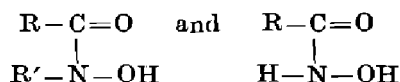


Separation of Niobium and Tantalum from Each Other with *N*-Benzoyl-*N*-*o*-tolylhydroxylamine

A. K. Majumdar and Bijoli K. Pal

N-Benzoyl-*N*-*o*-tolylhydroxylamine provides a satisfactory separation, in the cold, of Nb from Ta from a tartrate solution in the pH range of 5.0 to 6.5, even when these are present in the ratio of 1:17 to 21:1. Nb precipitates quantitatively from solutions with acidity ranging from 10% sulphuric acid to a pH of 6.7 and Ta, from 10% sulphuric acid solution to a pH of 1.8. Only Ti and Zr interfere in the determination of Nb at a higher pH 4.5 to 6.0, whereas Ti, Zr, MoO_4^{2-} , and WO_4^{2-} interfere in the determination of both Ta and Nb from a 10% sulphuric acid solution.

In previous communications¹⁻⁴, it was claimed that the organic reagents of the type



(where R, R' stand for alkyl or aryl groups) could be used effectively for the separation of niobium and tantalum from each other and from quite a large number of elements.

In a recent investigation, *N*-benzoyl-*N*-*o*-tolylhydroxylamine has been found to afford quantitative precipitations of both niobium and tantalum in the cold from a solution containing tartaric acid; the acid range for the quantitative precipitation of niobium is from 10% (v/v) sulphuric acid to a pH of 6.7 and that for tantalum is from 10% (v/v) sulphuric acid to a pH of 1.80. At and over a pH of 5.0, tantalum does not precipitate in the cold unless digested on a hot water bath when it precipitates even at a pH of 6.0. Thus the reagent in the cold affords a satisfactory separation by a single precipitation, even when the elements niobium and tantalum are present to the extent of 1:17 to 21:1. Moreover, from a 10% (v/v) sulphuric acid solution these can be separated from other common ions. Tungstate, molybdate, titanium, and zirconium seriously interfere, though the interference in niobium determination due to first two can be removed if the precipitation is undertaken at a pH between 4.5 and 6.0, adjusted with ammonium acetate solution.

Niobium, though forms a complex of definite composition, $(\text{C}_{14}\text{H}_{12}\text{NO}_2)_3 \text{Nb}=\text{O}$, stable at 110° for several hours, cannot be directly determined as such, as the complex has some solubility in hot water and the reagent, though soluble in hot water, is sparingly so in cold water.

EXPERIMENTAL

Reagents, chemicals, and standard solutions of niobium and tantalum were the same as reported in previous papers¹⁻³.

1. Majumdar and Mukherjee, *Anal. Chim. Acta*, 1959, **19**, 23; 1959, **21**, 245; 1960, **23**, 246; **22**, 514.
2. Majumdar and Pal, *ibid.*, 1961, **24**, 487; 1962, **27**, 356.
3. Majumdar and Mukherjee, *Z. anal. Chem.*, 1962, **189**, 339.
4. Majumdar and Pal, *Anal. Chim. Acta*, 1963, **29**, 168.

o-Nitrotoluene was reduced by zinc to *o*-tolylhydroxylamine⁵ and treated with benzoyl chloride⁶. *N*-Benzoyl-*N*-*o*-tolylhydroxylamine, thus obtained, was recrystallised from ethanol, m.p. 102-103°. Its composition as determined on analysis is C₁₄H₁₃O₂N. (Found: C, 73.99; H, 5.67; N, 6.16. Calc. for C₁₄H₁₃O₂N: C, 74.4; H, 5.6; N, 6.26%). The reagent, which is slightly soluble in cold water and moderately soluble in hot water, is highly soluble in ethanol; the presence of an excess of this last solvent should be avoided during the niobium precipitation as the complex of niobium also is somewhat soluble in it. In actual work, the reagent was dissolved in a minimum amount of 1:1 ethanol before being used as a precipitant.

Wash water comprised 0.1 g. of the reagent in 2-3 ml of ethanol and 100 ml of water containing 1-2 g. of ammonium chloride.

Effect of pH.—An aliquot portion of the standard solution of niobium or tantalum was taken in a 250-ml beaker and diluted to 100 ml with water. After the addition of 2-3g. of ammonium chloride, the pH of the solution was adjusted to a desired value, either with 20% (w/v) ammonium acetate solution along with dilute ammonia, if necessary, or with H₂SO₄ (dil.). The reagent solution was then added very slowly with thorough stirring after each addition and the precipitate so formed was allowed to settle for 1-2 hr., filtered, washed with wash water till free of sulphate, dried, ignited, and weighed. The precipitation of niobium was quantitative even when the acidity of the solution varied from 10% (v/v) H₂SO₄ to a pH of 6.7, whereas for complete precipitation of tantalum, the acidity could be as high as 10% (v/v) H₂SO₄ and as low as pH 1.8; pH higher than 4.5 kept tantalum completely in solution. Thus the pH range 5.0 to 6.5 is suitable for the separation of niobium from tantalum from a tartrate solution.

Separation of Niobium and Tantalum.—The solutions of niobium and tantalum (a few ml each) were mixed together and diluted to about 250 ml with water; after the addition of ammonium chloride (2-3g.) the pH of the solution was adjusted to any value between 5.0 and 6.5 and treated in the same way as already stated. The amount of the reagent should be at least 20 times in excess of the total oxides present.

The filtrate and the washings were then combined and from the mixture tantalum was precipitated on acidifying the solution to 10% (v/v) H₂SO₄ after addition of a few ml more of the reagent solution. The precipitate was then filtered, washed, and ignited to oxide (Table I).

TABLE I

Separation of niobium from tantalum.

Nb ₂ O ₅		Ta ₂ O ₅	
Taken.	Found.	Taken.	Found.
5.0 mg.	5.0 mg.	7.0 mg.	7.2 mg.
5.2	5.2	21.0	21.0
52.0	52.0	5.0	5.0
104.0	103.8	5.0	5.2
2.5	2.6	35.0	35.0
3.0	3.0	53.0	53.0

5. Bamberger and Rising, *Annalen*, 1901, 316, 278.6. Shome, *Analyst*, 1950, 75, 27.

On spectroscopic analysis, the precipitates of niobium were found to be completely free from tantalum, but those of tantalum contained a very slight trace of niobium.

Effect of Various Ions.—For the separation of niobium and tantalum from a large number of ions, an excess of tartaric acid, at least 2-3 times the total amount of the ions, was added to the mixture and then the acidity of the solution was adjusted to 10% (v/v) H_2SO_4 and the precipitation was effected, following the procedure as described above. Only titanium, zirconium, tungstate, and molybdate interfere. Niobium, but not tantalum, can, however, be separated from tungstate and molybdate by the precipitation of the former element from a solution kept at a pH of 4.5 to 6.0, rendered by ammonium acetate.

TABLE II

Ions added.	$Nb_2O_5 + Ta_2O_5$ taken.	$Nb_2O_5 + Ta_2O_5$ found.
Cr ³⁺ 100 mg.	5.2 + 5.0 = 10.2 mg.	10.4 mg.
Al ³⁺ 100		
La ³⁺ 100		
Ce ³⁺ 100		
Co ²⁺ 100		
Ni ²⁺ 100	5.2 + 5.0 = 10.2	10.2
Cu ²⁺ 100		
Zn ²⁺ 100		
Fe ³⁺ 200	5.2 + 5.0 = 10.2	15.6 ^a 10.0 ^b
VO ₃ ⁻ 150	7.6 + 5.0 = 12.6	19.4 ^a 12.6 ^b
Th ⁴⁺ 100	5.2 + 5.0 = 10.2	10.0
WO ₄ ²⁻ 100	7.6 + 5.0 = 12.6	7.6*
MoO ₄ ²⁻ 100	7.6 + 5.0 = 12.6	7.6*
UO ₂ ²⁺ 80	7.6 + 5.0 = 12.6	12.8

a Single precipitation.

b Double precipitation.

* pH 4.5-6.0, Nb alone precipitated

Spectrochemical analysis showed the oxides ($Nb_2O_5 + Ta_2O_5$) to be practically free from any adsorbed ions.