

## N-Aryl Hydroxamic Acids as Gravimetric Reagents for Niobium and Tantalum

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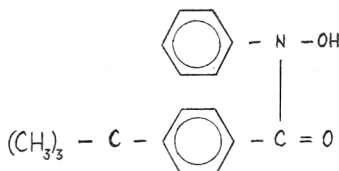
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Twenty six newly synthesized *N*-aryl-hydroxamic acids have been examined as reagents for gravimetric determination of niobium and tantalum. *N*-Phenyl-*p*-*ter*-butylbenzohydroxamic acid was found to be the most suitable reagent in the series examined and is proposed for the separation and gravimetric determination of niobium and tantalum. Niobium and tantalum are precipitated in the pH range of 3.5—6.5 and 0.8—1.8 respectively. The niobium and tantalum hydroxamates are ignited to oxides and weighed as niobium pentoxide and tantalum pentoxide. Niobium has also been estimated by direct weighing of the niobium hydroxamate. Separation of niobium and tantalum has been achieved using *N*-phenyl-*p*-*ter*-butylbenzohydroxamic acid by adjusting the pH of precipitation, without using any masking agent.

*N*-phenylbenzohydroxamic acid<sup>1,2</sup> and some of its analogues have been recommended for the separation and determination of niobium and tantalum<sup>3-5</sup>. Looking to the applicability of hydroxamic acids for gravimetric determination of niobium and tantalum, further investigation with twenty six new hydroxamic acids with different substituents have been carried out, to discover if other reagents with similar functional groups will be equally efficient.

It is a well established fact that the usefulness of a reagent can be altered by introducing different substituents in the molecule. Out of the twenty six *N*-arylhydroxamic acids examined *N*-phenyl-*p*-*ter*-butylbenzohydroxamic acid (I) is found to be the most suitable reagent for separation and gravimetric estimation of niobium and tantalum.



I

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The presence of the bulky tertiarybutyl group and its striking selectivity as a precipitant for niobium and tantalum at different pH have made it possible to determine and separate them gravimetrically in the presence of each other and a number of other associated ions. The accuracy obtained by this method is satisfactory and the separation of niobium and tantalum is achieved without the use of any masking agents, by a judicious control of pH.

#### EXPERIMENTAL

##### *Reagent Solutions*

All hydroxamic acids were prepared by the method reported earlier<sup>6,7</sup>. All chemicals used were of reagent grade. A 1% w/v alcoholic solution of the hydroxamic acid is used as precipitant.

##### *Solutions of Niobium and Tantalum*

Standard solutions of niobium and tantalum are prepared by the potassium-bisulphate, tartaric acid fusion method of Schoeller<sup>8</sup>.

##### *Solutions of Foreign Ions and Apparatus*

Solutions of foreign ions for interference studies were prepared following the method of West<sup>9</sup>, using A. R. Chemicals.

Narrow and wide range indicator papers were used for making pH measurements. Accurate measurements of pH were made by a Systronics portable pH Meter Type 323.

##### *General Procedure for Precipitation*

A suitable aliquot of the standard solution of niobium or tantalum obtained from tartarate fusion is taken in a 400 ml beaker and diluted to about 250 ml with distilled water. The solution is heated to 60 °C and 1% alcoholic solution of the N-aryl-hydroxamic acid is added with constant stirring, until precipitation is complete. The pH of precipitation is kept between 3.5 to 6.5 and between 0.8 to 1.8 for niobium and tantalum respectively. The pH is adjusted before addition of the reagent solution with the help of 10% (v/v) sulphuric acid or 20% ammonium acetate solution. The granular precipitate thus obtained is digested on a water bath for one hour and filtered through a quantitative filter paper, Whatman No. 542. The precipitate is washed thoroughly with a 0.1% solution of the reagent and warm water and finally with 10 ml of 10% aqueous ethanol, to remove traces of hydroxamic acid. The complexes are dried and ignited to pentoxides before weighing.

The niobium precipitate has a known composition and hence can also be weighed directly after filtering through a sintered glass crucible of porosity G4.

The tantalum precipitate has an indefinite composition; hence it cannot be weighed directly and has to be ignited to oxide.

In the method reported here all the complexes of niobium and tantalum are ignited to oxides after drying at 110 °C for uniformity. The results of niobium and tantalum determination with different hydroxamic acids are given in Table I.

##### *Effect of pH*

The experimental studies on the determination of niobium and tantalum in solutions of different pH values, keeping all the other factors identical, revealed that the precipitation starts at pH ~0.8 and ~3.5 and is quantitative in the range of 0.8–1.8 and 3.5–6.5 for tantalum and niobium, respectively.

##### *Amount of Reagent Solution*

It is found that 25 to 30 ml of 1% alcoholic solution is sufficient for every 10 mg of niobium or tantalum pentoxide in solution. A little excess is added for complete precipitation.

It has been found that most of the hydroxamic acids examined yield good results with niobium and tantalum in tartrate solutions. But *N-m*-chlorophenyl-*p*-

TABLE I

Gravimetric Determination of Niobium and Tantalum with *N*-Arylhydroxamic Acids  
 Wt. of  $\text{Nb}_2\text{O}_5$  = 20 mg, Wt. of  $\text{Ta}_2\text{O}_5$  = 15 mg, pH of precipitation of Nb = 4.8–5.5,  
 pH precipitation of Ta = 0.8–1.8.

S. No.	Hydroxamic acid	Weight of $\text{Ta}_2\text{O}_5$ found mg	Error	Weight of $\text{Nb}_2\text{O}_5$ found mg	Error mg
1	<i>N</i> -Phenylbenzo-,	19.95	−0.05	15.05	+0.05
2	<i>N</i> - <i>o</i> -Chlorophenylfuro-,	20.00	—	No precipitate	—
3	<i>N</i> - <i>m</i> -Chlorophenylfuro-,	19.82	−0.18	15.04	+0.04
4	<i>N</i> - <i>o</i> -Chlorophenylbenzo-,	19.88	−0.12	14.90	−0.10
5	<i>N</i> - <i>m</i> -Chlorophenylbenzo-,	20.02	+0.02	becomes oily	—
6	<i>N</i> - <i>o</i> -Chlorophenyl- <i>p</i> -chlorobenzo-,	20.12	+0.12	15.08	+0.08
7	<i>N</i> - <i>m</i> -Chlorophenyl- <i>p</i> -chlorobenzo-,	20.05	+0.05	14.95	−0.05
8	<i>N</i> - <i>o</i> -Chlorophenyl- <i>p</i> -toluic-,	20.00	—	14.90	−0.10
9	<i>N</i> - <i>m</i> -Chlorophenyl- <i>p</i> -toluic-,	No precipitate	—	Sticky precipitate	—
10	<i>N</i> - <i>o</i> -Chlorophenyl- <i>o</i> -methoxybenzo-,	19.94	−0.06	14.96	−0.04
11	<i>N</i> - <i>m</i> -Chlorophenyl- <i>o</i> -methoxybenzo-,	19.97	−0.03	15.05	+0.05
12	<i>N</i> - <i>o</i> -Chlorophenyl- <i>p</i> -methoxybenzo-,	19.95	−0.05	15.00	—
13	<i>N</i> - <i>m</i> -Chlorophenyl- <i>p</i> -methoxybenzo-,	20.05	+0.05	15.02	+0.02
14	<i>N</i> - <i>o</i> -Chlorophenyl-phenylaceto-,	19.98	−0.02	Stick precipitate	—
15	<i>N</i> - <i>m</i> -Chlorophenyl-phenylaceto-,	20.00	—	No precipitate	—
16	<i>N</i> - <i>o</i> -Chlorophenylcinnamo-,	20.04	+0.04	15.06	+0.06
17	<i>N</i> - <i>m</i> -Chlorophenylcinnamo-,	20.07	+0.07	15.02	+0.02
18	<i>N</i> -Phenyl- <i>p</i> - <i>ter</i> -butylbenzo-,	20.01	+0.01	15.05	+0.05
19	<i>N</i> - <i>o</i> -Chlorophenyl- <i>p</i> - <i>ter</i> -butylbenzo-,	20.02	+0.02	14.97	−0.03
20	<i>N</i> - <i>m</i> -Chlorophenyl- <i>p</i> - <i>ter</i> -butylbenzo-,	19.94	−0.06	15.00	—
21	<i>N</i> - <i>p</i> -Chlorophenyl- <i>p</i> - <i>ter</i> -butylbenzo-,	19.92	−0.08	14.98	−0.02
22	<i>N</i> - <i>o</i> -Tolyl- <i>p</i> - <i>ter</i> -butylbenzo-,	19.98	−0.02	15.04	+0.04
23	<i>N</i> - <i>m</i> -Tolyl- <i>p</i> - <i>ter</i> -butylbenzo-,	20.02	+0.02	15.06	+0.06
24	<i>N</i> - <i>p</i> -Tolyl- <i>p</i> - <i>ter</i> -butylbenzo-,	19.96	−0.04	14.97	−0.03
25	<i>N</i> -Phenyldiphenylaceto-,	20.03	+0.03	15.05	+0.05
26	<i>N</i> - <i>p</i> -Tolyldiphenylaceto-,	20.08	+0.08	15.04	+0.04

-toluichydroxamic acid and *N*-*m*-chlorophenylphenylacetohydroxamic acid formed no precipitate with tantalum under the employed experimental conditions. *N*-*o*-chlorophenyl-phenylacetohydroxamic acid gives a sticky brownish precipitate with tantalum solution. *N*-*m*-Chlorophenyl-*p*-toluichydroxamic acid does not give any precipitate with niobium, also under the experimental conditions.

On the other hand *N*-*m*-tolyl-*p*-*ter*-butylbenzo-, and *N*-phenyl-*p*-*ter*-butylbenzo-hydroxamic acids give a very good fine, granular precipitate with niobium and tantalum from tartrate solutions. Other reagents yielding good precipitates with these metals and *N*-*o*-chlorophenylcinnamo-, *N*-*o*-chlorophenyl-*p*-toluic-, *N*-*m*-chlorophenylfuro-, *N*-*o*-chlorophenylfuro-, *N*-*o*-chlorophenyl-*p*-*ter*-butylbenzo-, *N*-*o*-chlorophenyl-*o*-methoxybenzo-, *N*-*m*-chlorophenyl-*p*-methoxybenzo- and *N*-*o*-tolyl-*p*-*ter*-butylbenzo hydroxamic acids. All the precipitation reactions were carried out with tartrate solutions of niobium and tantalum.

In these studies *N*-phenyl-*p*-*ter*-butylbenzohydroxamic acid is found to be the most suitable hydroxamic acid for gravimetric determination of niobium and tantalum, hence, it has been examined in detail.

*Gravimetric Determination of Niobium and Tantalum with N-Phenyl-p-ter-Butylbenzohydroxamic Acid*

As discussed earlier *N*-phenyl-*p*-ter-butyl benzohydroxamic acid (N-PTBBHA) was found to be the most suitable reagent for gravimetric determination of niobium and tantalum. Hence, with this reagent detailed investigations were carried out. The general procedure for determining niobium and tantalum is the same as described earlier. The metal complexes are ignited to oxides and weighed. The results of the niobium and tantalum determination are given in Table II and III, respectively.

TABLE II  
*Precipitation of Niobium with N-PTBBHA*  
(pH = 5.5)

$\text{Nb}_2\text{O}_5$ taken mg	Wt of* Complex mg	$\text{Nb}_2\text{O}_5$ found mg	Error mg
15	51.52	14.97	-0.03
20	68.67	19.98	-0.02
25	85.86	25.02	+0.02
30	103.04	30.02	+0.02
35	120.20	34.96	-0.04

TABLE III  
*Precipitation of Tantalum with N-PTBBHA*  
(pH = 1.4)

$\text{Ta}_2\text{O}_5$ taken mg	$\text{Ta}_2\text{O}_5$ found mg	Error mg
10	9.96	-0.04
12	11.99	-0.01
16	16.01	+0.01
20	20.03	+0.03
24	23.98	-0.02

*Separation of Niobium and Tantalum Using N-PTBBHA*

A suitable aliquot containing a known amount of niobium and tantalum is taken in a 400 ml beaker and diluted to about 250 ml. The pH of the solution is adjusted to 5-6 with 20% ammonium acetate or 10% sulphuric acid. The solution is heated to 60 °C and niobium is precipitated by a slow addition of 1% alcoholic solution of the reagent. The precipitate is digested for about one hour over a boiling water bath and filtered through a quantitative filter paper, Whatman N. 542. The precipitate is washed thoroughly with 10 ml of a 0.1% solution of the reagent, warm water and finally with 10 ml of 10% aqueous ethanol. The precipitate is dried at 110 °C and ignited to oxide and weighed as niobium pentoxide.

The filtrate obtained after the precipitation of niobium is evaporated to 200 ml. Then pH of the solution is adjusted to 0.8-1.8 by adding 10% (v/v) sulphuric acid. The solution is heated to 70 °C and tantalum is precipitated and determined as described in general procedure. The results of the separation of niobium and tantalum are shown in Table IV.

TABLE IV

*Separation of Niobium and Tantalum with N-PTBBHA*  
(pH of precipitation of niobium and tantalum are 5.5 and 1.4 respectively)

Ta <sub>2</sub> O <sub>5</sub> taken mg	Nb <sub>2</sub> O <sub>5</sub> found mg	Error	Nb <sub>2</sub> O <sub>5</sub> taken mg	Ta <sub>2</sub> O <sub>5</sub> found mg	Error mg
15	14.98	-0.02	10	9.95	-0.05
20	19.99	-0.01	12	11.98	-0.02
25	25.02	+0.02	16	16.02	+0.02
30	29.97	-0.03	20	20.03	+0.03
35	35.04	+0.04	24	24.02	+0.02

## RESULTS AND DISCUSSION

*Effect of pH*

As given earlier, we have found that for quantitative precipitation of niobium with *N*-PTBBHA the optimum pH is from 3.5 to 6.5 and for tantalum it is from 0.8 to 1.8. For quantitative precipitation and separation of niobium from tantalum the pH should be kept in the range 5 to 6. At lower pH some tantalum also precipitated and at higher pH the precipitation of niobium is not quantitative. In the studies on separation of niobium from tantalum and other associated foreign ions the pH was maintained around 5.5. The precipitation was carried at about 60 °C.

For precipitation of tantalum and its separation from foreign ions the pH was maintained at around 1.4. At lower acidity a colloidal precipitate of tantalum was obtained which was difficult to filter. The precipitation of tantalum was slow at lower temperature, hence it was done at 70–80 °C.

For complete precipitation of the metal 25–30 mg of the reagent per mg of the metal is sufficient. The optimum concentration of the reagent in the final precipitation is about three times the theoretical quantity.

*Effect of Foreign Ions*

For making interference studies, an aliquot of the standard niobium or tantalum solution was mixed with a few ml of the ion whose effect was to be studied. The solution was diluted to about 250 ml and pH was adjusted by 20% ammonium acetate or 10% v/v H<sub>2</sub>SO<sub>4</sub>. The niobium and tantalum were then precipitated, washed and weighed as described before. 100 mg of each of the following ions do not interfere in the gravimetric determination of 15 mg of each of niobium and tantalum:

Alkali metals, Al (III), Bi(III), Ca(II), Cd(II), Cr(III), Cu(II), Fe(III), Hg(II), La(III), Mg(II), Ni(II), Pr(III), Th(IV), Ti(I), U(VI), Zn(II), Acetate, Carbonate, Citrate and tartrate.

Ti(IV) and Zr(IV) interfere with the determination of niobium and Zr(IV), Mo(VI), W(V) and PO<sub>4</sub><sup>3-</sup> interfere with the determination of tantalum with this reagent. No masking agents were employed for determination of niobium and tantalum in the presence of each other and of foreign ions. It may be noted that Zr(IV), Ti(IV) normally interfere with the determination of niobium

and tantalum with other reagents also<sup>3,5</sup>. The interference from these ions can be removed by using masking agents like EDTA and citrates. Larger quantities of the metal ions examined were also tolerated in several cases.

### Composition of the Complex

The composition of the niobium complex as determined by analysis is  $(C_{17}H_{18}NO_2)_3NbO$  and the conversion factor for niobium is 0.10176.

Tantalum complex is of indefinite composition, hence for gravimetry it is necessary to ignite it to pentoxide before weighing. Similar finding have been reported by other workers<sup>3,5</sup>.

### Conclusion

The determination of niobium and tantalum by means of *N*-phenyl-*p*-*terc*-butylbenzohydroxamic acid is satisfactory. The method is fairly selective and several foreign ions do not interfere.

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### SAŽETAK

#### *N*-Arihidroksamne kiseline kao gravimetrijski reagensi za niobij i tantal

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Sintetizirano je 26 novih *N*-arilhidroksamnih kiselina, koje su ispitane kao mogući reagensi za gravimetrijsko odjeljivanje i određivanje niobija i tantala. *N*-Fenil-*p*-(*terc*-butil)benzohidroksamna kiselina pokazala se kao najpogodniji reagens u tu svrhu. Za gravimetrijsko odjeljivanje niobija i tantala taloženjem s *N*-fenil-*p*-(*terc*-butil)benzohidroksamnom kiselinom potrebno je jedino ugađanje pH otopine bez upotrebe maskirajućih agensa. Niobij precipitira u području  $3,5 < \text{pH} < 6,5$ , a tantal precipitira u području  $0,8 < \text{pH} < 1,8$ . Hidroksamati niobija i tantala spaljuju se u okside i važu kao pentoksidi. Niobij je također određen direktnom odvagom odgo-varajućeg hidroksamata.

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