[CONTRIBUTION FROM THE RARE AND PRECIOUS METALS EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

CRITICAL STUDIES ON THE FUSION OF RARE METAL ORES. III. DETERMINATION OF TANTALUM AND COLUMBIUM[1]

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In a previous investigation[3] it was shown that tantalum and columbium can be completely separated from each other by the action of concentrated sulfuric acid on the compounds obtained by fusion with sodium pyrosulfate at 835 to 875 °C. Fusion under these conditions renders the tantalum insoluble in concentrated sulfuric acid while the columbium remains soluble. This action was explained on the basis that the sodium salts of tantalic and columbic acids are formed during the fusion and that the sodium tantalate is decomposed at 835° while the corresponding columbium compound remains unaffected at temperatures as high as 875°. The present investigation was undertaken in order to find the conditions, if possible, whereby these reactions can be applied to a quantitative determination of the two elements.

Among the available methods for the determination of tantalum and columbium, those involving the difference in solubility of the potassium double fluorides appear to be the most satisfactory. All of these[4] necessitate the fractional precipitation of tantalum as K_2TaF_7. The double fluoride is weighed as such or is converted to the oxide and weighed as Ta_2O_5. The columbium remaining in the solution is usually converted to the oxide and weighed as Cb_2O_5, although it may be determined volumetrically by reduction and subsequent oxidation with standard potassium permanganate. Titanium, which usually occurs with tantalum and columbium, is not removed by the double fluoride method and is weighed with the columbium. Its estimation colorimetrically with hydrogen peroxide has been found by Chesneau[4] to involve an error of at least 0.5%. Treadwell,[5] and also Schoeller and Waterhouse,[6] investigated the methods of reducing columbium and found that in no case could it be reduced to the tervalent state and that the degree of reduction varied so much with conditions that

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[3] Geo. W. Sears, THIS JOURNAL, **48**, 343 (1926).

[4] H. E. Roscoe and C. Schorlemmer, "Treatise on Chemistry," MacMillan Co., London, **1913**, Vol. II, p. 955; W. B. Giles, *Chem. News*, **99**, 1, 25 (1909); E. S. Simpson, *ibid.*, **99**, 243 (1909); G. Chesneau, *Compt. rend.*, **149**, 1132 (1909); E. Meimberg, *Z. angew. Chem.*, **26**, 83 (1913).

[5] W. D. Treadwell, *Helv. Chim. Acta*, **5**, 806 (1922); *C. A.*, **17**, 505 (1923).

[6] W. R. Schoeller and E. F. Waterhouse, *Analyst*, **49**, 215–220 (1924).

a definite factor was not possible. The method was therefore declared unsatisfactory. Schoeller and Powell[7] attempted a separation and determination by fusing with potassium carbonate. The greater solubility of the columbium compound afforded a fairly complete separation after two or three fusions. Interfering elements, however, make the method unreliable for the determination of tantalum.

It may be concluded, therefore, that the present methods for the determination of tantalum and columbium involve fractionation processes which are at best only approximate. Interfering elements are very difficult to remove and hence often contaminate the precipitated tantalum and columbium. Iron and titanium, almost universally found associated with tantalum and columbium, are among the most troublesome and most difficult elements to remove.

Experimental Part

Since titanium sulfate, formed by fusion with sodium pyrosulfate below 700°C., is soluble in hot 3 N hydrochloric acid[8] and both tantalic and columbic acids are known to be relatively insoluble in water and dilute mineral acids, fusion of the ore or mixed oxides with sodium pyrosulfate should offer a possible means of separating any titanium that might be present. Iron and other more basic elements should also be soluble under these conditions.

Solubility of Tantalic and Columbic Acids in Dilute Hydrochloric Acid.—Tantalic and columbic acids were obtained by fusing the mixed oxides with sodium pyrosulfate and leaching the cold melt with water. This procedure dissolved a large proportion of the excess sodium sulfate and left all the tantalum and columbium as a fine granular or flocculent residue, the density of which depended somewhat on the temperature at which the fusion was made. The residue was allowed to settle and the liquid decanted through a filter. Three normal hydrochloric acid was then added to the residue remaining in the beaker and the mixture was digested near the boiling temperature for some time. It was then filtered and the filtrate evaporated to a few cubic centimeters and tested for columbium according to the method outlined in the previous paper.[3] Several experiments were carried out in this way on mixtures that had been fused at different temperatures. In no case was even a trace of columbium detected. Although the tests for tantalum are somewhat less satisfactory than for columbium, tests were made by adding hydrofluoric acid and potassium chloride to the concentrated filtrate, allowing excess water to evaporate, and examining the residue under the microscope for the needle-like crystals of K_2TaF_7. No evidence of tantalum was obtained in any case. It was therefore assumed that no loss of either tantalum or columbium would result from washing with hot 3 N hydrochloric acid.

Removal of Contaminating Substances.—From the difficulties encountered a number of years ago in washing large quantities of tantalic and columbic acids free from potassium sulfate it seemed probable that similar difficulties might arise in the removal of the sodium sulfate obtained during the fusion. Accordingly a number of samples of the mixed oxides were

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[7] W. R. Schoeller and A. R. Powell, *J. Chem. Soc.*, **119**, 1927 (1921).

[8] George W. Sears and Laurence Quill, THIS JOURNAL, **47**, 922 (1925).

fused with sodium pyrosulfate, the cold melt was leached with water and the residue washed with hot 3 *N* hydrochloric acid. By repeated digestion in the hot wash liquid it was found that no further test for sulfate could be obtained after six or seven washings if the sample taken for analysis was less than half a gram. Larger samples were much more difficult to wash free from sulfate. In order to determine whether sodium sulfate might be occluded in such a way as to prevent its being washed out, two samples of pure potassium fluotantalate were fumed with sulfuric acid to remove the fluorine and then analyzed for tantalum oxide as described above. The results are given in Table I.

TABLE I

DETERMINATION OF Ta_2O_5 IN K_2TaF_7

K_2TaF_7 taken, g.	Ta_2O_5 found, g.	Ta_2O_5 present, g.	Error, g.
0.6227	0.3520	0.3512	+0.0008
.5180	.3914	.3917	− .0003

The removal of iron presented a somewhat greater difficulty. The iron compound obtained during the fusion appeared to be almost completely insoluble in water, regardless of whether the fusion was made at a low or high temperature. Repeated digestion with hot 3 *N* hydrochloric acid proved efficient for removing the iron when the fusion was carried out at a low temperature. High-temperature fusions, however, appeared to decompose the iron compound or otherwise render it very difficultly soluble in the dilute acid. By fusing at a low temperature (about 650°) and leaching the cold melt with water to remove it from the crucible, much of the excess sodium sulfate was dissolved and the tantalum and columbium were left as a fine, white, granular residue that settled readily. All iron and sodium sulfate could be removed from the residue by repeated digestion with hot 3 *N* hydrochloric acid and final washing with water. When the insoluble residue of tantalic and columbic acids which had been washed until the washings gave no further test for iron or sulfate was filtered, dried and ignited, a pure white powder was obtained.

The results so far obtained, together with the fact that the fusion of titanium ores below 700° renders the titanium completely soluble[8] in hot 3 *N* hydrochloric acid, made it seem quite probable that titanium could be quantitatively removed along with the iron. In order to test this point a sample of pure tantalum oxide, to which was added a small amount of titanium oxide, was fused with the pyrosulfate at about 650° and analyzed as described above. The final washing with hot 3 *N* hydrochloric acid was continued until no further test for titanium was obtained in the washing liquid when tested with hydrogen peroxide. A portion of the residue was then fused and tested for titanium and gave a negative result. It was evident, therefore, that the chief interfering substances could be removed by fusing at about 650°, washing first with hot 3 *N* hydrochloric acid and then with water.

Separation of Tantalum and Columbium

In order to effect a separation between the tantalum and columbium by means of the pyrosulfate fusion the temperature of the fusion mixture must reach 835 to 875°. In the earlier investigation[3] fusions were made in platinum over a Bunsen flame and the temperatures were obtained by means of a thermocouple placed in the fused mass. Since this procedure was not feasible for a quantitative determination, it was decided to use an electric resistance cup furnace as the source of heat. The thermocouple was suspended just above the crucible containing the melt. A number of experiments were carried out in order to determine the furnace temperature and the rate of heating necessary to decompose completely the tantalate without affecting the columbate. It was soon found that time is a factor in the decomposition of the tantalate. This fact did not appear in the earlier investigation, probably because the temperature had to be raised much more slowly in order to prevent boiling when the flame was used as the source of heat. A satisfactory separation was found possible if the temperature was held at 835 to 850° for ten to fifteen minutes.

Determination of Total Tantalum and Columbium

For the purpose of a quantitative determination of the two elements by this method, a filter medium unaffected by the hot concentrated sulfuric acid would be necessary. A Gooch crucible provided with an asbestos pad seemed to be the most logical substance available; hence a quantity of the washed asbestos fiber commonly used in quantitative analysis was heated with concentrated sulfuric acid for two to three hours and then carefully washed with water to remove the sulfuric acid and any other soluble material that might have been present. A suspension of this was made in the usual way and used in a series of determinations made with pure potassium fluotantalate. The procedure consisted in converting a weighed quantity of the fluotantalate to the oxide by fuming with sulfuric acid in a platinum crucible, evaporating the excess sulfuric acid and fusing the residue with twelve parts of sodium pyrosulfate at about 850°. The cold melt was then leached with water to remove it from the crucible and dissolve as much of the sodium sulfate as possible. It was then filtered through a Gooch crucible provided with an asbestos pad, the dry weight of which had previously been determined.

The residue of tantalic acid was washed with hot 3 *N* hydrochloric acid and finally with water until no further test for sulfate could be obtained in the washings. The residue of tantalic acid together with the asbestos pad was transferred to the original beaker with as little water as possible and 10 to 15 cc. of concentrated sulfuric acid was added. The resulting mixture was carefully evaporated until dense white fumes of sulfur trioxide appeared, and was then held at that temperature for about ten minutes. When cold the mixture was filtered through a weighed Gooch crucible, washed, dried, ignited and weighed.

The results were irregular, showing some unexpected interfering factor. It seemed, therefore, that the asbestos was being attacked by the sulfuric acid. In order to determine to what extent this was being done, a weighed quantity of the asbestos was subjected to the action of hot concentrated sulfuric acid in a manner similar to that required by the analysis. Several determinations of this kind showed a small but distinct loss of weight during the treatment. A number of alundum filtering crucibles were tested in a similar manner, but they were found to be much less resistant than the asbestos. The solvent action of hot concentrated sulfuric acid on platinum indicated that a Monroe crucible would be little better for this purpose than the ordinary Gooch. From these results it seemed doubtful whether a material entirely resistant to the action of the hot acid could be found.

Two possible methods of procedure presented themselves. A correction might be made for the asbestos dissolved during the treatment with sulfuric acid or the weight of tantalum oxide could be obtained by difference. Investigation of these two methods was carried out in the following manner, using a mixture of the oxides of tantalum and columbium containing a small amount of iron oxide. From 0.2 to 0.3 g. of the mixed oxides was weighed in a platinum crucible, 4.5 to 5.0 g. of sodium pyrosulfate added and the mixture fused over a Bunsen flame at as low a temperature as possible to obtain a clear fusion. By keeping the crucible covered and the flame just high enough to keep the mass liquid but not boiling, a satisfactory fusion could be obtained in about forty-five minutes to an hour. The crucible containing the cold melt was placed in a beaker containing enough water to cover it and was allowed to stand for one to two hours, when the undissolved residue was disintegrated and easily removed from the crucible. After thorough mixing the residue was allowed to settle and the liquid was decanted through a filter. A small quantity of 3 *N* hydrochloric acid was then added and the mixture digested near the boiling temperature for 10 to 15 minutes. This served to dissolve most of the iron, which was decanted through the same filter. By repeating this process three to four times no further test for iron could be obtained in the washings. Several washings with hot water were required to remove all the sulfate. The residue was then transferred quantitatively to the filter, dried, ignited and weighed. In all cases the ignited residue was pure white, indicating the absence of iron. A small portion held in the flame by means of a platinum wire gave no yellow color, showing the absence of sodium. A small amount of silica, however, was found to be present. This was removed by treatment with hydrofluoric and sulfuric acids. The final residue was assumed to be the pure oxides of tantalum and columbium. Consecutive analyses gave results calculated in per cent. as follows: 98.00, 98.20, 98.11, 97.97, 98.04; average, 98.06.

Separation and Determination of Columbium

For the separation and determination of columbium the pure oxides obtained by the above method were fused as before over a Bunsen flame. When the fusion was complete and a clear liquid resulted, the crucible and contents were placed in the furnace, the temperature was brought to 850° and maintained at approximately that temperature for ten to fifteen minutes. At the end of this time they were removed from the furnace and allowed to cool. Fumes of sulfur trioxide ceased to be evolved sometime before the temperature of the furnace reached 850°, and the mass solidified. When taken from the furnace it was quite porous and had a flaky appearance. This was most easily removed from the crucible by digesting for one to two hours with water kept near the boiling temperature. A small portion, however, clung very tenaciously to the crucible. It was found impossible to remove this except by fusing again with the pyrosulfate at a low temperature. Since this would necessarily introduce an error into the determination, some container other than a platinum crucible would be necessary for the high-temperature fusion. A silica crucible not being available at the time, a Coors glazed porcelain crucible was tried. The results were very satisfactory. Not only was the fused mass very easily and completely removed from the crucibles but the loss in weight caused by the fusion was very much less than that sustained by the platinum. In five fusions two porcelain crucibles lost a total of 3.0 and 2.3 mg., respectively, while a platinum crucible similarly treated lost 7.7 mg. Porcelain was therefore used for all high-temperature fusions thereafter. The cold melt was leached with water and washed with two or three portions of hot 3 *N* hydrochloric acid to remove any iron that might have been introduced with the pyrosulfate, decanting each time through a Gooch crucible provided with an asbestos pad.

The residue of tantalic and columbic acids, together with the asbestos pad, was then transferred to the original beaker with the aid of as little water as possible, and 15 cc. of concentrated sulfuric acid was added. The mixture was evaporated until the white fumes of sulfur trioxide appeared. The beaker was then covered with a watch glass and the heating continued for twelve to fifteen minutes; this served to dissolve all of the columbium without affecting the tantalum. On cooling, it was filtered through a weighed Gooch crucible, washed with two or three portions of cold 6 *N* sulfuric acid,[3] and then with water until the washings gave no further precipitate with ammonia.

A good deal of difficulty was encountered in this filtration owing to the fact that the finely divided tantalum residue tended to pass through the filter. After the sulfuric acid treatment the tantalum is left as a dense, granular mass, some of which is very finely divided. A small amount may pass into the filtrate and entirely escape notice since it appears to give little or no cloudiness to the concentrated acid solution. Until its presence was suspected and the solution carefully examined for it, a good many unaccountably high columbium values were obtained.

On diluting the filtrate containing the columbium it was noticed that in most cases a distinct cloudiness developed, indicating hydrolysis, although in some cases the solution remained perfectly clear. It seemed probable, therefore, that the concentrated acid solution might be diluted without fear of hydrolysis if the correct conditions could be found. After some investigation it was found that no hydrolysis occurred and that a complete separation could be obtained if the cold acid solution were slowly poured, with constant stirring, into about 100 cc. of water kept cold with ice or running water.[9] This simplified very much the process of filtering and washing the residue free from columbium.

[9] After this work was completed and the paper had been sent to Washington, an article by S. J. Kiehl and David Hart, appeared (THIS JOURNAL, **50**, 1608 (1928)) describing a similar method for diluting a sulfuric acid solution of columbic oxide without causing precipitation.

The most favorable conditions found for the precipitation and separation of columbium were to neutralize the solution, which had been diluted to about 300 cc., with ammonia and then heat to boiling. This caused the precipitate to settle well and make it more easily washed. A number of attempts were made to precipitate the columbium by means of hydrolysis in acid solution but conditions could not be obtained under which complete precipitation could be assured. The precipitate of columbium usually contained a small amount of silica, which was removed by treatment with hydrofluoric and sulfuric acids. Consecutive analyses gave results calculated in per cent. as follows: 21.90, 21.86, 22.42; average, 22.06.

Attempts to obtain the weight of the tantalum oxide by igniting and weighing the residue did not meet with success. The correction for the asbestos which had to be placed in the hot concentrated sulfuric acid apparently was not constant in value and could not be obtained for each determination.

Method of Analysis

The procedure finally adopted as giving the most satisfactory results consisted in fusing the weighed sample at about 650° with 12 to 13 parts of sodium pyrosulfate and leaching the cold melt with water to remove it from the crucible and dissolve most of the excess sodium sulfate. The clear supernatant liquid is then decanted through a filter, the residue digested with hot 3 *N* hydrochloric acid to remove iron and titanium, transferred to the filter, washed free from sulfate with hot water, dried and ignited. This product contains all of the tantalum and columbium along with a small amount of silica, which is removed by treatment with hydrofluoric and sulfuric acids. After weighing the pure mixed oxides, a definite portion is transferred to a porcelain crucible and fused in the furnace with 5 g. of sodium pyrosulfate. The temperature is slowly raised to 850° and held at 835 to 850° for ten to fifteen minutes. It is then removed from the furnace, leached with water, filtered through a Gooch crucible, provided with an asbestos pad and washed two or three times with hot 3 *N* hydrochloric acid. The residue, together with the asbestos pad, is then transferred to the original beaker, with the aid of as little water as possible, and 15 cc. of concentrated sulfuric acid is added. The mixture is then evaporated to the appearance of white fumes and kept at that temperature for ten to fifteen minutes with occasional stirring. When cold the concentrated acid solution is slowly poured with constant stirring into 100 cc. of water kept cold with ice or running water. The mixture is then filtered, washed with cold water, and the columbic acid precipitated from the filtrate with ammonia. The precipitate is filtered, dried, ignited, and the silica removed by treatment with hydrofluoric and sulfuric acids. The final residue is weighed as Cb_2O_5.

Summary and Conclusion

The pyrosulfate fusion as a means for the quantitative determination of tantalum and columbium has been studied with results and conclusions as follows.

1. When fused at a low temperature (about 650°) iron and titanium are completely separated from the tantalum by digestion near the boiling temperature with 3 *N* hydrochloric acid. The tantalic and columbic acids are left in the insoluble portion.
2. When the fusion mixture is held at 835 to 850° for ten to fifteen minutes, the columbium only is dissolved by fuming with concentrated sulfuric acid. The solution may be diluted without precipitation if the cold acid mixture is slowly poured into water kept cold with ice or running water.
3. A method of procedure for the determination of tantalum and columbium is given.
4. The possibility of more economic extraction and separation of tantalum and columbium is indicated in the method used for the removal of iron and titanium and in the fact that the sulfuric acid solution may be diluted without precipitation of columbium.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY SECTION, PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

THE EQUILIBRIUM BETWEEN METHANOL, CARBON MONOXIDE AND HYDROGEN. PRELIMINARY PAPER[1]

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Introduction

Although our work on the equilibrium between methanol, carbon monoxide and hydrogen is still in progress, it has been decided to present the results so far obtained. The results heretofore available are very conflicting and no direct experimental measurements of equilibrium appear to have been made. The many inquiries which have been received concerning the data indicate the general interest and practical importance attached to the thermodynamic properties of methanol.

Published values of the free energy of methanol have been obtained in several ways. Kelley[4] has calculated his value from the specific heat of

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[4] Kelley, *Ind. Eng. Chem.*, **18**, 78 (1926).