	Expt.	1.	2.	3.	4.	5.	6.	7.
Ta ₂ O ₅	taken.....	0.2151	0.1449	0.2040	0.1414	0.0411	0.0552	0.0178
	found.....	0.2130	0.1437	0.2019	0.1431	0.0477	0.0704	0.0304
Cb ₂ O ₅	taken.....	0.0162	0.0525	0.1052	0.1043	0.1998	0.4875	0.4267
	found.....	0.0183	0.0537	0.1073	0.1026	0.1932	0.4723	0.4141

The maximum divergence of the results found from the amount taken is about 3% of the total amount taken, and is in the most cases much less. The errors are far smaller than those to which the Marignac method is liable. In simplicity and speed, the superiority of the separation proposed over the Marignac method is very marked. An analysis of the mixed oxides may be begun and completed in a few hours, using the

selenium oxychloride-sulfuric acid method, while days or even weeks are required by the Marignac method.

It is believed, therefore, that the method proposed for the separation of columbium and tantalum is superior to any other yet proposed.

Procedure for the Preparation of Pure Oxides.

To prepare pure columbium pentoxide, the mixed oxides should be extracted with sufficient solvent to dissolve all of the columbium. The boiling should not be prolonged until all of the columbium is dissolved, since the object is to dissolve as little tantalum pentoxide as possible. The dissolved oxide is precipitated with water and ammonia, filtered, and ignited. Some tantalum pentoxide will inevitably be dissolved during the extraction, but by repeating the treatment upon the oxide obtained by the first extraction, very pure columbium pentoxide may be obtained, since the amount of tantalum pentoxide present during the second purification is so small that virtually no tantalum will be dissolved.

To prepare pure tantalum pentoxide, it is only necessary to extract the oxide with the reagent until all of the columbium is dissolved, sacrificing the portion of the tantalum which goes into solution. The complete removal of the columbium may be expedited by increasing the proportion of sulfuric acid in the reagent.

Summary.

A method for the separation of columbium and tantalum, both for purposes of analysis and of purification, by means of selenium oxychloride and sulfuric acid, has been described.

This work was performed by the author while acting as research assistant to Professor Victor Lenher.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]
**THE SEPARATION OF MOLYBDENUM AND TUNGSTEN BY
MEANS OF SELENIUM OXYCHLORIDE.¹**

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It was found by Lenher² that molybdenum trioxide is soluble in selenium oxychloride, while tungstic oxide is insoluble in this reagent. Since none of the methods hitherto known for the separation of molybdenum and tungsten is entirely satisfactory, it was felt that this observation of Lenher's which appeared to afford a new method of separation, should be studied further. The purpose of the present investigation was to determine

¹ Abstract of a portion of a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the University of Wisconsin, 1921. This work was financed in part by a grant from the University research fund.

² Lenher, *THIS JOURNAL*, 43, 29 (1921).