

**On the Stabilization of
Nb^V-Solutions by
Zr^{IV} and Hf^{IV}**

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Abstract. Niobium cannot be separated from zirconium or hafnium when these elements occur together in solution with common anions such as Cl⁻ and SO₄⁻⁻. This is ascribed to the copolymerisation of Nb^V and the hydrolyzed ionic species of Zr^{IV} and Hf^{IV} by which the colloidal particles are masked as Zr- and Hf-compounds.

In HCl the particles are positively charged as opposed to when they are in sulphate solution where the Zr- and Hf-sulphate complexes confer a negative charge. The two cases are considered separately.

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1. INTRODUCTION

During a work on recovery of Zr and Nb from a complex Zr-ore a crucial point was the separation of these elements. It was coped with by means of solvent extraction (1), but before that we studied the classic precipitation method which is based on the extreme proneness to hydrolytic decomposition shown by niobium solution. Weiss and Landecker (2) stated that precipitation is complete from perchloric acid solution and Silverman (3) used this principle for determining of Nb in steel. However, in our case the expected precipitation did not take place at all.

It turns out that this reaction may be less specific in the presence of certain elements such as titanium and zirconium. Marignac (4) has shown that by hydrolyzing a solution of Nb and Ti some Nb remains in solution while on the other hand some Ti is precipitated. This effect has been termed "loss of individuality".

As to Zr, Schoeller mentions that it may prevent the precipitation of Nb_2O_5, aq (5) and Chekmarev et al. (6) conclude from extraction data that Nb and hydrolyzed Zr probably form compounds in solution.

As the available information seemed rather vague we have carried out the investigation below of the Zr-Nb relationship in solution.

The similarity between Zr and Hf makes it natural to include Hf in this investigation. Thereby it becomes possible to use radioactive Hf^{181} as a tracer. Zr has no convenient radioactive isotopes.

During the work we found a marked difference in behaviour between systems in Cl^- and SO_4^{--} -based solutions. Consequently the two cases are considered separately.

Since the above-mentioned Zr-Nb ore also contained Ta, which is even more inclined to hydrolyze than Nb, limited attention has been paid to the behaviour of Ta.

1.1. Materials and methods

1.1.1. Preparation of solutions

Nb in hydrochloric acid

One gramme of KNbO_3 dissolved in 10 ml of H_2O is poured slowly while vigorously stirring into a beaker containing 20 ml of conc. HCl . The mixture is heated to the boiling point whereupon water is added until the solution is completely clear. This occurs when the volume is about 60 ml. All is then transferred to a Visking dialysis tube and allowed to dialyze in a large amount of 0.2 N HCl . After 24 hours a clear solution of $(\text{Nb}_2\text{O}_5, n\text{H}_2\text{O})_x$ remains in the tube.

Nb in sodium hydrogen sulphate

0.2 gr. of Nb_2O_5 is melted with 20 gr. of NaHSO_4 in a quartz crucible. After cooling to about 50°C a few ml of saturated NaHSO_4 -solution are added, followed by small additions of water while stirring and heating in between until all is dissolved. The resulting solution should be clear and nearly saturated with NaHSO_4 .

1.1.2. Turbidimetry

The optical density (OD) of the solutions has proved a reproducible measure of their stage of polymerisation. Using a Zeiss spectrophotometer, the OD was measured in 1 cm cells at 400 m μ chosen as a convenient wavelength.

1.1.3. Methods of separation

Dialysis

The Visking dialysis tube mentioned above is manufactured from cellulose by Union Carbide. A tube of 1/2 inch width with 24 Å pores was used. When the tube containing a solution is placed in water, small ions and molecules pass quickly through the membrane. With increasing molecular weight the mobility decreases, but it appears that a practically stationary condition is reached after 3 days. The 24 Å pores then retain particles larger than 10,000 MWU which comprises by far the greater part of the polymer species.

Precipitation

Hydrosols are often precipitated by admixture of organic solvents such as alcohol or acetone. This is true also of the above prepared hydrochloric Nb₂O₅-solution. ZrOCl₂ and HfOCl₂ in the concentration range used are fully soluble after addition of the double volume of acetone, which presents a method for their separation from the polymers. The sulphates of Zr and Hf are slightly soluble in acetone-water, so in the sulphate case this method is of no avail.

1.1.4. Analysis

Tagging with the radioactive isotopes Nb⁹⁵ and Hf¹⁸¹ allows us to determine the distribution of these elements by gamma-counting in a well-type NaI-crystal. Precipitates are ignited and weighed. With knowledge of the amount of starting material, it is then possible to calculate the composition of the products obtained.

1.2. RESULTS AND DISCUSSIONS

1.2.1. Behaviour of Nb in hydrochloric acid without or with addition of Zr and Hf

Measurement of stability by turbidimetry

At first the instability of pure Nb-solutions in dilute acid was established.

The prepared experimental solution, which at room temperature remains clear for weeks, was heated at 95°C with varying concentrations of HCl. The degree of instability was measured by the time elapsed before turbidity just becomes visible. The results shown in Table 1 reasonably agree with the finding by Nabivanets (7) that $Nb_2O_4^{++}$ ions tend to polymerize at H^+ -concentration below 2 N. If $ZrOCl_2$ or $HfOCl_2$ was added to the Nb-solution before heating, the stability was greatly changed.

Table I. Time elapsed before turbidity is just visible in 0.03 M Nb_2O_5 -solutions at 95°C.

HCl	Minutes
0.5 M	5
1.0	15 ;
1.5	90
2.5	200

Solutions were prepared with varying $[H^+]$ and two different ratios $[Zr]/[Nb]$ and $[Hf]/[Nb]$. After heating for 6 hours at 95°C the optical density of the solutions were measured. The results seen in figs. 1 and 2 show that the solutions stay clear inside an $[H^+]$ interval which becomes wider the higher the ratio $[Zr]/[Nb]$. The same holds true for Hf, but the stability interval is somewhat narrower.

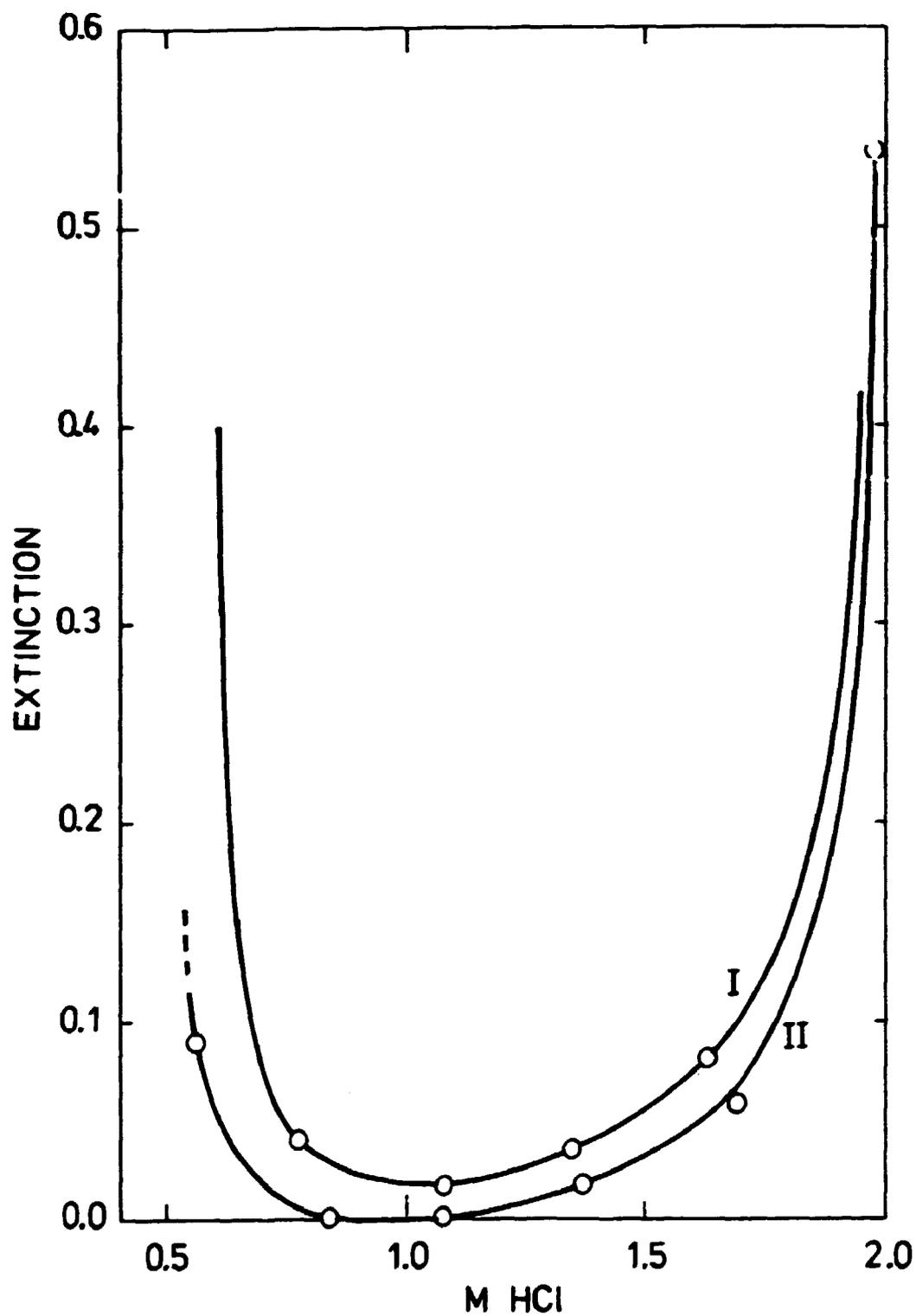


Figure 1. Optical density of solutions of NbV - ZrIV 0,028 M in Nb in varying concentrations of HCl after heating at 95°C for 6 hours. The respective unheated solutions were used for reference.

Curve I corresponds to the atomic ratio Zr/Nb = 0.50.
Curve II corresponds to the atomic ratio Zr/Nb = 0.62.

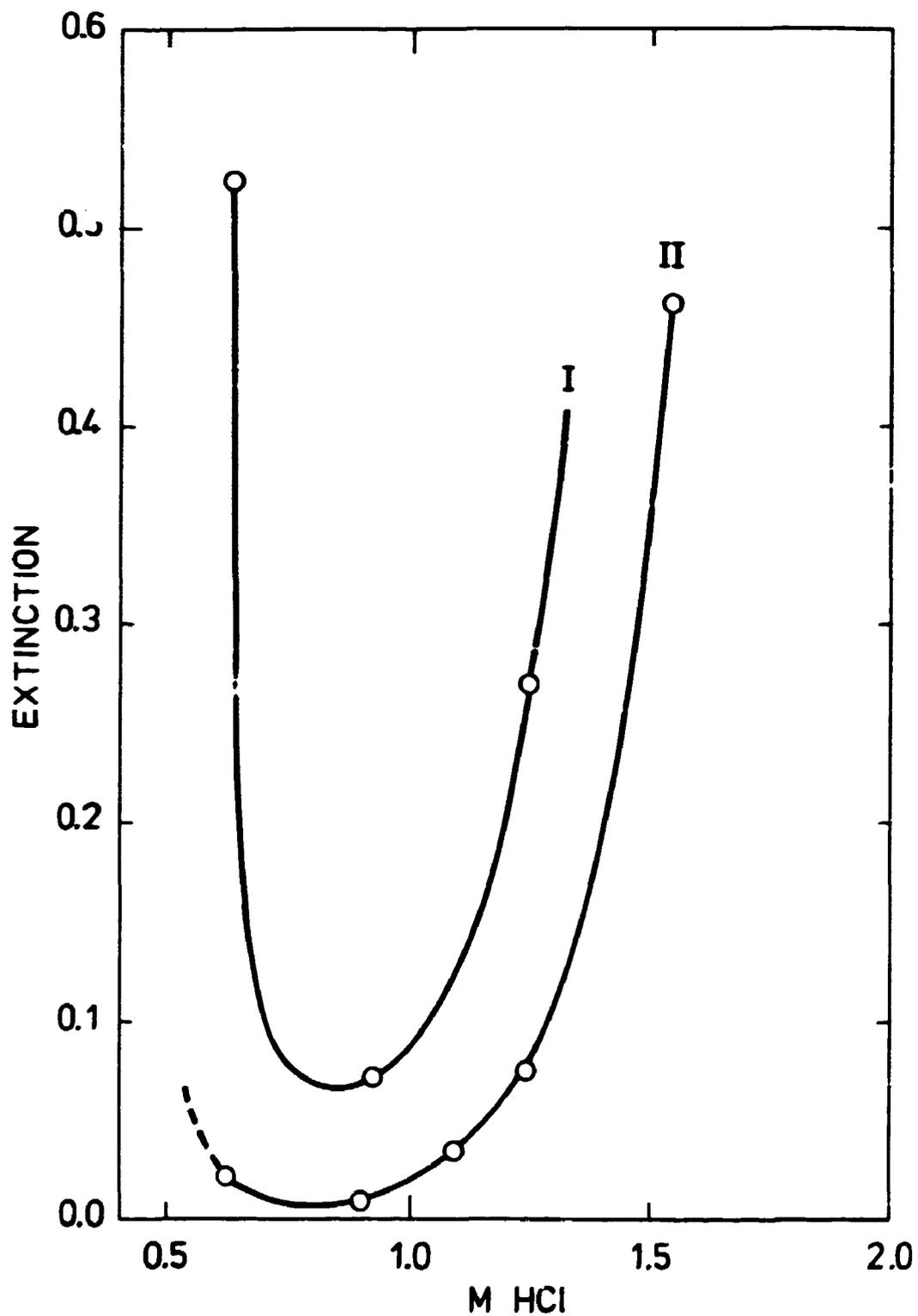


Figure 2. Optical density of solutions of $\text{NbV} - \text{HfIV}$ 0,0275 M in Nb at similar conditions as in fig. 1.

Curve I Hf/Nb (atomic) = 0.50.

Curve II Hf/Nb (atomic) = 0.62.

At the upper $[H^+]$ limit the solutions are turbid but fairly stable; at the lower $[H^+]$ limit the solutions coagulate. The precipitate contains Zr and Hf even though these metals are otherwise fully soluble at the acid concentration considered.

The hypothesis that hydrolyzed species of Zr^{IV} and Hf^{IV} copolymerize with Nb^V is supported by the following experiments:

Separation of the polymer by dialysis

HfOCl₂ containing radioactive Hf¹⁸¹ was mixed with Nb₂O₅-solution so as to obtain an atomic ratio Hf/Nb = 0.35 (6.5 g/l of HfO₂, 11.7 g/l of Nb₂O₅). This low ratio was chosen in order to make the effect of copolymerisation more perceptible. The HCl-concentration was 1.7 M.

Samples were subjected to four different treatments:

- 1) No heating.
- 2) Heating to 95°C during 3 minutes, then cooling to 25°C during 1 minute.
- 3) Heating to 95°C for 36 minutes.
- 4) Heating to 95°C for 60 minutes.

The samples were then placed in Visking tubes surrounded by an equal volume of pure 1.7 N HCl. After dialysis for 3 days the ratio between Hf inside and Hf outside was determined in each sample by gamma counting (see Table II).

Table II. Equilibrium ratio of $[Hf]$ in the inner and outer liquid after dialysis of differently treated mixtures with Nb₂O₅ in hydrochloric solution.

Treatment	$[Hf]_{in}/[Hf]_{out}$	Per cent of Hf trapped
No heating	1.0	0
Heating to 95°C during 3 minutes followed by cooling to 25°C during 1 minute	1.3	13
Heating to 95°C for 36 minutes	2.9	49
Heating to 95°C for 60 minutes	5.0	67

Hf-ions pass freely through the visking membrane as evidenced by the distribution 1:1 in the unheated sample. After heating to 95°C Hf is more or less retained within the dialysis tube depending on the duration of heating. This retention is ascribed to an association with the colloid particles of Nb₂O₅,aq. Assuming the same concentration of free Hf-ions on both sides of the membrane and remembering that the volumes are equal, we find the expression:

$$\frac{[\text{Hf}]_{\text{in}} - [\text{Hf}]_{\text{out}}}{[\text{Hf}]_{\text{in}} + [\text{Hf}]_{\text{out}}}$$

for the fraction of Hf which has joined the colloid particles. (See right-hand column, Table II)

Precipitation of the polymer by addition of acetone

HfOCl₂ containing Hf181 was mixed with Nb₂O₅ solution so as to obtain an atomic ratio Hf/Nb = 0.4 (4.2 g/l HfO₂, 6.6 g/l Nb₂O₅). The HCl-concentration was 0.85 N.

The mixture was heated to 95°C and samples taken after 10, 34, and 60 minutes. Each sample was added to the double volume of acetone; the precipitates were collected and analysed with the results shown in Table III.

Table III. Composition of acetone precipitate from Hf-containing Nb₂O₅-solutions in HCl, which have been heated for different periods.

Time of heating at 95°C	Nb and Hf in acetone precipitate				Atomic ratio Hf/Nb in ppt.
	milligrammes		per cent of initial amount in solution		
	Nb ₂ O ₅	HfO ₂	Nb ₂ O ₅	HfO ₂	
Minutes	Nb ₂ O ₅	HfO ₂	Nb ₂ O ₅	HfO ₂	
10	6.87	1.13	50	13	0.104
34	10.92	4.68	80	54	0.271
60	11.94	7.36	87	85	0.391

In an analogous experiment solutions with the same Nb₂O₅ content but different Hf/Nb ratios were all heated to 95°C for 60 minutes before precipitation by addition of the double volume of acetone. The composition of the precipitates are shown in Table IV.

Table IV. Composition of acetone precipitate from Hf-containing Nb₂O₅-solutions of varying Hf/Nb-ratio, all heated to 95°C for 60 minutes.

Time of heating at 95°C	Nb and Hf in acetone precipitate				Atomic ratio Hf/Nb in ppt.
	milligrammes		per cent of initial amount in solution		
	Nb ₂ O ₅	HfO ₂	Nb ₂ O ₅	HfO ₂	
Minutes					
0.50	38.8	23.4	81	60	0.38
0.66	31.5	22.4	66	43	0.45
0.83	18.4	17.5	39	27	0.60

It appears that the ratio Hf/Nb of the precipitate keeps pace with that of the solution. On the other hand the absolute amount of precipitate decreases with increasing Hf-content.

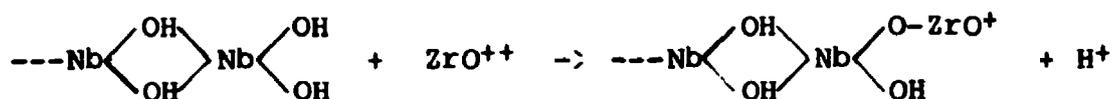
General properties of the polymer

The silky residue left by gentle evaporation of a dilute hydrochloric solution of NbV- ZrIV as well as the curdled solid obtained by addition of acetone can be redissolved in water. When NH₃ is added to the solution a "hydroxide" is formed, which can be redissolved in HCl. Electromigration confirms that the niobium is contained in positively charged particles.

Discussion

It was demonstrated that in solutions of NbV with HCl-concentrations less than 2N a hydrolytic polymerisation proceeds until

turbidity or eventually a precipitate is produced. The inhibitory effect of ZrO^{++} or HfO^{++} is assumed to be due to the reaction:



by which the colloid particles are studded with ZrO^+ or HfO^+ . The resulting increase in charge density leads to a virtual stability of the solution.

The precipitate formed by addition of excess NH_3 is soluble in HCl , indicating that a majority of bonds are similar to those occurring in Zr- and Hf-hydroxide.

The upper and the lower $[H^+]$ -limits of the stability interval in figs. 1 and 2 are caused by decreasing charge of the colloidal particles, but for different reasons. High $[H^+]$ leads to a gradual rupture of the -O-bridges whereby ZrO^{++} or HfO^{++} are split off.

The solution becomes more and more turbid, but keeps fairly stable. At low $[H^+]$ the positive charges are neutralized by OH^- , and coagulation occurs within a narrow $[H^+]$ -range. Since the coagulate cannot be redissolved in acids, it is assumed to be a Nb_2O_5 ,aq-polymer. The co-precipitated Zr and Hf are trapped in the structure by occlusion and are thus also made insoluble. By comparing figs. 1 and 2 it appears that the stability interval of the Hf-compounds is shifted towards less $[H^+]$ corresponding to the slightly more electropositive character of Hf.

* The symbols ZrO^{++} and HfO^{++} are used for convenience to designate the more complex positive ions actually occurring.

The results of the dialysis experiment, shown in Table II, confirm that the HfO^{++-} ions are caught by the colloid particles and further it shows that this process continues for more than 60 minutes at 95°C . The same is evidenced by the precipitation experiment (Table III). Here the sorting of particles by size is brought about by the acetone-water solvent. The amount of Nb precipitated is seen to increase with time, which suggests that the particles grow during the heating period. This is due to the aforementioned low Hf/Nb-ratio in these experiments. Table IV shows that a higher Hf/Nb leads to a smaller amount of Nb precipitated. This indicates a smaller particle size and accordingly a higher surface-to-volume ratio the size being maintained by the hafnium covering.

1.2.2. Behaviour of Nb in NaHSO_4 -solution without and with addition of Zr and Hf

Stabilization of Nb-solution by precipitation of hydroxide and redissolution

If the prepared solution of Nb in concentrated NaHSO_4 is diluted, it will polymerize immediately. Simple addition of Zr- or Hf-salts will not prevent this polymerisation. If, however, ZrOCl_2 or HfOCl_2 is mixed with concentrated NaHSO_4 -Nb-solution and the mixture is poured into an excess of NH_4OH , then the precipitate formed can subsequently be dissolved in H_2SO_4 to form a stable solution. The same is obtained by melting Nb_2O_5 and ZrO_2 together with NaHSO_4 from the beginning.

The prepared solution of Nb_2O_5 in NaHSO_4 was divided in eight equal samples which were supplied with varying amounts of ZrOCl_2 or HfOCl_2 . After homogenization NH_4OH was added, whereupon the resulting precipitates were washed, redissolved in 2 ml of 2 M H_2SO_4 each, supplied with 2 ml of 2M Na_2SO_4 and with water to make up a final volume of 8 ml.

After heating to 95°C for 6 hours it appeared that stabilization of these mixtures was obtained for the atomic ratio $Zr/Nb > 3$ and $Hf/Nb > 2$. Figure 3 shows the plot of the optical density versus the respective value of Zr/Nb and Hf/Nb .

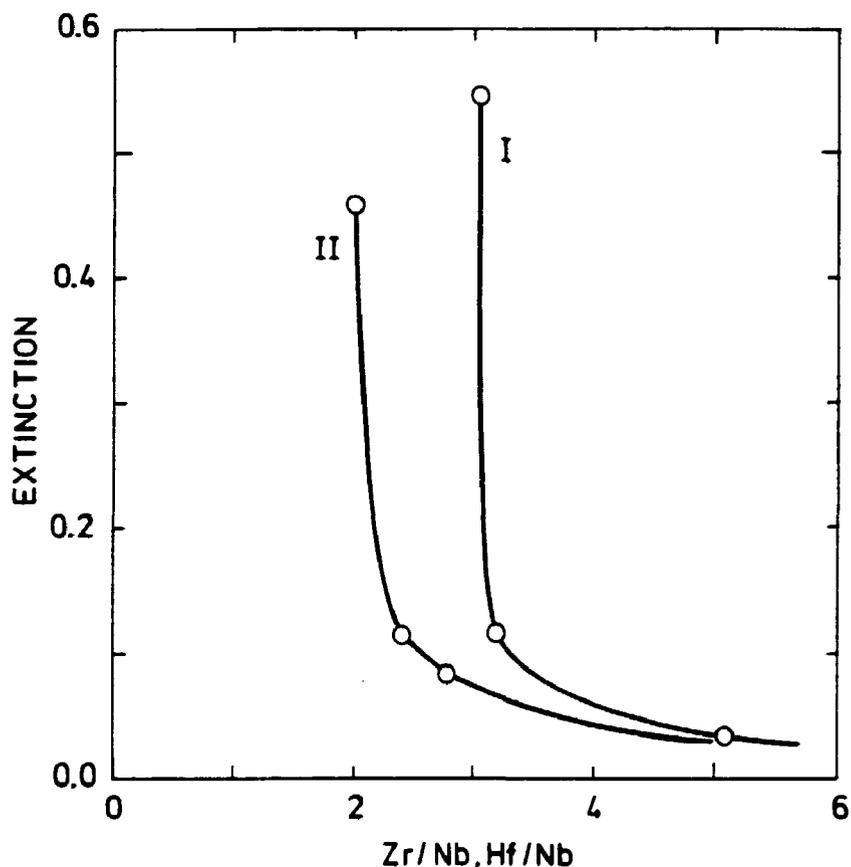


Figure 3. I Optical density of sulphate solutions of NbV - ZrIV 0,0235 M in Nb at pH = 1.8 at varying atomic ratio Zr/Nb.

II Optical density of solutions of the corresponding Hf-compound.

Separation of the polymer by dialysis

Excess of SO_4^{--} (hf,Zr) O^{++} and H^+ can be removed by dialysis. If this is done stepwise, alternating with heating periods, solutions are obtained which remain stable up to approx. pH=1.8, the highest value permissible to retain a clear solution of zirconium sulphate (8).

These solutions of pure, colloid Nb, Zr- or Nb, Hf-sulphate will coagulate by addition of only a slight amount of free H^+ unless the SO_4^{--} -concentration is simultaneously increased. It appears that in the Zr-case the ratio $[H^+]/[SO_4^{--}]$ must be less than 1.2, and in the Hf-case less than 1.0 if the solutions should stay clear for 6 hours at 95°C.

General properties of the polymer

Voluntary evaporation leaves a clear glass that breaks into scales with a conchoidal fracture. It redissolves easily in water from where it may again be precipitated by addition of acetone. This property is not as useful as in the chloride case, since also zirconium sulphate as well as sulphate in general are precipitated from aqueous solutions by acetone. Electromigration shows that the colloidal particles are negatively charged.

Discussion

The positively charged $(Nb_mZr_n(OH)_xH_2O)_y^{5m+4n-x}$ particles will upon addition of SO_4^{--} form negatively charged sulphate complexes, and the presence at the same time of particles of opposite charges leads to coagulation. Therefore a particular preparation method must be employed.

In the strong $NaHSO_4$ -solution, Nb and Zr or Hf are prevented from getting in close contact by the complexing sulphate-ligands. Upon dilution Nb will hydrolyze first and polymerize without being protected by Zr or Hf. With the addition of excess of NH_3 copolymerisation becomes possible. When the redissolved precipitate is cured at suitable concentrations of H^+ and SO_4^{--} a copolymerized Zr or Hf sulphate is formed, which presumably surrounds the Nb_2O_5 particles.

Since aggregation is prevented by maintaining a negative charge on the particles, it is evident that sulphate ions act as a stabilizer, whereas hydrogen ions have the reverse effect.

The higher SO_4^{--} - concentration required in the Hf-case is probably due to a lower complexity constant of hafnium sulphate as compared with zirconium sulphate. On the other hand, there seems to be no obvious reason for the marked difference between the atomic ratios Zr/Nb and Hf/Nb, which are just sufficient to stabilize the respective solutions (fig. 3).

1.2.3. Behaviour of Nb in carbonate solutions

It is well known that ZrO^{++} forms soluble carbonate complexes. This is also true for the Zr-Nb compounds, although with some reservations.

20 ml solutions of the chloride and the sulphate, each containing 10 mg of Nb_2O_5 and 100 mg of ZrO_2 , were added to 20 ml 1 M Na_2CO_3 . In the Cl^- -case a precipitate was seen immediately and in the SO_4^{--} -case a few seconds later. The same experiments with 20 ml in NH_4HCO_3 instead of Na_2CO_3 yielded a precipitate in the Cl^- -case after 1 hour, but not before 24 hours in the SO_4^{--} -case. Tagging with radioactive Nb-95 made it simple to determine the Nb-distribution after precipitation. Table V shows that a considerable fraction of the niobium in all cases remains in the solution.

Table V. The figures indicate the percentage of Nb left in solution after precipitation with the reagents quoted and standing for 24 hours.

Anions	Per cent of original Nb in solution	
	Sodium carbonate	Ammonium bicarbonate
Cl^-	15	32
SO_4^{--}	36	50

Discussion

The missing precipitation of Nb by carbonate, which is otherwise complete even in the presence of complexing agents, appears to be a strong evidence of the masking effect exerted by ZrO^{++} on colloidal Nb_2O_5 .

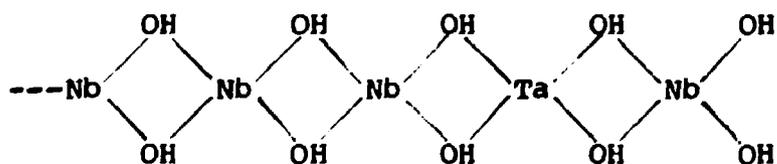
The transformation into the carbonate form takes place with a smaller precipitation loss when the particles are negatively charged beforehand, as in the sulphate solution. Further, the solubility is better in ammonium bicarbonate than in sodium carbonate because of the lower OH^- -concentration.

1.2.4. Tantalum compounds

It was attempted to prepare solutions of Ta stabilized with Zr analogous with those of Nb, but they appeared always to be turbid, probably because Ta is even more prone to hydrolyze than Nb. However, with Ta, Nb and Zr in the atomic ratio 0.2:1:5 clear stable solutions can be obtained both in dilute hydrochloric and sulphate media.

The oxides are melted together with $NaHSO_4$ and the cooled mass dissolved as described under preparation of solutions in $NaHSO_4$. Conversion to the chloride form is accomplished by precipitation by NH_4OH and washing of the hydroxide followed by addition of HCl in an amount just sufficient to dissolve it.

It has been known for a long time (5) that in mixtures of Nb and Ta a certain amount of one of these elements can be masked as the other. Lassner and PUSchel (9) indicate the following scheme for forming a heteropolymer:



Increasing the share of Ta leads to turbid solutions. It may be expected that colloidal particles of the composition shown require a higher $[ZrO^{++}]$ than those of pure Nb_2O_5, aq in order to prevent more extensive polymerisation.

1.3. CONCLUSIONS

In solutions of weakly complexing anions, Nb_2O_5, aq adsorbs ionic species of Zr^{IV} and Hf^{IV} . Thereby the solutions are stabilized and to a certain extent assume the behaviour of Zr- and Hf- compounds in a H^+ domain where they would otherwise undergo hydrolytic precipitation. In the presence of sulphate, complex formation causes a negative charge of the particles; for this reason the solution is sensitive to H^+ unless it is stabilized by an excess of SO_4^{--} .

The higher the Zr/Nb ratio the more Nb loses its chemical individuality; thus it becomes able to follow Zr in carbonate solution and in phase distribution equilibria (solvent extraction).

Tantalum, to the extent it is masked by niobium, behaves in the same manner.

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In HCl the particles are positively charged as opposed to when they are in sulphate solution where the Zr- and Hf-sulphate complexes confer a negative charge. The two cases are considered separately.

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