THE ESTIMATION OF NIOBIUM IN PRESENCE OF TANTALUM, AND SOME REACTIONS OF TANTALUM COMPOUNDS.

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INTRODUCTION.

THE most generally trusted method for the separation of niobium and tantalum at the present time still appears to be Marignac's old method of fractionally crystallising the double potassium fluorides. The drawbacks of this method, its inaccuracy and tediousness, are familiar to every chemist who has worked with it, and quite a number of attempts have been made to find a method to supplant it.

As far back as 1885 Osborne (*Amer. J. Sci.*, 1885 [3], **30**, 328), basing his work on some earlier experiments of Marignac, described a method for the volumetric estimation of niobium in presence of tantalum, and extended it to include the presence of titanium. His work may be summarised as follows : Dissolving potassium niobium oxyfluoride (K_2NbOF_5) in hydrochloric acid, and reducing with amalgamated zinc and a piece of platinum foil at a temperature of about 80° C., he found (apparently as the result of one experiment only) that reduction went as far as a hypothetical oxide (Nb_8O_{13}), which is fairly close to another oxide, (Nb_3O_5), mentioned by Marignac. This degree of reduction was only reached, however, if concentrated hydrochloric acid was used. If even a small quantity of water was present, reduction stopped short at a point depending on the concentration of the acid. This result seems to me not very probable. When the acid has reached a temperature of 80° C., its composition should be much the same, whether concentrated acid or concentrated acid *plus* a little water was used in the first place. The quantity of acid left would indeed be different, but Osborne states that (within limits) the quantity of acid used is immaterial. Osborne next applied his method to the analysis of a sample of mixed oxides of niobium and tantalum of known composition, obtained by precipitation with ammonia and drying at 100° C. Five estimations on this sample gave 46·64 to 47·45 (average 46·95) per cent. Nb_2O_5 as against a theoretical 47·36.

Osborne then added 0·0900 and 0·3728 grm. respectively of potassium fluoride to two portions of a little over 6·5 grms. each of mixed oxides supposed to contain 45·99 per cent. of Nb_2O_5. He found 43·83 and 43·87 per cent. respectively, and concluded that potassium salts inhibited reduction to an extent independent of their amount. This, however, appears to be in conflict with his earlier experiment, in which he worked with potassium niobium oxyfluoride.

Osborne finally showed that titanium solutions are completely reduced to Ti_2O_3 by his method, both when the titanium is alone and when it is mixed with niobium

and tantalum. When both titanium and niobium are present together, they are estimated together by his reduction method, and then titanium is determined colorimetrically by Weller's method (*Ber.*, 1882, **15**, 2592). Since, however, hydrofluoric acid prevents the colour, and hydrochloric acid deepens it, it is necessary to precipitate the oxides by ammonia, and then to redissolve (without filtering) in the smallest possible amount of sulphuric acid.

Piecing together Osborne's method as given in various parts of his paper, to estimate niobium in a mineral containing tantalum as well, the mixed oxides are obtained as usual and ignited. They are then fused with potassium bisulphate, digested with water, filtered, washed, and dissolved in hydrofluoric acid; the excess of acid is evaporated off (in one place he says "nearly dry") on the water-bath, 50 c.c. concentrated hydrochloric acid, some amalgamated zinc and a piece of platinum foil are added, and reduction carried out for about three-quarters of an hour at 80° C. in an atmosphere of carbon dioxide. After cooling, the reduced solution is poured into a beaker, diluted to about 350 c.c., and titrated with potassium permanganate.

I have described Osborne's work at some length, as it forms the basis of my own experiments; moreover, the details of his work are but little known.

Warren (*Amer. J. Sci.*, 1906 [4], **22**, No. 132; *Chem. News*, 1906, **94**, 298) carried out six experiments by Osborne's methods on mixtures containing in five cases about as much titanium oxide as niobium oxide; in four cases smaller quantities of tantalum oxide were also present. The quantity of permanganate used was always less than that calculated by a large and irregular amount, and Warren concluded that the method was hopeless. It should be said, however, that he misread Osborne's paper and based his calculations on a supposed reduction to Nb_2O_3 instead of to the Nb_8O_{13}, as stated by Osborne. Correcting for this, in five cases the minus errors become very considerably smaller, although even so the results are far from good. It seems obvious that there is grave danger of reoxidation of both niobium and titanium during the transfer of the solution from the reduction flask to the beaker in which the titration is made.

Metzger and Taylor (*School of Mines Quart.*, 1909, **33**, No. 4; *Zeitsch. Anorg. Chem.*, 1909, **62**, 383) have described a method in which succinic acid is used to prevent precipitation of the mixed oxides on diluting a sulphuric acid solution of a potassium bisulphate melt; the dilute solution is passed through a Jones reductor containing amalgamated zinc and the reduced solution titrated with permanganate. Niobium is reduced to an oxide of the formula $Nb_2O_{3\cdot 107}$, 1 c.c. of $\frac{N}{10}$ solution corresponding to 0·007052 grm. Nb_2O_5. The degree of amalgamation, and probably the acidity of the solution, are of great importance, and the details given by the authors must be closely followed. The test results given by Metzger and Taylor for pure niobium solutions are excellent, but for mixtures of niobium and tantalum of known composition they are not nearly so good, the error of the niobium oxide taken (0·05 to 0·22 grm.) ranging from +0·0007 to −0·0079 (average −0·0032) grm. in the eleven estimations given. Duplicate analyses on the same mineral sometimes differ by as much as 1·2 per cent. reckoned on the mineral.

None of the newer gravimetric methods—all modifications of Marignac's method, or Weiss and Landecker's process, which depends on an entirely different principle—

have come into general use. Foote and Langley's specific gravity method will be mentioned in an appendix.

The standard textbooks are mostly silent as to the volumetric methods for determining niobium. Moissan, however, in his "Traité de Chimie Minérale," Paris, 1905, vol. ii., states that reduction of potassium niobium oxyfluorides with zinc in hydrochloric acid solution goes as far as $Nb_3O_5(=Nb_2O_4.NbO)$, but gives no details except to state that alkali fluorides prevent the reduction. Beckurts' "Massanalyse," Braunschweig, 1913, p. 595, gives both Osborne's method * and Metzger and Taylor's, and states that the last-named is at present the best.

EXPERIMENTAL.

Contrary to the usual textbook statements, both niobium and tantalum oxide are readily soluble in hydrofluoric acid, even after strong ignition. The simplicity with which a fluoride solution of the mixed oxides, as they are ordinarily obtained in the analysis of tantalum minerals, can be produced in this way, led me to determine whether, in spite of Warren's adverse criticism, Osborne's method or a modification could not be made to work. The experiments described below are the outcome.

The method followed at first was to dissolve weighed portions of pure niobium pentoxide in about 3 to 5 c.c. of hydrofluoric acid in a 25 c.c. platinum crucible, and then to evaporate to dryness. Both solution and evaporation were occasionally carried out on a water-bath, but in the great majority of cases on a hot plate, at a temperature below the boiling-point. The residue was taken up in concentrated hydrochloric acid, the solution transferred to a glass flask, using a glass rod, the crucible being rinsed out with successive portions of hydrochloric acid, and finally with water. The solution so obtained was generally slightly cloudy. Ten grms. of zinc were then added, and when the reaction slackened, usually at the end of ten minutes, the flask was gently warmed on a hot plate. As soon as all the zinc was dissolved, generally in about thirty minutes from the start, the contents of the flask were diluted, and the titration was carried out *at once* with an approximately $\frac{N}{10}$ potassium permanganate solution.

The first few experiments were made in flasks provided with a rubber stopper carrying a Bunsen valve. On account of the presence of so much chloride, however, the reduced solution must be considerably diluted before titrating, and ordinary flasks of sufficient size will not often stand the pressure created when the solution cools. Transfer from a smaller flask to a larger vessel is to be avoided on account of the risk of reoxidation. Consequently, reduction was later carried out in a 500-c.c. conical flask provided with a double-bored rubber stopper carrying an inlet tube for hydrogen and an ordinary thistle funnel, the stem of which terminated at such a height that it was still above the liquid at the end of the titration, at which stage the flask holds nearly 400 c.c. This thistle funnel serves as the exit tube for

* Beckurts states that Osborne removed the last traces of hydrogen fluoride " by heating in a glass vessel." Osborne merely mentioned that most of the fluorine left appears to go off as SiF_4 during the reduction.

the hydrogen during the reduction, and to add the diluting solution before the titration. By filling the funnel with the solution and simultaneously loosening the rubber stopper slightly, the solution can be added easily without introducing any air. The permanganate solution is also run in through this thistle funnel.* Hydrogen, washed with copper sulphate solution, was used to give an inert atmosphere during reduction and titration. Carbon dioxide would probably do as well, but coal-gas cannot be used, as it rapidly reduces permanganate.

To keep the method as simple as possible, unamalgamated zinc was used throughout. In order to lessen the briskness of the reaction somewhat, a certain amount of water was usually added to the hydrochloric acid, the standard quantities finally adopted being 40 c.c. of concentrated hydrochloric acid to 20 c.c. of water and 10 grms. of zinc. The zinc was in fairly massive form, the thicker pieces only from a sample of granulated zinc being used for the earlier experiments, Nos. 1 to 22, and zinc "shot," 23 of which usually weighed 10 grms., being used for the later ones. In Experiments 1 to 5 and 11 to 13 the reduced solution was diluted simply with from 150 to 300 c.c. of water. The end-point so obtained was fairly sharp, but very transient ; hence in Nos. 6, 14, and 15, 10 c.c. of concentrated sulphuric acid were also added. Whilst this improved matters somewhat, it was found that a very much sharper end-point could be obtained by adding sodium phosphate solution as well, and after two trials with larger quantities of phosphate, Experiments 7 to 10 and from 18 (inclusive) on were made by diluting the reduced solution with a mixture of 270 c.c. of water, 10 c.c. of concentrated sulphuric acid, and 20 c.c. of a cold saturated solution of sodium phosphate. This diluting solution should be cold and free from air. The reduced and diluted solution need not be further cooled. The permanganate solution was run in at such a rate that single drops could just be distinguished until the originally dark brown solution became almost colourless. From this point on the permanganate was added a few drops, and finally one drop at a time, each successive addition being washed down the funnel with a little water. The pink colour so obtained persists for at least two minutes. With very little practice, it is easy to ascertain when the end-point is near, the solution becoming perfectly colourless a little before this point. A complete control was run whenever a new chemical was employed. It generally amounted to 0·25 c.c. of $\frac{N}{10}$ solution. Two slightly different, but nearly $\frac{N}{10}$ solutions of potassium permanganate were used during the course of the work. To facilitate comparison of results, all figures have been calculated to $\frac{N}{10}$ strength, and the figures so obtained are given. The actual burette readings were only to 0·05 c.c. It may also be stated that the order in which the experiments are given in the tables is not quite that in which they were made, some of the experiments in Table II. being made before the later ones of Table I.

Note.—In the fourth column of Tables I., II., and IV., and the fifth column of Table II., after the first result, all zeros are omitted, significant figures only being given.

* Alternatively, the flask may be closed by a three-holed stopper. Two of the holes serve for inlet and exit of the gas. The diluting liquid, and afterwards the tip of a long-stemmed burette, are introduced through the third.

TABLE I.

Evaporation carried to Dryness.

No.	Nb_2O_5 taken.	$\frac{N}{10}$ $KMnO_4$ required.	Nb_2O_5 per C.C.	Hydrochloric Acid present.	Water present.	
	Grm.	C.C.	Grm.	C.C.	C.C.	
1	0·0590	5·85	0·01009	50	Nil	} Bunsen
2	0·0508	6·14	0·00827	,,	A little	} valve flask.
3	0·0592	5·56	0·1065	,,	30	
4	0·1139	13·56	0·0840	,,	,,	
5	0·0794	9·36	0·0848	,,	,,	
6	0·1292	13·95	0·0925	,,	50	
7	0·0626	5·90	0·1061	40	20	
8	0·0582	4·63	0·1257	,,	,,	
9	0·0711	7·66	0·0928	,,	,,	
10	0·1023	11·60	0·0882	,,	,,	

TABLE II.

Evaporation carried nearly to Dryness.

No.	Nb_2O_5 taken.	$\frac{N}{10}$ $KMnO_4$ required.	Nb_2O_5 per C.C.	Deviation from mean, 0·00833.	Hydrochloric Acid present.	Water Present.
	Grm.	C.C.	Grm.	Grm.	C.C.	C.C.
11	0·0954	11·12	0·00858	+ 0·00025	50	20
12	0·0584	7·02	0·00832	− 0·00001	,,	30
13	0·0996	12·14	0·00820	− 0·00013	,,	30
14	0·1202	14·53	0·00827	− 0·00006	,,	20
15	0·1394	17·07	0·00817	− 0·00016	,,	5
16	0·1186	14·19	0·00836	+ 0·00003	40	20
17	0·1243	15·12	0·00822	− 0·00011	,,	,,
18	0·1134	13·60	0·00834	+ 0·00001	,,	,,
19	0·1168	13·80	0·00846	+ 0·00013	,,	,,
20	0·0712	8·53	0·00835	+ 0·00002	,,	,,
21	0·1041	12·48	0·00834	+ 0·00001	,,	,,
22	0·1699	20·38	0·00833	± 0·00000	,,	,,
23	0·1111	13·36	0·00832	− 0·00001	,,	,,
24	0·1026	12·26	0·00837	+ 0·00004	,,	,,

The results obtained in this way are given in detail in Table I., the first two experiments being made in a flask with Bunsen valve and the others in the flask fitted with the thistle funnel described above. It will be seen that the results are very irregular, reduction usually stopping far short of the oxide Nb_8O_{13}. The procedure just mentioned near the end of Osborne's paper of evaporating *nearly* to dryness was next tried. For this purpose the final evaporation was carefully carried out on a moderately warm " hot " plate until only a few drops of solution remained,

and crystals separated out when the crucible was lifted off the hot plate and cooled a little. The residue so obtained, which gave a perfectly clear solution in hydrochloric acid, was reduced, diluted, and titrated exactly as before, with the results given in Table II.

These results may fairly be said to be good for a titration which appears to be as delicate as the one under consideration. The average of all the results in Table II. is $0\cdot00833$ grm. of Nb_2O_5 for the equivalent of 1 c.c. $\frac{N}{10}$ permanganate solution. Excluding Nos. 11, 13, 15, 17, and 19, all of which differ from the mean by more than $0\cdot00010$, the almost identical figure $0\cdot00834$ is obtained, which has been adopted in the subsequent work. This happens to be the equivalent of a hypothetical oxide $Nb_{10}O_{17}$, which may be written $4Nb_2O_3.Nb_2O_5$. The degree of reduction obtained by different observers is summed up in Table III. It will be seen that in the present method reduction does not go as far as in any of the others, which may be an advantage, in that the less one aims at the more likely one is to obtain that little. The higher permanganate equivalent is, of course, a slight disadvantage.

TABLE III.

Degrees of Reduction found by Different Observers.

Observer.	Reduced Oxide.	Acid present.	Nb_2O_5 per C.C. of $\frac{N}{10}$ Solution.
			Grm.
Marignac	$Nb_3O_5 = Nb_{120}O_{200}$	HCl	$0\cdot00763$
Osborne	$Nb_8O_{13} = Nb_{120}O_{195}$	and a little	$0\cdot00801$
Author	$Nb_{10}O_{17} = Nb_{120}O_{204}$	HF	$0\cdot00834$
Metzger and Taylor	$Nb_2O_{3\cdot107} = Nb_{120}O_{186\cdot42}$	H_2SO_4	$0\cdot00705$

A higher permanganate equivalent might, of course, be due to impurity in the niobium pentoxide used. This had been repeatedly ignited; finally at a temperature of 1,000° C. (measured) for one hour, and may be taken as free from SO_3 and water. It seemed possible that it might contain some tantalum. Part of it was therefore fractionated by Marignac's method, nearly equal quantities of soluble and insoluble double potassium fluorides being obtained. Experiments 23 and 24 were made on portions of the more soluble oxides, and are in good agreement with the others made on unfractionated material. Hence tantalum was not present.

Some possible sources of error were next examined, with results collected in Table IV.

In Experiments 25, 26, and 27, evaporation was not carried nearly as far as before, with the result that a little more hydrofluoric acid remained in the liquid, and reduction stopped short of the point reached before. Hence some little care is needed in the final stage of the evaporation. On one hand, enough hydrofluoric acid must be present to give a perfectly clear solution in hydrochloric acid; on the other, the quantity must be so small as not to interfere with the reduction. The

operation is quite similar to the corresponding stage in the separation of bismuth as oxychloride from copper.* It was found that whenever the correct degree of evaporation was reached, a bulky white precipitate separated out from the solution shortly after the end of the titration, usually within fifteen to thirty minutes, or even less. If this precipitation does not take place, the result obtained should be treated with suspicion, probably being too low. Unfortunately, this indication is only given at the end of the whole determination.

TABLE IV.

Various Sources of Error.

No.	Nb_2O_5 taken.	$\frac{N}{10}$ $KMnO_4$ required.	Nb_2O_5 per C.C.	Conditions.
	Grm.	C.C.	Grm.	
25	0·0972	10·78	0·00902	Too much HF left.
26	0·1168	13·70	0·00853	„ „ „
27	0·1334	15·21	0·00877	„ „ „ 0·13 grm. Ta_2O_5 present.
28	0·0930	10·73	0·00866	Concentrated HCl ; no water.
29	0·1116	12·92	0·00864	„ „ „
30	0·0916	10·29	0·00890	Too finely divided Zn.
31·	0·0584	5·90	0·00990	„ „ „
32	0·0462	2·93	0·01576	No hydrogen.
33	0·0362	2·69	0·01345	Poor supply of hydrogen.
34	0·0842	8·97	0·00939	„ „ „

Two experiments, Nos. 28 and 29, were made to see whether in concentrated hydrochloric acid reduction will go further than in the 2 : 1 mixture used. In Experiment 28 the reduction flask was cooled in water during the first part of the reduction, whilst in No. 29 it stood on the bench as usual. In both cases reduction did not go as far as when a little water is present.

Experiments 30 and 31 were made using very small pieces of granulated zinc. Dissolution only took a short time, and reduction was not complete. In Experiment 32 no hydrogen was passed into the reduction flask ; in Nos. 33 and 34 the hydrogen-supply was purposely interrupted for short periods during reduction. As was expected, these experiments gave poor results. It is advisable to insert the stopper and to start a good current of hydrogen as soon as the zinc has been placed in the flask. By doing this one is sure of having swept all air out of leading tubes, etc., by the time the evolution of hydrogen in the reduction flask itself slackens.

Mixtures of niobium pentoxide with tantalum pentoxide were next analysed by this method, using the factor 0·00834 found above. The results are given in Table V. They are nearly as good as those found with pure niobium oxide, with the exception

* An easier, if less simple, alternative is possible : The original solution may be evaporated to dryness, and the residue taken up by heating with 10 c.c. of very dilute (1 : 30) hydrofluoric acid. Solution is complete in less than ten minutes. I have used this variation in a few cases with good results.

of the last three, in which the proportion of niobium oxide to tantalum oxide is small. I believe that this represents the difficulty of driving off enough of the hydrofluoric acid in presence of much tantalum fluoride. If much tantalum is present, it appears to be best to conduct the final evaporation at as high a temperature as possible without boiling, as otherwise tantalum is apt to separate out in a gelatinous form before the proper degree of concentration is reached.

TABLE V.

Mixtures of Nb_2O_5 and Ta_2O_5.

No.	Nb_2O_5 taken.	Ta_2O_5 taken.	$\frac{N}{10}$ $KMnO_4$ required.	Nb_2O_5 found.	Error.
	Grm.	Grm.	C.C.	Grm.	Grm.
35	0·0946	0·0803	11·17	0·0932	− 0·0014
36	0·1215	0·1272	14·48	0·1208	− 0·0007
37	0·1329	0·0798	15·85	0·1322	− 0·0007
38	0·0442	0·1000	5·27	0·0440	− 0·0002
39	0·1516	0·1766	18·19	0·1517	+ 0·0001
40	0·1073	0·0750	12·92	0·1077	+ 0·0004
41	0·0314	0·1400	3·54	0·0295	− 0·0019
42	0·0146	0·1704	1·37	0·0114	− 0·0032
43	0·0070	0·0750	0·39	0·0033	− 0·0037

Finally, some experiments were made on a sample of mixed oxides of niobium and tantalum, the results being given in Table VI. Experiments 44 to 47 were made using the method given above. In Experiments 48 and 49 the effect of having alkali present was studied. For this purpose the mixed oxides, together with 1 grm. of potassium fluoride, were dissolved in 5 to 7 c.c. of hydrofluoric acid, and the solution carefully evaporated almost to dryness on the hot plate. The residue was then further heated over a Bunsen burner, very cautiously at first, more strongly as the melt solidifies, and finally to redness, when a clear melt is obtained. The melt was broken up by warming with a little water in the crucible, transferred to the reduction flask, the remainder of the 20 c.c. water and 40 c.c. of concentrated hydrochloric acid was added, solution completed, and the estimation finished as before. It will be seen that the results obtained in this way agree well with those obtained in the absence of alkali. This is at variance with Osborne's results, though, as noted above, these are mutually contradictory.* Experiment 50, though not made on the mixed oxides, but on nearly pure niobium oxide, may be cited here. The procedure was the same as for Experiments 48 and 49, except that the residue obtained by evaporation was not fused but only heated very gently—*i.e.*, much of the acid potassium fluoride was left undecomposed. Only 85·86 per cent. of the Nb_2O_5

* In Marignac's well-known test (*Zeitsch. anal. Chem.*, 1868, **7**, 112) for titanium in presence of niobium, which depends on the non-reduction by zinc of niobium in presence of potassium fluoride, the conditions are very different, very dilute hydrochloric acid (sp. gr. 1·015, or even less) being used, and the solution being perfectly cold.

present was found, showing the need for fusing and expelling as much hydrogen fluoride as possible.   To test the influence of more dilute acid in presence of alkali, Experiments 51 and 52 were made, proceeding as in Experiments 48 and 49, except that in Experiment 51, 45 c.c. hydrochloric acid and 45 c.c. water were used, and in Experiment 52, 40 c.c. hydrochloric acid and 40 c.c. water.   The results obtained are considerably lower than those given by the stronger acid.   Experiments 53 and 54 were next made on mixtures of these mixed oxides with more tantalum oxide, proceeding as in Nos. 48 and 49, but using 2 grms. potassium fluoride.   The results obtained are much too low.   Experiment 55, in which twice the usual quantity of all the reagents was used in order to diminish the concentration of the alkali fluoride, gave a higher result, but still much below the truth.

TABLE VI.

Experiments on a Sample of Mixed Oxides of Nb and Ta.

No.	Nb_2O_5 taken.	Ta_2O_5 taken.	Mixed Oxides taken.	$\frac{N}{10}$ $KMnO_4$ required.	Nb_2O_5 found.	Nb_2O_5 found.	Nb_2O_5 found. Average.	Remarks.
	Grm.	Grm.	Grm.	C.C.	Grm.	Per Cent.	Per Cent.	
44	—	—	0·2002	14·30	0·1192	59·54 ⎱		
45	—	—	0·2012	14·35	0·1197	59·50 ⎰	59·39	Standard fluoride method.
46	—	—	0·2212	15·72	0·1311	59·27		
47	—	—	0·1978	14·05	0·1172	59·24 ⎱		
48	—	—	0·2217	15·87	0·1324	59·67 ⎱	59·44	Fusion with 1 grm. KF.
49	—	—	0·2076	14·74	0·1229	59·21 ⎰		
50	0·1064	0·0007	—	10·95	0·0914	85·86	—	1 grm. KF ; not fused.
51	—	—	0·2084	14·50	0·1210	58·03	—	45 c.c. HCl, 45 c.c. H₂O ⎱ 1 grm. KF fusion.
52	—	—	0·2040	14·06	0·1172	57·48	—	40 ,, 40 ,, ⎰
53	—	0·2650	0·1170	5·90	0·0492	42·07*	—	40 ,, 20 ,, ⎱ 2 grms. KF fusion.
54	—	0·2650	0·0966	4·13	0·0345	35·67*	—	40 ,, 20 ,,
55	—	0·3060	0·1092	6·53	0·0545	49·87*	—	80 ,, 40 ,, ⎰
56	—	—	0·2030	17·34	0·1223	60·24 ⎱		
57	—	—	0·2108	17·78	0·1254	59·50 ⎰	59·85	Metzger and Taylor's method.
58	—	—	0·2317	19·65	0·1386	59·81		

One-half grm. of the same mixed oxides was next analysed by Marignac's method, only one crystallisation being made : 45·36 per cent. of tantalum oxide and 54·33 of niobium oxide were obtained.   Instead of carrying out a second fractionation as usual, each oxide was analysed by the volumetric method.   The niobium portion gave 54·10 per cent. of niobium oxide—that is, it was nearly pure ; the tantalum fraction gave 4·67 per cent. of niobium oxide, or a total of 58·77 per cent. of niobium oxide.   The fact that this is 0·62 per cent. below the value 59·39 per cent. found volumetrically I ascribe to the tendency previously noticed of the volumetric method to give low results in mixtures containing much tantalum oxide.   The tantalum portion probably contained more niobium oxide than that here found.

The same sample of mixed oxides was finally analysed by Metzger and Taylor's method, Experiments 56, 57 and 58 of Table VI.   The procedure given by these

* These percentages are calculated on the "mixed oxides" taken, and are directly comparable with all others in the same column, except No. 50, which relates to the Nb_2O_5 taken.

authors was closely followed, with the exception of three unimportant details : (1) As a matter of convenience, hydrogen was used as inert gas instead of carbon dioxide. (2) An ordinary burette tube of ½-inch bore was used as reductor instead of the ¾-inch bore tube recommended. The succinic acid solution froths slightly, however, and probably the wider tube permits easier working. (3) Instead of adding the 20 c.c. succinic acid solution in a fine stream from a wash bottle, it was poured in a little at a time along a stirring rod. There was no trace of turbidity at this point. A blank of 0·3 c.c. was found. The method works well, and the results obtained do not differ more from each other than those found by Metzger and Taylor on similar samples. The average result is 0·46 per cent. higher than the average of the fluoride method, which seems fair agreement.

One point may be mentioned here : Metzger and Taylor state that succinic acid is not affected by permanganate in acid solution. This seems to be true only if the temperature is kept low. To test this point, 3 grms. of succinic acid were dissolved in 390 c.c. water and 45 c.c. sulphuric acid, this being the approximate concentration of the reduced solution in Metzger and Taylor's method, 10 grms. of zinc dissolved in the solution, and its action on potassium permanganate solution noted. At 48° C. it required several c.c. to produce a red colour ; by the time the liquid had cooled to 36° C., several c.c. more could be run in before a red colour appeared. In another experiment 0·1101 grm. of succinic acid was dissolved in 50 c.c. of water and 5 c.c. of sulphuric acid. After heating, the solution required 3·25 c.c. $\frac{N}{10}$ permanganate solution before a permanent red colour was obtained, the temperature at the end of the titration being 67° C. Although the end-point in Metzger and Taylor's method seems perfectly sharp, I am inclined to attribute an occasional high result to this oxidation of succinic acid, and would advise that the receiving flask be cooled whilst the solution runs through the reductor.

Comparing Metzger and Taylor's with the fluoride method, the first can be carried out in about one to one and a half hours, and works smoothly, but demands nearly continuous attention. The second takes about one and a quarter to two hours, and requires little attention except for a short time during the final evaporation, but this operation demands a small amount of judgment. The fluoride method has a tendency to give low results with low percentages of niobium oxide, but, even so, the results are at least as concordant as those given by the succinic acid method. Both volumetric methods give results which appear to be more accurate than those given by Marignac's method in a very much shorter time and with less labour.

THE SOLUBILITY OF TANTALUM AND NIOBIUM OXIDES IN HYDROFLUORIC ACID, AND THE VOLATILITY OF TANTALUM FLUORIDE.

In 1900, in the course of experiments made in the laboratory of Mr. B. Blount, I noticed that tantalum and niobium oxides, both separately and when mixed together, are readily soluble in hydrofluoric acid of ordinary strength (48 per cent.), even after strong ignition (ANALYST, 1901, **26**, 64). The solubility is a little irregular ; at moderate temperatures considerable quantities of acid can be evaporated in contact with the oxides without much solution taking place. At temperatures near but

well below the boiling-point, however, solution is quite rapid, especially if the liquid is brought to this temperature quickly. Thus, in one experiment 0·14 grm. of tantalum oxide which had been ignited for three-quarters of an hour in a covered crucible at the hottest temperature of a coal-gas air blowpipe flame dissolved completely in less than ten minutes in about 5 c.c. hydrofluoric acid heated to about 90° C. Niobium oxide is still more easily soluble.

Most of the standard textbooks continue to state the contrary. Thus, Roscoe and Schorlemmer (vol. ii., p. 935, 1907 edition) state that "the ignited (tantalum) oxide does not dissolve in any acid, but volatilises completely when ignited with ammonium fluoride." Even Moissan's "Traité de Chimie Minérale" (vol. ii., p. 158, 1905) states that "strongly ignited niobium oxide is insoluble in sulphuric, hydrochloric, nitric, and *hydrofluoric* acids, and on p. 151 that "tantalum oxide is not soluble in acids even on boiling."

Ruff and Schiller (*Zeitsch. anorg. Chem.*, 1911, **72**, 349), on the other hand, have more recently found that even quite dilute hydrofluoric acid dissolves the ignited oxides on prolonged boiling under a reflux condenser, and that stronger acid effects solution readily at a boiling temperature.

In the same paper (p. 334) Ruff and Schiller give four experiments, in two of which tantalum oxide was dissolved in hydrofluoric acid, the solution evaporated to dryness, *the residue dried* and ignited. In the other two the procedure was similar, but sulphuric acid was added to the fluoride solution. The authors state that there was no loss in any of these experiments. (As a matter of fact, in three experiments there were losses of 0·30, 0·62, and 0·27 per cent.; in the fourth there was a gain of 0·15 per cent., probably due to SO₃.) They conclude that tantalum fluoride solutions can be evaporated to dryness and the residue ignited without any loss, both when sulphuric acid is present and when it is not. They also state that tantalum oxide can be repeatedly ignited with ammonium fluoride without any loss, and that the double fluoride of potassium and tantalum can be ignited without loss of tantalum.

Some of these conclusions are in direct opposition to results found by me in the paper cited above. I there stated that "it was found that neither niobic nor tantalic oxide volatilises when treated with HF and H₂SO₄, and that niobic oxide does not form volatile compounds even when treated with HF alone, but that tantalic oxide by the action of HF loses in weight each time the operation is repeated," and on fusing a mixture of about two-thirds niobium oxide and one-third tantalum oxide with acid potassium fluoride a loss of over 7 per cent. was noticed. My results were largely in accord with Rose's (*Pogg. Annal.*, 1856, **99**, 481), who found very large losses of tantalum on igniting (a) residues from fluoride solutions, (b) mixtures of tantalum oxide with ammonium fluoride, and (c) the double potassium tantalum fluoride. Rose also found, however, small losses (about 1 per cent.) when sulphuric acid was present in the tantalum fluoride solutions, and the incorrectness of this result, familiar to every analyst, has thrown doubt on the rest of his work.

Ruff and Schiller's statements led me to repeat some of my work of fourteen years ago, as follows :

0·1530 grm. of pure tantalum oxide was ignited for twenty minutes over a blowpipe ; it then weighed 0·1529 grm. It was next dissolved in about 5 c.c. of

hydrofluoric acid, the solution evaporated to dryness on a hot plate as quickly as possible without boiling, and the residue ignited first very gently over a Bunsen burner, then more strongly, and finally for twenty minutes over the blowpipe. Dense white fumes came off during the early stage of the ignition, which in small part settled on the upper portion of the crucible. The weight at the end of the operation was 0·1182 grm., a loss of 22·7 per cent. The operation was repeated, but this time the residue was baked for about ten minutes on the hot plate before igniting; the weight obtained was 0·0988 grm., a loss of 16·2 per cent., appreciably less than in the first experiment.

This 0·0988 grm. of tantalum oxide was next dissolved in 5 c.c. of hydrofluoric acid together with 1 grm. of potassium fluoride, the whole evaporated nearly to dryness on the hot plate, and then heated over a Bunsen burner, at first very cautiously, then more strongly, and finally at a red heat until a clear fusion was obtained. It was kept at this temperature for about five minutes, allowed to cool, heated with sulphuric acid for about twenty minutes, and boiled with water. The oxide was filtered off and ignited as before. It weighed 0·0790 grm., showing a loss of 20·0 per cent. The operation was repeated, but this time the potassium fluoride melt was only just melted at a red heat and allowed to cool at once. The weight obtained was 0·0744 grm., or a loss of only 5·8 per cent. The hydrofluoric acid used in all these experiments was taken from a freshly opened bottle. The experiments were made in a room free from all fumes.

Finally, a single experiment was made in which 0·0828 grm. of well-ignited tantalum oxide was heated with 1 grm. of ammonium fluoride, at first very gently, and finally to redness. The melt behaved much like the double potassium fluoride, but near a red heat copious and dense white fumes were evolved, which I have not observed with the potassium salt. The ignited oxide obtained weighed 0·0442 grm., a loss of 46·6 per cent.

Whilst Ruff and Schiller's experiments show that there are special conditions which minimise the loss on igniting residues from tantalum fluoride solutions, potassium tantalum fluoride, and mixtures of tantalum oxide with ammonium fluoride, I think that the experiments just cited, together with my earlier work, show that in general the loss to be expected in these operations is very considerable.

SUMMARY.

A volumetric method for the estimation of niobium in presence of tantalum is described. The method is based on the fluoride method of Osborne, but reduction only goes as far as an oxide, $Nb_{10}O_{17}$, with an $\frac{N}{10}$ permanganate equivalent of 0·00834 grm. per c.c.

It is shown that large losses of tantalum are caused by (a) dissolving tantalum oxide in hydrofluoric acid and igniting the residue obtained on evaporation to dryness; (b) igniting potassium tantalum fluoride with excess of potassium fluoride at a red heat; and (c) igniting mixtures of tantalum oxide and ammonium fluoride.

APPENDIX.

Metzger and Lamme on the Specific Gravities of Niobium and Tantalum Oxides.

Foote and Langley (*Chem. News*, 1911, **103**, 52; in ANALYST, 1911, **36**, 239) have determined the specific gravities of mixtures of niobium and tantalum oxides precipitated and ignited together, and show that the results do not fall on a straight-line curve. Their somewhat irregular curve is reproduced and apparently adopted by Mellor ("Quantitative Inorganic Chemistry," 1913, p. 423).

It was my intention, if time permitted, to make some experiments by this method, but I find that the field has been pretty well covered by M. A. Lamme working under Dr. Metzger ("Columbia University Dissertation," 1909). By the latter's kindness I am permitted to refer here to these results, which have never been published.

Lamme found that the specific gravity of both oxides varied with the degree of ignition, and to a much smaller extent with the method of preparation. He obtained his oxides by decomposition of the fluorides with sulphuric acid, using a small amount of ammonia in the final washing. Ignition of from thirty to ninety minutes in a coal-gas air blowpipe flame was necessary to give constant results. The specific gravity of niobium oxide decreases, whilst that of tantalum oxide increases, with prolonged ignition. On account of many difficulties with water, the specific gravities were finally compared with that of chloroform at its boiling-point. Quantities of a little over 1 grm. were generally used. The results obtained are given in Table VII.

TABLE VII.

Metzger and Lamme's Results for Specific Gravities of Mixtures of Nb_2O_5 and Ta_2O_5 referred to that of Boiling Chloroform.

Ta_2O_5 per cent. ...	0	10·20	20·06	30·10	40·05	50·02	59·98	69·94	79·95	89·80	100
Nb_2O_5 ,, ,, ...	100	89·80	79·94	69·90	59·95	49·98	40·02	30·06	20·05	10·20	0
Sp. gr.	3·265	3·316	3·484	3·686	3·908	4·074	4·925	5·227	5·530	5·843	6·201

On plotting these, it is seen that up to 40 per cent. of Nb_2O_5 the results lie on a straight line a little below and parallel to that connecting the specific gravity of the pure oxides. From 50 to 90 per cent. of Nb_2O_5, the results lie on a second straight line considerably below and inclined to the pure oxide line. Between 40 and 50 per cent. there is a very sharp break in the curve.

A mineral which by Metzger and Taylor's volumetric method showed on an average 54·21 per cent. of Nb_2O_5 and 22·75 per cent. of Ta_2O_5, was analysed in triplicate by this method. The specific gravities found were 3·612, 3·616, and 3·577, which, allowing for the slightly different amounts of total oxides obtained, gave values 57·43, 57·47, and 58·75 per cent. of Nb_2O_5 and 19·82, 19·68, and 18·16 per cent. of Ta_2O_5 respectively, differing by 2·93, 2·87, and 4·59 per cent. of Ta_2O_5 respectively from the results of the volumetric method.

Lamme concludes that the method can only be relied on to an accuracy of about 5 per cent. (on the mineral).

Incidentally, Lamme mentions a fact which I have often noticed—namely, that crystallised potassium bisulphate decomposes the mixed oxides (and some minerals) more rapidly than does the fused pyrosulphate. My experience is that the bisulphate should be fused at a low temperature just before the oxides are added. If pyrosulphate only is available, it may be made much more active by adding a little concentrated sulphuric acid.

In conclusion, I have great pleasure in thanking Professor F. J. Metzger for the generous gift of some of his carefully purified tantalum and niobium oxides. To the authorities of the Department of Metallurgy, more especially to Emeritus Professor Henry M. Howe, I am greatly indebted for permission to carry out this work at the School of Mines, Columbia University, in the City of New York.

DISCUSSION.

The PRESIDENT, in inviting discussion, remarked that the increase which had taken place during recent years in the commercial value of minerals containing niobium and tantalum made the estimation of these elements a matter of the greatest importance, while its difficulty was illustrated by a case which had recently been brought to his notice, in which the results obtained by three expert analysts had varied in an extraordinary manner. The method dealt with by Mr. Levy depended on the reduction of the higher oxides, not to some definite, well-defined oxide, but to an intermediate stage of oxidation. Under such circumstances it was necessary that the conditions of reduction should be very clearly defined, and he thought that perhaps the chief merit of Mr. Levy's paper was that he had done more than any of his predecessors in laying down those conditions clearly. The necessity for such clear definition was illustrated by the case of the closely related element vanadium, V_2O_5 being reduced to V_2O_4 by sulphur dioxide, to V_2O_3 by magnesium, and to V_2O_2 by zinc. About ten years ago, in a paper read before the Society relating to molybdenum and vanadium, he had called attention to the very different results that one obtained, not merely when using different reducing reagents, but when using different qualities of zinc. Thus, he had shown that different results were obtained with an alloy of zinc and platinum on the one hand, in which case the potential of the hydrogen was low, and an alloy of zinc and cadmium on the other, when the potential of the hydrogen was higher. In another paper communicated to the Society he had detailed some experiments on the reduction of molybdenum and vanadium oxides with palladium-hydrogen, and it might be interesting to know to what extent the reduction would go in the case of tantalum and niobium. His impression had hitherto been that tantalum oxide was not easily volatilised on heating with ammonium fluoride, and he had quite recently repeated the experiment. On heating 0·244 grm. of pure ignited tantalum pentoxide with 3 grms. of ammonium fluoride, the ultimate loss of weight was found to be only 0·009 grm., or 3·7 per cent.—a result which seemed to indicate that tantalum oxide was not as volatile under these conditions as was usually stated in the textbooks. He

thought the Society was to be distinctly congratulated on this admirable communication, and it was a further source of gratification that the work had been carried out under the Society's Investigation Scheme.

Dr. W. R. SCHOELLER agreed that the solution of the problem of estimating niobium in presence of tantalum lay in a volumetric method, the conditions of the reduction being very carefully laid down. The method of fractional crystallisation and precipitation of the niobium-potassium oxyfluoride would only be successful in the hands of a highly experienced chemist, and would not be of much use for the purposes of a commercial laboratory. The determination of the specific gravity, after Foot and Langley's method, had the disadvantage of requiring rather a large quantity of the chemically pure mixed oxides, such as it was difficult to obtain by decomposition of the ore. He had found that in the presence of succinic acid the pink colour produced by permanganate vanished very quickly, and if this modification could be adopted it would be a distinct advantage. It was much more difficult, in the presence of tantalum, to estimate small quantities of niobium than large quantities. In Marignac's process the quantity of potassium fluoride added was rather important. If too much were used, the separation was much more imperfect than with the exact quantity prescribed.

Mr. BLOUNT agreed that the conditions must be very carefully defined, because it was not to be supposed that the oxide obtained was a definite oxide, nor that the extent of oxidation would not vary if the conditions were altered. It was obvious that the process of Marignac was out of the question for ordinary commercial work, but there was no doubt that for really crucial work Marignac's process was the best.

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