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ELECTROMETRIC INVESTIGATIONS ON THE FORMATION OF CERIUM(III) TUNGSTATES AS A FUNCTION OF pH

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ABSTRACT: The course of reaction between cerium(III) nitrate and different sodium tungstates (Na_2WO_4, $Na_{10}W_{12}O_{41}$ and $Na_6W_{12}O_{39}$) has been followed by means of pH and conductometric titrations between the reactants at different pH levels, in aqueous and alcoholic media, with each of the reagents alternatively used as titrant. The electrometric experiments provide definite evidence of the formation of *normal*-$Ce_2O_3.3WO_3$ and *para*- $5Ce_2O_3.36WO_3$ tungstates of cerium in the vicinity of pH 6.2 and 5.3. The formation of normal tungstate is almost quantitative and the pH titrations offer a simple means for determination of cerium(III) or tungstate solutions at suitable concentrations and pH range.

KEYWORDS: Tungstates, cerium(III), electrometry.

Introduction

In aqueous solutions molybdates, tungstates, vanadates, and to smaller extent, niobates, tantalates, and chromates, undergo complex hydrolysis-polymerization reactions upon acidification. The major species generated by such reactions are isopolyanions, of which $Cr_2O_7^{2-}$, and heptamolybdate, $Mo_7O_{24}^{6-}$, are well-characterized examples[7]. There is no doubt that the formation of isopolytungstates on acidification of the solutions of normal tungstate, WO_4^{2-}, is the most complex and the least understood system[5]. The difficulties are at least three fold. Firstly there is the instability to obtain well-defined crystalline salts with many of the isopolytungstate anions, and hence the structural basis remains somewhat speculative. Secondly many workers have used solutions containing buffers, many of which contain anions that preferentially form complexes with the tetrahedrally coordinated normal tungstate rather than the octahedrally coordinated polytungstates. Thirdly the rates of formation of some isopolytungstates are very slow[2,3].

Despite extensive investigations the problem of number and composition of the polymeric species has not been completely solved. It is reported[4,6] that even in a solution initially containing only orthotungstate and acid may exist eight types of species with $H^+:WO_4^{2-}$ ratio as 1:3, 2:3, 7:6, 3:2 and 2:1. The degree of aggregation in solutions increases as the pH is lowered, and numerous tungstates $M_2^IO.nWO_3.mH_2O$, differing in the value of *n*, have been reported from the solutions at different pH's[1].

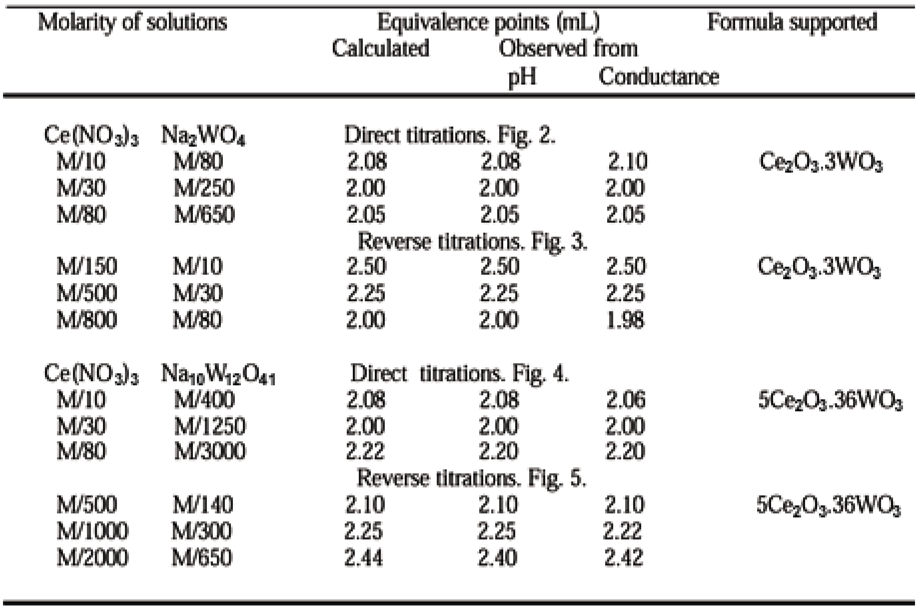
In earlier publications the authors have reported the effect of pH variation on tungstate anions[10] and formation of different chromium tungstates[12]. In view of the interesting results obtained it was considered worthwhile to investigate the composition of cerium tungstates obtained by action of Ce^{3+} on different tungstate anions at specific pH levels by means of electrometric techniques, which have provided conclusive evidences on thiotungstates[9], thiomolybdates[8], molybdates[14] and vanadates[13]

Experimental

$Na_2WO_4.2H_2O$, $Ce(NO_3)_3$, HNO_3 and ethanol of extra-pure grade were used, and their solutions were prepared with deionized distilled water. Concentration of the sodium tungstate solution was further verified by tannin-antipyrine method[16a]. The variations of pH of Na_2WO_4 solutions were obtained by progressive additions of determined quantities of nitric acid[10].

The pH-meter, conductometer, electrodes and titration cells were used as reported earlier[11]. Stoichiometric points in pH titrations were obtained from the sharp inflections in the titration curves. Conductivity values after correcting for dilution effect were plotted as a function of mL of titrant solution added and the end-points were judged from the breaks in titration curves. 25.00 mL of solution was taken in the cell each time and thermostated at 25.0± 0.1°C. The same strengths of solutions were employed in both the techniques for the sake of comparison of results. The electrometric titration results are summarized in Table 1.

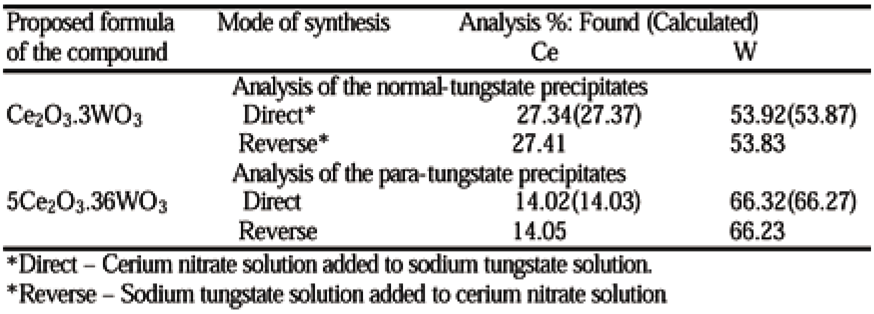
Table 1 - Summary of results of electrometric study.
Volume of titre solution taken in the cell = 25.00 mL.



Molarity of solutions		Equivalence points (mL) Calculated	Observed from pH	Conductance	Formula supported
$Ce(NO_3)_3$	Na_2WO_4	Direct titrations. Fig. 2.			
M/10	M/80	2.08	2.08	2.10	$Ce_2O_3.3WO_3$
M/30	M/250	2.00	2.00	2.00	
M/80	M/650	2.05	2.05	2.05	
		Reverse titrations. Fig. 3.			
M/150	M/10	2.50	2.50	2.50	$Ce_2O_3.3WO_3$
M/500	M/30	2.25	2.25	2.25	
M/800	M/80	2.00	2.00	1.98	
$Ce(NO_3)_3$	$Na_{10}W_{12}O_{41}$	Direct titrations. Fig. 4.			
M/10	M/400	2.08	2.08	2.06	$5Ce_2O_3.36WO_3$
M/30	M/1250	2.00	2.00	2.00	
M/80	M/3000	2.22	2.20	2.20	
		Reverse titrations. Fig. 5.			
M/500	M/140	2.10	2.10	2.10	$5Ce_2O_3.36WO_3$
M/1000	M/300	2.25	2.25	2.22	
M/2000	M/650	2.44	2.40	2.42	

Analytical investigations were also carried out with a view to substantiate the electrometric results. Different cerium tungstates were precipitated by mixing solutions of sodium tungstate at specific pH levels 8.0, 5.9 and 4.0 with cerium nitrate. Tungsten[16a] was determined as oxinate and cerium[16b] volumetrically. From the proportions of cerium and tungsten in the compounds thus obtained their composition was established. The results are summarized in Table 2.

Table 2 - Summary of analytical results of the precipitates.



Proposed formula of the compound	Mode of synthesis	Analysis %: Found (Calculated) Ce	W
	Analysis of the normal-tungstate precipitates		
$Ce_2O_3.3WO_3$	Direct*	27.34(27.37)	53.92(53.87)
	Reverse*	27.41	53.83
	Analysis of the para-tungstate precipitates		
$5Ce_2O_3.36WO_3$	Direct	14.02(14.03)	66.32(66.27)
	Reverse	14.05	66.23

*Direct – Cerium nitrate solution added to sodium tungstate solution.
*Reverse – Sodium tungstate solution added to cerium nitrate solution

Results and discussion

The solution of Na_2WO_4 was prepared in deionized distilled water. When nitric acid is gradually added to Na_2WO_4 solution, it changes to sodium paratungstate $Na_{10}W_{12}O_{41}$ and metatungstate $Na_6W_{12}O_{39}$ around pH 5.9 and 4.0 corresponding to the ratios 6W:7H and 6W:9H, respectively[10]. Fig. 1 illustrates the curves of pH and conductometric titrations of Na_2WO_4 solution with nitric acid. The pH titration curve shows two inflections at 6W:7H and 6W:9H corresponding to the formation of $Na_{10}W_{12}O_{41}$ and $Na_6W_{12}O_{39}$, respectively. The position of the inflections is further checked by the curve of dpH/dV. Similar results are obtained by conductometric titrations (Fig. 1). The stepwise degradation of Na_2WO_4 by the gradual addition of HNO_3 can be represented by the following equations[10]:

$12Na_2WO_4 + 14HNO_3 = Na_{10}W_{12}O_{41} + 14NaNO_3 + 7H_2O$

$12Na_2WO_4 + 18HNO_3 = Na_6W_{12}O_{39} + 18NaNO_3 + 9H_2O$

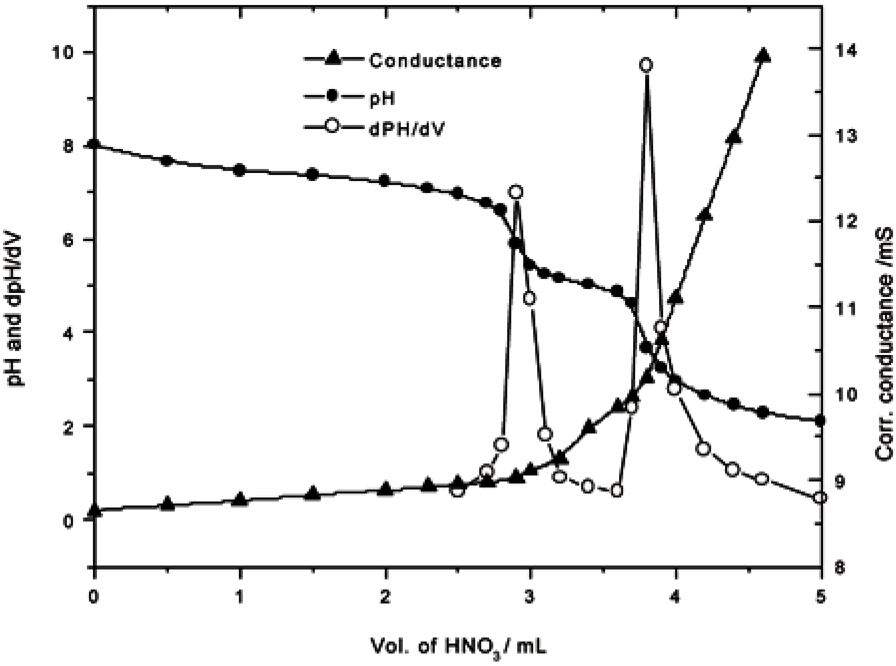


FIGURE 1 – pH and conductometric titrations of 25 mL of M/10 N_2WO_4 with 1 M HNO_3

Cerium normal tungstate

Figures 2 and 3 illustrate the curves of the pH and conductometric titrations performed between the solutions of the normal tungstate and cerium nitrate. In direct titrations (Fig. 2), when $Ce(NO_3)_3$ solution (pH 4.6) was added to the Na_2WO_4 solution (pH 8.0) a sharp fall in pH was noted with an inflection at molar ratio of Ce^{3+}:WO_4^{2-} as 2:3 in the vicinity of pH 6.2, corresponding to the stoichiometry for the formation of cerium tungstate, $Ce_2O_3.3WO_3$. This sharp fall in pH occurs because of the presence of unreacted acidic (pH 4.6) $Ce(NO_3)_3$ in the cell just after completion of precipitation of cerium tungstate. In reverse titrations (Fig. 3), when Na_2WO_4 solution was added to the cerium nitrate solution, the pH first changed very slowly, but at the end-point it jumped upwards corresponding to the formation of the same compound in accordance with the following equation:

$2Ce(NO_3)_3 + 3Na_2WO_4 = Ce_2O_3.3WO_3 + 6NaNO_3$

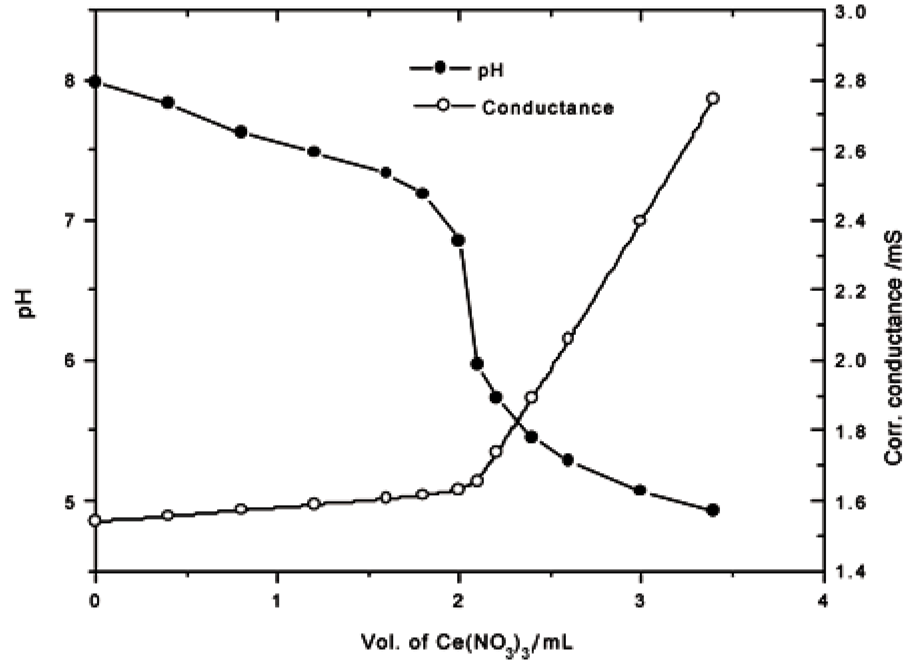


FIGURE 2 – pH and conductometric titrations of 25 mL of M/80 Na_2WO_4 with M/10 $Ce(NO_3)_3$.

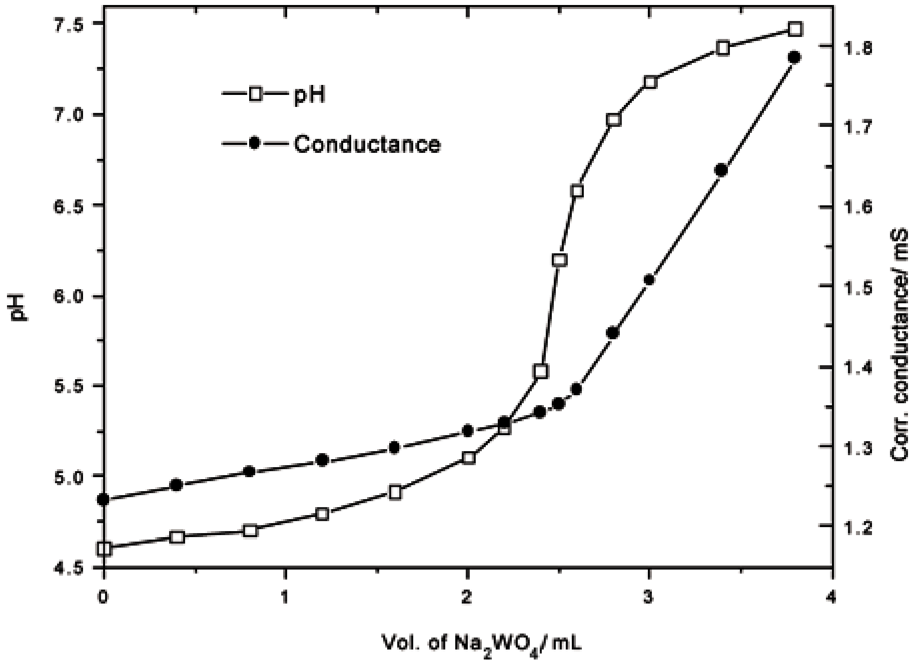


FIGURE 3 – pH and conductometric titrations of 25 mL of M/150 $Ce(NO_3)_3$ with M/10 Na_2WO_4.

Employing similar concentrations of the reactants, both direct (Fig. 2) and reverse (Fig. 3) conductometric titrations between the solutions of $Ce(NO_3)_3$ and Na_2WO_4 gave well-defined breaks at 2:3 molar ratio of Ce^{3+}:WO_4^{2-}, confirming the stoichiometry for formation of the cerium tungstate $Ce_2O_3.3WO_3$, as suggested by the pH study.

Cerium paratungstate

The solution of sodium paratungstate, $Na_{10}W_{12}O_{41}$, was prepared by addition of nitric acid to Na_2WO_4 in the molar ratio 7:6. Figures 4 and 5 illustrate the changes occurring in pH and conductance when $Ce(NO_3)_3$ solution (pH 4.6) is treated with $Na_{10}W_{12}O_{41}$ solution (pH 5.9). In direct titrations (Fig. 4) when $Ce(NO_3)_3$ solution was added from microburette to $Na_{10}W_{12}O_{41}$ solution, a gradual change in pH was observed till at the stoichiometric end-point (the stage at which the reaction ends if simple double decomposition takes place), a sharp fall in pH was noted with the inflection corresponding to the molar ratio of $Ce^{3+}:W_{12}O_{41}^{10-}$ as 10:3, suggesting the formation of cerium paratungstate $5Ce_2O_3.36WO_3$ in the vicinity of pH 5.3. In case of reverse titrations (Fig. 5) the first addition of $Na_{10}W_{12}O_{41}$ solution to $Ce(NO_3)_3$ caused a slight decrease in pH till about half the volume of titrant required for the precipitation of cerium paratungstate was added. This initial lowering in pH value was due to the presence of hydrolyzed acid from the cerium salt. Later on, with the progress of the reaction, pH began to rise and a pronounced upward jump was obtained at the stoichiometric point corresponding to the formation of cerium paratungstate. Employing similar concentrations of the reactants a series of direct (Fig. 4) and reverse (Fig. 5) conductometric titrations were performed between the solutions of $Ce(NO_3)_3$ and $Na_{10}W_{12}O_{41}$. The titration curves provide well-defined breaks at a point where the molar ratio of $Ce^{3+}:W_{12}O_{41}^{10-}$ is 10:3 (Table 1), thus confirming formation of the paratungstate as suggested by the pH study. The appreciable increase in conductance values in the initial stage of the inverse titration (Fig. 5) provides strong support to the observation noted in the reverse pH titrations. The formation of the paratungstate can be represented as follows:

$$10Ce(NO_3)_3 + 3Na_{10}W_{12}O_{41} = (5Cr_2O_3.36WO_3) + 30NaNO_3$$

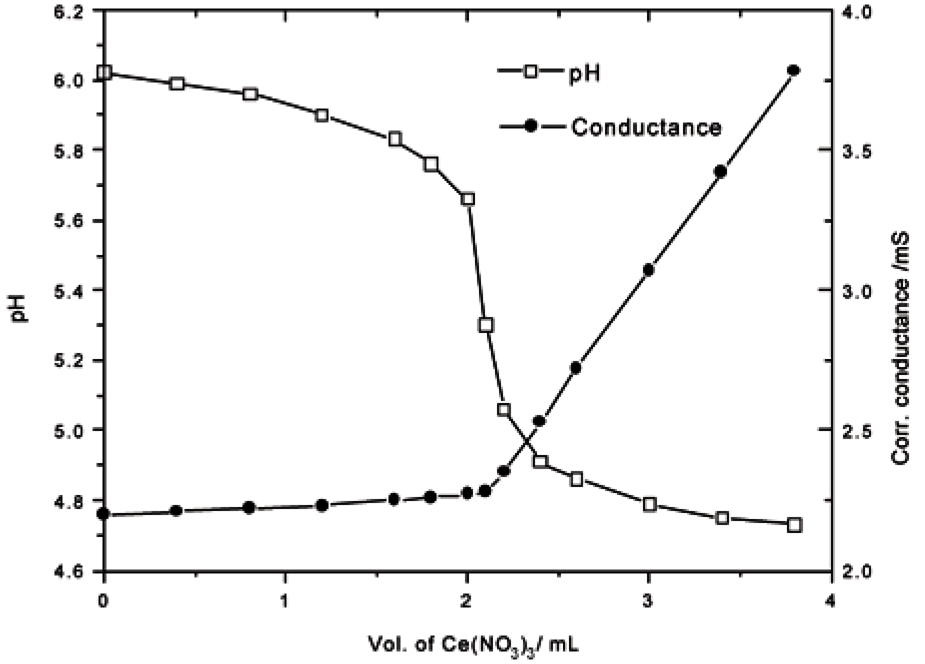


FIGURE 4 - pH and conductometric titrations of 25 mL of M/400 $Na_{10}W_{12}O_{41}$ with M/10 $Ce(NO_3)_3$.

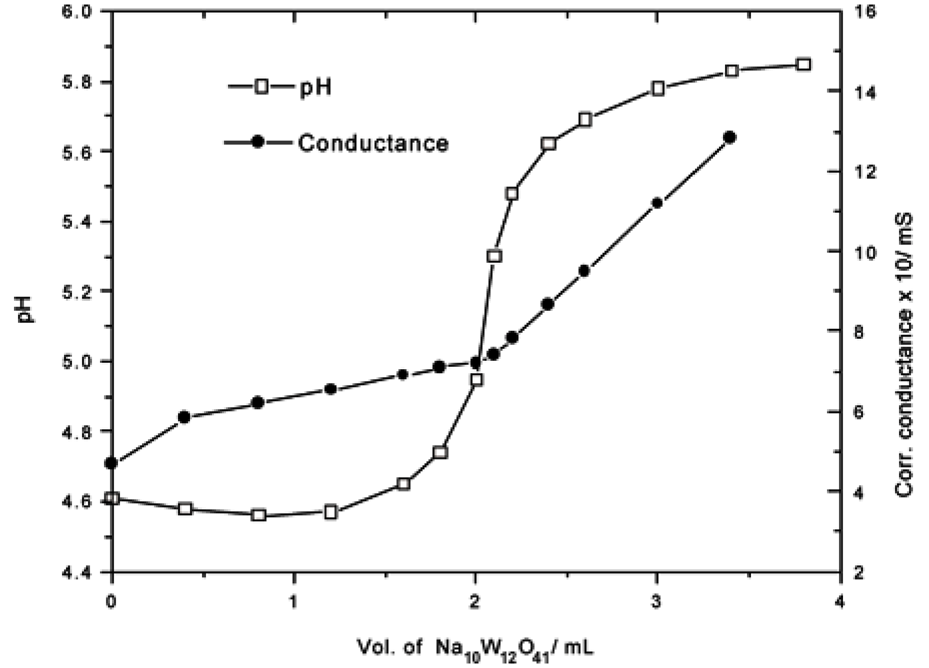


FIGURE 5 – pH and conductometric titrations of 25 mL of M/500 $Ce(NO_3)_3$ with M/140 $Na_{10}W_{12}O_{41}$

The reaction between cerium nitrate and sodium metatungstate, $Na_6W_{12}O_{39}$, has also been studied by pH and conductometric titrations but curves did not exhibit sharp inflections and breaks. This may be ascribed to the small difference in pH values of the reactants and the presence of $NaNO_3$ in appreciable amounts preventing the occurrence of breaks in the conductometric titration curves.

It was noted that after each addition of the titrant, it takes a little time for the pH and conductance values to become steady. A thorough stirring in neighborhood of the equivalence point has a favorable effect. The presence of ethanol (20%) improves position of the end-point and increases magnitude of the jump in pH curves, as it decreases solubility of the precipitates formed and minimizes hydrolysis and adsorption. For this reason all the titrations were performed in presence of 20% ethanol. The precipitation of normal tungstate was found to be almost quantitative. The titrations are simple and rapid and offer a quantitative method for determination of cerium(III) or tungstate solutions at suitable concentrations and pH range.

Analytical results

The results of the quantitative elemental analysis of the precipitates were used to calculate the proportions of the elements present in the compounds. From these proportions, the composition of the compounds was established which was found to be the same as obtained by the electrometric techniques (see Table 2).

The present electrometric and analytical investigations confirm the formation and precipitation of two cerium tungstates, viz. *Normal*-$Ce_2O_3.3WO_3$ and *para*-$5Ce_2O_3.36WO_3$ in the vicinity of pH 6.2 and 5.3, respectively.

As structure of these compounds is not known they are represented as double oxides, the manner which is usually adopted for such compounds[15].

Acknowledgement

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PRASAD, S. et al. Investigações eletrométricas sobre a formação de tungstatos de cério(III) em função do pH. *Ecl. Quím (São Paulo),* v.25, p. 2000.

RESUMO: *Através de técnicas eletrométricas envolvendo titulações potenciométricas e condutométricas entre os reagentes, foi estudada a reação do nitrato de cério(III) com diferentes tungstatos de sódio (*Na_2WO_4*,* $Na_{10}W_{12}O_{41}$ *e* $Na_6W_{12}O_{39}$*) em níveis diferentes do pH, em meios aquoso e alcoólico, com cada reagente usado alternadamente como titulante. Os resultados obtidos fornecem definitivas evidências de formação dos normal-*$Ce_2O_3.3WO_3$ *e para-*$5Ce_2O_3.36WO_3$ *tungstatos de cério nas vizinhanças de valores de pH iguais, respectivamente, 6,2 e 5,3. A precipitação do tungstato normal de cério foi quase quantitativa e as titulações potenciométricas oferecem um método simples para determinação de cério(III) ou tungstato nas soluções a concentrações e faixa do pH apropriadas.*

PALAVRAS-CHAVE: *Tungstatos; cério(III); eletrometria.*

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