

# Studies on the Formation of Thorium Niobates as a Function of pH.

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A estequiometria de compostos formados pela interação de nitrato de tório e niobiato de potássio a níveis específicos de pH 12,0; 10,8 e 7,6 foi estudada com emprego de técnicas eletrométricas envolvendo titulações po pH-métricas e condutométricas. As nítidas inflexões e quebras nas curvas fornecem perfeita evidência da formação e precipitação de orto-  $3\text{ThO}_2 \cdot 2\text{Nb}_2\text{O}_5$  e hexa- $2\text{ThO}_2 \cdot 3\text{Nb}_2\text{O}_5$  niobatos de tório, nas proximidades dos valores de pH iguais, respectivamente, a 7,8 e 6,4. Foram realizadas, também, investigações analíticas dos compostos, confirmando os resultados dos estudos eletrométricos.

The stoichiometry of the compounds formed by the interaction of thorium nitrate and potassium niobate at specific pH levels 12.0, 10.8 and 7.6 have been studied by electrometric techniques involving pH and conductometric titrations. The well defined breaks and inflections in the titration curves provide cogent evidence for the formation and precipitation of thorium ortho- $3\text{ThO}_2 \cdot 2\text{Nb}_2\text{O}_5$  and hexa- $2\text{ThO}_2 \cdot 3\text{Nb}_2\text{O}_5$  niobates in the vicinity of pH 7.8 and 6.4 respectively. Analytical investigations of the compounds have also been carried out which substantiate the results of the electrometric study.

**Key words:** *thorium niobates; electrometric study.*

## Introduction

An outstanding character of niobates is their strong tendency to form condensed ions in solutions<sup>1,2</sup> and from these polyniobates crystallize, depending upon the  $\text{H}^+$  concentration which plays an important role on the aggregation process. Some of these compounds have ferroelectric and piezoelectric properties and have been found to be attractive alternatives to quartz as *frequency filters* in communications devices. A number of nonstoichiometric *bronzes* are also known<sup>3</sup> which like tungsten bronzes, are characterized by high electrical conductivity and characteristic colours. The great importance of niobates interested the author to start investigations on their formation.

In an earlier publication<sup>4</sup> the author has shown that the solution containing the species  $\text{NbO}_3^{3-}$  on treatment with dilute acid decomposes into  $\text{Nb}_2\text{O}_5 \cdot \text{aq}$ . via formation of various intermediate anions depending upon the hydrogen ion concentration of the medium. In view of the interesting results obtained, it was considered worthwhile to investigate precisely the composition of thorium niobates obtained by the interaction of thorium nitrate on various niobate species at different pH levels by means of electrometric techniques which have provided more conclusive evidences on the composition of these and related compounds<sup>5</sup>. There is however, no reference available in the literature on the study of thorium niobates as a function of pH.

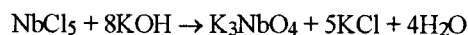
## Experimental

Nitric acid, KOH,  $\text{NbCl}_5$  and  $\text{Th}(\text{NO}_3)_4$  of extra-pure grade were used and their solutions were prepared in carbonate-free conductivity water. The solution of potassium orthoniobate was prepared by digesting  $\text{NbCl}_5$  in KOH solution of required strength. The concentration of  $\text{K}_3\text{NbO}_4$  solution was further verified by determining the niobium as pentoxide<sup>2b</sup>. Calculated amounts of  $\text{HNO}_3$  were then added to  $\text{k}_3\text{SbO}_4$  solutions in definite molecular proportions to vary the pH.

pH and conductometric measurements were carried out as usual<sup>5</sup>. Using different concentrations of the reactants, a series of pH and conductometric titrations were performed both by direct and reverse methods. Similar concentrations of the reactants were taken in the two techniques for comparison of the results.

## Results and Discussion:

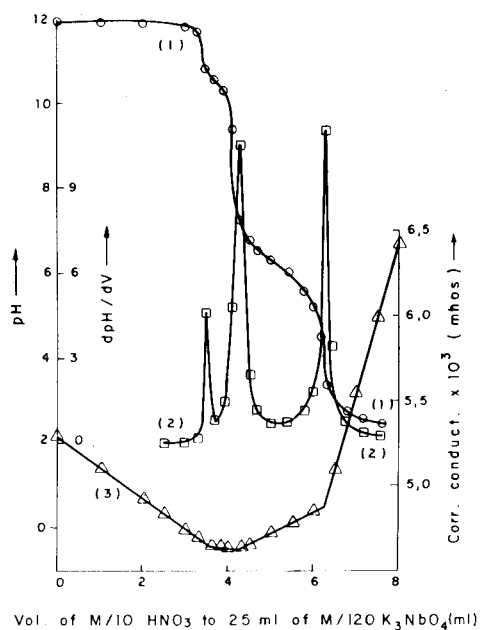
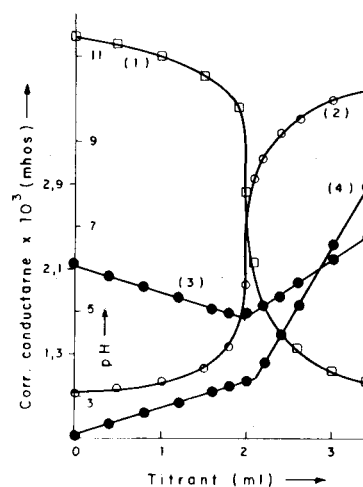
Potassium niobate solution was prepared by digesting  $\text{NbCl}_5$  in a KOH solution in 1:8 molecular ratio.

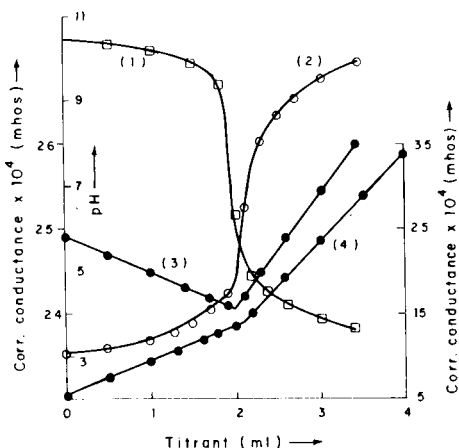


When acid ( $\text{HNO}_3$ ,  $\text{HCl}$  or  $\text{CH}_3\text{COOH}$ ) is gradually added to  $\text{K}_3\text{NbO}_4$ , it changes to hexaniobate  $\text{Nb}_6\text{O}^{8-}$ , meta-niobate  $\text{NbO}_3^-$  and finally to the oxide  $\text{Nb}_2\text{O}_5 \cdot \text{aq}$ . around pH

**Table 1:** Summary of results of the electrometric titrations. Volume of titre solution taken in the cell = 25 ml.

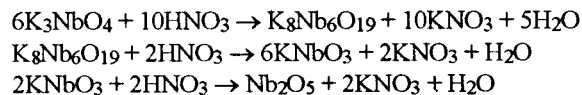
Molarity of Solutions	Equivalence Points (ml)		Formula Supported			
	Calc.	Observed from	pH	COND.		
Th(NO <sub>3</sub> ) <sub>4</sub> K <sub>3</sub> NbO <sub>4</sub>	Direct titrations, Fig. 2, curves 1 and 3					
	M/20	M/175	2.14	2.15	2.15	3ThO <sub>2</sub> .2Nb <sub>2</sub> O <sub>5</sub>
	M/40	M/375	2.00	2.00	2.00	
	M/60	M/500	2.25	2.25	2.30	
	Reverse titrations, Fig. 2, curves 2 and 4					
	M/500	M/30	2.00	2.00	2.00	3ThO <sub>2</sub> .2Nb <sub>2</sub> O <sub>5</sub>
	M/800	M/50	2.08	2.05	2.05	
	M/1000	M/70	2.33	2.35	2.30	
	Th(NO <sub>3</sub> ) <sub>4</sub> K <sub>8</sub> Nb <sub>6</sub> O <sub>19</sub>	Direct titrations, Fig. 3, curves 1 and 3				
		M/20	M/500	2.00	2.00	2.00
M/40		M/900	2.22	2.20	2.20	
M/60		M/1400	2.14	2.15	2.15	
Reverse titrations, Fig. 3, curves 2 and 4						
M/250		M/50	2.50	2.50	2.50	2ThO <sub>2</sub> .3Nb <sub>2</sub> O <sub>5</sub>
M/600		M/100	2.08	2.10	2.10	
M/800		M/150	2.34	2.35	2.35	

**Figure 1:** pH (curves 1 and 2) and conductometric (curve 3) titrations between HNO<sub>3</sub> and K<sub>3</sub>NbO<sub>4</sub>.**Figure 2:** Ortho-niobate titrations. Curves (1) and (3): M/40 Th(NO<sub>3</sub>)<sub>4</sub> added to 25 ml of M/375 K<sub>3</sub>NbO<sub>4</sub>. Curves (2) and (4): M/50 K<sub>3</sub>NbO<sub>4</sub> added to 25 ml of M/800 Th(NO<sub>3</sub>)<sub>4</sub>.

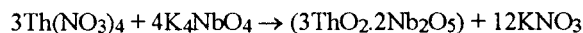


**Figure 3:** Hexa-niobate titrations. Curves (1) and (3):  $M/20$   $Th(NO_3)_4$  added to 25 ml. of  $M/500$   $K_8Nb_6O_{19}$ . Curves (2) and (4):  $M/100$   $K_8Nb_6O_{19}$  added to 25 ml of  $M/600$   $Th(NO_3)_4$ .

10.8, 7.6 and 3.8 corresponding to the ratios 3Nb:5H, 3Nb:6H and 3Nb:9H, respectively<sup>2a,4</sup>. These studies<sup>4</sup> did not evidence the existence of the other forms, such as  $HNb_6O_{19}^{7-}$  and  $Nb_2O_4^{7-}$ , as reported in the literature<sup>2a,6</sup>. The behaviour of  $K_3NbO_4$  with  $HNO_3$  is shown in Fig. 1. Curve 1 illustrates the pH titration result showing three inflections at 3Nb:5H, 3Nb:6H and 3Nb:9H corresponding to the formation of  $Nb_6O_8^{19-}$ ,  $NbO_3$  and  $Nb_2O_5.aq.$ , respectively. The position of the inflections is further checked by  $dpH/dV$  graphs (curve 2). Similar results are obtained by conductometric titrations (curve 3). The reactions can be represented<sup>2a,4</sup> by the following equations:



**Ortho-niobate Titrations:** Using different concentrations of thorium nitrate (pH 3.0) and  $K_3NbO_4$  (pH 12.0), a series of pH titrations was carried out. In direct titrations (Fig. 2, curve 1), when  $K_3NbO_4$  solution was used as titre, a gradual decrease in pH value was observed till at the stoichiometric end-point (the stage at which the reaction ends if simple double decomposition takes place), a sharp downward jump in pH was observed when the molar ratio of  $Th^{4+}:NbO_3^{3-}$  is as 3:4, corresponding to the formation of white coloured precipitate of thorium ortho-niobate,  $3ThO_2.2Nb_2O_5$ , in the neighbourhood of pH 7.8. This sharp fall in pH value is the result of removal of the last traces of strongly alkaline  $NbO_3^{3-}$  ions in the form of  $3NbO_2.2Nb_2O_5$  precipitate. In the case of inverse titrations (Fig. 2, curve 2) the pH at first gradually increases till in the vicinity of the end-point, when the last traces of thorium ions have been removed by precipitation, further addition of alkali niobate causes a marked upward jump in pH and the inflection corresponds to the molar ratio for the formation of  $3ThO_2.2Nb_2O_5$  according to the reaction:



Employing similar concentrations of the reactants, direct, (Fig. 2, curve 3) and reverse (Fig. 2, curve 4) conductometric titrations between thorium nitrate and potassium ortho-niobate gave well-defined breaks at 3:4 molar ratio of  $Th^{4+}:NbO_3^{3-}$ , confirming the formation of thorium ortho-niobate. In direct titrations, when thorium nitrate solution was added from the microburette to the solution of alkali ortho-niobate, a decrease in conductance was observed (due to

**Table 2:** Summary of the analytical results.

Proposed Formula Of The Compound	Mode of Synthesis	Analysis %: Found(calculated)	
		Th	Nb
Analysis of the ortho-niobate precipitates			
$3ThO_2.2Nb_2O_5$	Direct*	52.53 (52.59)	28.10 (28.07)
	Reverse*	52.62	28.05
Analysis of the hexa-niobate precipitates			
$2ThO_2.3Nb_2O_5$	Direct	34.96 (35.01)	42.11 (42.05)
	Reverse	35.04	42.03

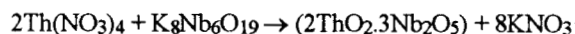
\* Direct - Thorium nitrate solution added to potassium ortho-niobate solution.

\* Reverse - Potassium ortho-niobate solution added to thorium nitrate solution.

removal of the

$\text{NbO}^{3-}_4$  ion in the form of a precipitate) till the stoichiometric end-point after which conductance increased with the increase in ionic concentration. In case of reverse titrations, as comparatively more mobile potassium ions are introduced in the cell, the conductance values show a gradual increase from the very beginning of the titration.

**Hexa-niobate Titrations:** The slope and nature of pH and conductometric titrations curves (Fig. 3) between potassium hexa-niobate and thorium nitrate are similar to those of the ortho-niobate. The curves provide well-defined inflections at molar ratio 2:1 of  $\text{Th}^{4+}:\text{Nb}_6\text{O}^{8-}_{29}$  suggesting the formation of  $2\text{ThO}_2 \cdot 3\text{Nb}_2\text{O}_5$  around pH 6.4. The reaction can be represented by the following equation:



The reaction between thorium nitrate and potassium meta-niobate was also studied by pH and conductometric titrations but the curves do not exhibit any appreciable breaks and inflections. This may be ascribed to small difference in pH values of the reactants; and the presence of potassium nitrate in appreciable amounts preventing the occurrence of breaks in conductometric titration curves.

**Analytical:** The precipitates obtained at the end-points of the titrations were also analysed by classical methods. Thorium<sup>7</sup> was determined as oxalate and niobium<sup>8</sup> as oxide. The results obtained (see Table 2) confirm those obtained by the electrometric study. The contents of the elements present in the precipitates of thorium niobates were also analysed by atomic absorption spectrophotometer (Varian, AA-175) which gave similar results as obtained by the classical methods.

The present electrometric and analytical investigations confirm the formation of  $3\text{ThO}_2 \cdot 2\text{Nb}_2\text{O}_5$  and  $2\text{ThO}_2 \cdot 3\text{Nb}_2\text{O}_5$  in the vicinity of pH 7.8 and 6.4 respectively. As the structure of these compounds is not known they are represented in the form of double oxides.

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