# STUDIES IN TANTALUM AND NIOBIUM.

## PART I. ANALYSIS OF MIXTURES OF PENTOXIDES OF NIOBIUM AND TANTALUM.

*By K. R. Krishnaswami and D. Suryanarayana Murthi.*

Owing to the close similarity in properties of the derivatives of tantalum and niobium, methods of determination which involve a preliminary separation are neither rapid nor simple. The oldest as well as the best known of such methods is the one devised by Marignac (*Ann. Chem. Phys.,* 1866, **8**, 60) which depends on the fact that potassium tantalifluoride ($K_2TaF_7$) and potassium niobium oxyfluoride ($K_2NbOF_5$) are soluble to different extents in hydrofluoric acid. Several crystallisations are, however, necessary to effect a satisfactory separation. Meyer and Hauser (Die Analyse der seltenen Erden u der Erdsauren, 1912, p. 177) state that an accuracy of 0.5 per cent. can be achieved by careful work, if 15–30 g. of the mixture is available. Ruff and Schiller (*Z. anorg. Chem.,* 1911, **72**, 348) reinvestigated the method in detail, and simplified it considerably, but its accurate application was still restricted to fairly large quantities (20 g.) of material. Another method for the estimation of niobium in a mixture of niobium and tantalum is based on the observation that, in acid medium, hydrogen reduces pentavalent compounds of niobium but not those of tantalum. The reduction, however, is attended with great uncertainty as it does not always proceed to the trivalent state, but stops earlier, (Treadwell, *Helv. chim. Acta.,* 1922, **5**, 806) and empirical factors have to be employed. Recently, however, Lundell (Hillebrand and Lundell, Applied Inorganic Analysis, p. 484) effected some modifications in the method and obtained satisfactory results. The most recently developed method for the separation and estimation of niobium and tantalum is due to Schoeller and Powell (*Analyst* , 1925, **50**, 485; 1932, **57**, 530). This is based on the observation that oxaloniobic and oxalotantalic acids yield adsorption complexes with tannin under different conditions, and these are coloured vermilion and sulphur-yellow respectively. Our experience with this method leads us to the conclusion that especially in the case of mixtures containing roughly equal quantities of niobium and tantalum, pure precipitates are obtained only after several precipitations and the method is laborious.

Ruff (*Z. anorg. Chem.,* 1926, **156**, 215) devised a method by making use of the fact that when a mixture of the pentoxides of niobium and tantalum is heated in a stream of hydrogen, niobium pentoxide is quantitatively reduced to the tetroxide, whereas tantalum pentoxide remains unaffected. The method consists in heating the mixed oxides in a stream of hydrogen until no further loss in weight is observed. The reduced mixture is weighed and then reheated in air when the niobium tetroxide is oxidised to the pentoxide. The oxidised mixture is weighed and from the observed increase in weight, the quantity of niobium pentoxide is calculated in accordance to the equation

$$2Nb_2O_4 + O_2 = 2Nb_2O_5$$

As Ruff has not given sufficient details regarding the conditions of working, and has not specified even approximately the temperature at which the reduction is to be carried out, and as in two experiments he obtained the large errors of 2.3 and 6 p.c. respectively, we decided to reinvestigate the method as we anticipated that it might prove helpful in our investigations concerning niobium and tantalum.

## EXPERIMENTAL.

The niobium pentoxide required for this work was prepared from a specimen of potassium niobium fluoride supplied by Kahlbaum, whilst the tantalum pentoxide was prepared from a pure specimen of potassium tantalum fluoride obtained by one of us in the course of his work on the atomic weight of tantalum. The double fluorides were decomposed with sulphuric acid and the precipitated oxides washed free from sulphate. The washed oxides were ignited on a Meker burner, and then crushed to fine powder in an agate mortar and preserved for analysis.

*Reduction in Hydrogen.*—Hydrogen obtained by electrolysis of dilute sulphuric acid was purified by passage over heated platinum sponge and then dried by means of calcium chloride and phosphorus pentoxide. A porcelain boat containing niobium pentoxide was placed in a silica tube (45 × 1.5 cm.), a portion of which could be kept heated at any temperature up to 1000° by means of a moveable nichrome-wound tube-furnace which surrounded it for a length of about 15 cm. The silica tube was closed at both ends by rubber stoppers through which passed inlet and outlet tubes for hydrogen. As no information was available regarding the lowest temperature at which niobium pentoxide is quantitatively reduced to the tetroxide, it was found necessary to carry out the following experiments. A weighed quantity (0.5 g.) of finely powdered niobium pentoxide contained in a porcelain boat was placed in the silica tube referred to above, and hydrogen admitted into the apparatus. The furnace current was then switched on and adjusted to the value required to give the desired temperature. After heating for 1½–2 hours, the furnace was moved away and the tube allowed to cool, the hydrogen supply being maintained till the tube had cooled down to about 100°. The boat containing the oxide was then taken out and weighed. The results of these experiments are as follows:— The reduction appears to start at 700° but proceeds at a very slow rate at this temperature. Even after heating for 2 hours, the loss in weight was only 0.4 mg. whereas quantitative reduction corresponds to a loss of nearly 30 mg. At 800°, however, heating for one hour was sufficient to effect quantitative reduction. The product obtained was a black powder and the loss in weight corresponded almost exactly with what is to be expected from the equation

$$Nb_2O_5+H_2=Nb_2O_4+H_2O.$$

Further heating at various temperatures up to 1000° resulted in no loss in weight. The results obtained are given in Table I (At. wt. of Nb = 93.5).

TABLE I.

| Expt. No. | $Nb_2O_5$ taken g. | $Nb_2O_4$ obtained g. | Loss in wt. mg. | $Nb_2O_5$ g. | Error p.c. |
|---|---|---|---|---|---|
| 1 | 0·5990 | 0·5630 | 36·0 | 0·6008 | 0·3 |
| 2 | 0·5938 | 0·5579 | 35·9 | 0·5993 | 0·9 |
| 3 | 0·5014 | 0·4714 | 30·0 | 0·5007 | 0·1 |
| 4 | 0·7476 | 0·7025 | 45·1 | 0·7530 | 0·9 |

*Oxidation of Niobium tetroxide.*—When heated in air at a temperature of about 600°, the tetroxide of niobium, which is black in colour, is quickly oxidised to the pentoxide which is snow white in appearance. Weighed quantities of niobium tetroxide (0.1–0.5 g.) were taken in a platinum crucible and heated at dull red heat to constant weight. Heating for 15 minutes was found to be sufficient to effect oxidation of the entire material. The observed increase in weight attending this conversion was found to be in fair agreement with that required by the equation

$$2Nb_2O_4+O_2 = 2Nb_2O_5$$

The results obtained are shown in Table II.

TABLE II.

| Expt. No. | $Nb_2O_4$ taken g | $Nb_2O_5$ obtained |  | Error p.c. |
|---|---|---|---|---|
|  |  | actual g. | calc. g. |  |
| 1 | 0·1000 | 0·1056 | 0·1064 | 0·8 |
| 2 | 0·1095 | 0·1168 | 0·1165 | 0·3 |
| 3 | 0·4724 | 0·5000 | 0·5025 | 0·5 |
| 4 | 0·2106 | 0·2556 | 0·2560 | 0·2 |

The next step was the preparation of mixtures in which $Nb_2O_5/Ta_2O_5$ varied from 1 : 1 up to 1 : 10. Carefully weighed quantities of the two oxides were transferred to an agate mortar and mixed intimately by grinding. The analyses of these mixtures were carried out as indicated earlier, *viz.*, a known weight of the mixture which was contained in a porcelain boat was heated in a stream of hydrogen at 800° for 1 hour after which the boat was allowed to cool and its contents reweighed. From the loss in weight observed, the quantity of niobium pentoxide present was calculated in the manner already mentioned. The reduced mixture obtained was in every case heated in air for about ½ hour and reweighed when it was found that the weight obtained was exactly the same as that of the mixture originally taken for analysis (Table III, col. 3). This procedure served to ensure that there was no mechanical loss of material from the boat during the experiment. The results obtained are shown in Table III.

TABLE III.

| Expt. No. | $Nb_2O_5/Ta_2O_5$ | Mixture taken g. | Loss in wt. mg. | $Nb_2O_5$ in mixture found g. | taken g. | Error p.c. |
|---|---|---|---|---|---|---|
| 1 | 1 | 0·5000 | 15·0 | 0·2504 | 0·2500 | +0·2 |
| 2 | „ | „ | 15·2 | 0·2537 | „ | +1·4 |
| 3 | $\frac{1}{4}$ | 1·0000 | 12·0 | 0·2003 | 0·2000 | +0·2 |
| 4 | „ | 1·1772 | 14·2 | 0·2370 | 0·2354 | +0·8 |
| 5 | $\frac{1}{10}$ | 2·2000 | 12·0 | 0·2003 | 0·2000 | +0·2 |
| 6 | „ | 2·7500 | 15·2 | 0·2537 | 0·2500 | +1·4 |

The reduced mixture in the boat was always found to be in the form of fine powder and was free from lumps. We mentioned earlier that Ruff (*loc. cit.*) obtained large errors because the material in the boat formed into lumps which prevented the reduction of the entire mass. We believe that this was due to heating it too strongly and suddenly with a blast-flame. In our experiments the mixture was heated more gradually and to a lower temperature than in the experiments carried out by Ruff and we consider that this procedure is necessary if satisfactory results are to be obtained.

This method has the great merit that it does not involve any operations of uncertainty like fusion, filtration, and transference of material from one vessel to another. The reaction underlying it seems to be perfectly simple and proceeds always to a definite stage. Owing to these reasons, the error in the determination will usually be not much more than the actual error in weighing.

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*Department of General Chemistry,*
*Indian Institute of Science,*
*Bangalore.*

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