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 Cr₂O₇²⁻ and heptamolybdate, Mo₇O₂₄⁶⁻, are well-characterized examples [1].

There is no doubt that the formation of isopolytungstates on acidification of the solutions of normal tungstate, WO₄²⁻, is the most complex and the least understood system [2]. 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 [3,4].

Tungstate solutions can absorb considerable quantities of strong acid by mechanism leading to formation of isopolytungstates [5]. 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⁺:WO₄²⁻ ratio as 7:6 and 9:6 in the pH ranges 5.7-6.0 and 3.6-4.1, respectively. The interaction of lanthanum nitrate with sodium tungstate solutions, at specific pH levels 8.0, 5.9 and 4.0 was also studied by pH and conductometric titrations, 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-La₂O₃.3WO₃, para-5La₂O₃.36WO₃ and meta-La₂O₃.12WO₃ tungstates in the vicinity of pH 6.3, 5.0 and 4.2, respectively. Analytical investigations on the precipitates formed confirm the results of the electrometric study.

Keywords: isopolytungstates; lanthanum; electrometry; polyanions.
so many isopolyanions seems to be doubtful; moreover, there is a great variance in the results published by earlier workers which allows no satisfactory interpretation of the mechanism of the condensation process. A further verification of the tungstate system seems very desirable with a view to rationalizing the conflicting details of the previous workers by employing electrometric techniques, which have provided more conclusive evidences on such systems [7,8,9]. After establishing for suitable conditions for the stability of different tungstate polyanions, the investigations for the formation of lanthanum tungstates as a function of pH were also carried out as no reference could be traced out in the literature about their formation.

### Experimental details

Na₂WO₄·2H₂O, La(NO₃)₃, HNO₃ 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 [10a].

pH measurements were carried out on Metrohm Herisau pH-meter using Scott Gerate glass combination electrode. Conductance values were recorded by employing a Metrohm conductometer. The sodium tungstate solution (25.00 mL) was placed in the cell each time and thermostated at 25.0±0.1°C. Using different concentrations of HNO₃ and Na₂WO₄, a series of glass electrode and conductometric titrations have been carried out.

The formation of lanthanum tungstates was investigated by the action of lanthanum nitrate with different vanadate anions at specific pH levels 8.0, 5.9 and 4.0 using different concentrations of the reactants. A series of pH and conductometric titrations was performed by direct and reverse methods, i.e. when lanthanum nitrate solution from the microburette was added to sodium tungstate solution and vice versa (Table 2). 25.00 mL of ethanolic solution (20%) was taken in the cell, which was thermostated at 25.0±0.1°C.

The precipitates obtained at the end-points of titrations between lanthanum nitrate and sodium tungstates were also analyzed to substantiate the electrometric results. The different lanthanum tungstates were precipitated by mixing stoichiometric amounts of lanthanum nitrate solutions with sodium tungstate solutions at specific pH levels 8.0, 5.9 and 4.0. The precipitates obtained were washed several times with 20% ethanolic solution and dried in a vacuum desiccator for 40 h. A known amount (ca. 2 g) of each of the precipitates was used for analysis tungsten and lanthanum. Tungsten [10a] was determined as oxinate and lan-

### Table 1. Summary of results of electrometric titrations of HNO₃ with Na₂WO₄

<table>
<thead>
<tr>
<th>Molarity of solutions</th>
<th>Equivalence points (ml) for the formation of</th>
<th>para-tungstate</th>
<th>meta-tungstate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Calculated</td>
<td>A&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>HNO₃</td>
<td>Na₂WO₄</td>
<td></td>
<td>2.92</td>
</tr>
<tr>
<td>M/10</td>
<td>M/100</td>
<td></td>
<td>2.59</td>
</tr>
<tr>
<td>M/20</td>
<td>M/225</td>
<td></td>
<td>2.78</td>
</tr>
<tr>
<td>M/50</td>
<td>M/525</td>
<td></td>
<td>2.50</td>
</tr>
<tr>
<td>M/100</td>
<td>M/1100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Volume of Na₂WO₄ solution taken in the cell = 25 mL.
<sup>b</sup> A and B represent results obtained from pH and conductometric titrations, respectively. The titrations were performed in triplicate (sd = ±0.005).
thanum [10b] with oxalate. From the proportions of lanthanum and tungsten in the compounds thus obtained their composition was established. The results are summarized in Table 3. The analytical results were also confirmed by atomic absorption spectroscopy.

### Results and Discussions

The pH titrations of the acid against sodium tungstate are shown in Fig. 1 (curves 1 and 2). Two points of inflection were obtained; the first at $H^+:WO_4^{2-}$ as 7:6 corresponding to the for-

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**Table 2. Summary of results of electrometric study on formation of lanthanum tungstates.**

Volume of titre solution taken in the cell = 25.00 mL.

<table>
<thead>
<tr>
<th>Molarity of solutions</th>
<th>Equivalence points (mL)</th>
<th>Formula supported</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Observed from</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>Conductance</td>
</tr>
<tr>
<td>La(NO₃)₃</td>
<td>Na₃WO₄</td>
<td>Direct titrations*</td>
</tr>
<tr>
<td>M/30  M/250</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>M/50  M/400</td>
<td>2.08</td>
<td>2.08</td>
</tr>
<tr>
<td>M/80  M/650</td>
<td>2.05</td>
<td>2.05</td>
</tr>
<tr>
<td>Reverse titrations*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M/375 M/20</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>M/675 M/40</td>
<td>2.40</td>
<td>2.40</td>
</tr>
<tr>
<td>M/900 M/60</td>
<td>2.50</td>
<td>2.50</td>
</tr>
<tr>
<td>La(NO₃)₃</td>
<td>Na₁₀W₁₂O₄₄</td>
<td>Direct titrations*</td>
</tr>
<tr>
<td>M/30  M/1200</td>
<td>2.08</td>
<td>2.08</td>
</tr>
<tr>
<td>M/50  M/1750</td>
<td>2.38</td>
<td>2.38</td>
</tr>
<tr>
<td>M/80  M/3000</td>
<td>2.22</td>
<td>2.20</td>
</tr>
<tr>
<td>Reverse titrations*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M/900 M/240</td>
<td>2.22</td>
<td>2.22</td>
</tr>
<tr>
<td>M/1600 M/480</td>
<td>2.25</td>
<td>2.25</td>
</tr>
<tr>
<td>M/2000 M/650</td>
<td>2.44</td>
<td>2.40</td>
</tr>
<tr>
<td>La(NO₃)₃</td>
<td>Na₁₂W₁₅O₄₉</td>
<td>Direct titrations*</td>
</tr>
<tr>
<td>M/30  M/750</td>
<td>2.00</td>
<td>-</td>
</tr>
<tr>
<td>M/50  M/1000</td>
<td>2.50</td>
<td>-</td>
</tr>
<tr>
<td>M/80  M/1750</td>
<td>2.29</td>
<td>-</td>
</tr>
<tr>
<td>Reverse titrations*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M/1500 M/240</td>
<td>2.00</td>
<td>-</td>
</tr>
<tr>
<td>M/2800 M/480</td>
<td>2.14</td>
<td>-</td>
</tr>
<tr>
<td>M/3600 M/600</td>
<td>2.08</td>
<td>-</td>
</tr>
</tbody>
</table>

* Typical curves of these titrations of normal- para- and meta- tungstates are shown in Figs. 2, 3 and 4, respectively.
mation of paratungstate and the second at 
H+:WO₄²⁻ as 9:6 due to the formation of 
paratungstate anions. In the first stage of the for-
mation, when H+:WO₄²⁻ is less than 7:6, the addi-
tion of the acid brings about a gradual change in 
pH with a rapid attainment of its equilibrium 
value. When the ratio of the acid to normal 
tungstate passed 7:6, the initial pH dropped 
sharply leading to the observed inflection due to 
the formation of paratungstate anion in the pH 
range 5.7-6.0. But in contrast to the earlier part of 
the titration, the pH value showed an increasing 
tendency on waiting after each addition of the 
titrant and took a long time for attaining the equi-
librium value, leading to a partial disappearance 
of the paratungstate A (HW₆O₂₁⁵⁻) to a more stable 
ion, paratungstate Z (W₁₂O₄₁⁰⁻). The 
increase in pH value observed on standing should 
be the result of an increase in negative charge 
(from -5 on HW₆O₂₁⁵⁻ to -10 on W₁₂O₄₁⁰⁻) on 
the formation of higher polymer of a weaker 
acid. The existence of these two species is in 
agreement with the ultracentrifuge results [11-
14]. The paratungstate formation may be repre-
sented in a simplified way as follows:

\[
6\text{WO}_4^{2-} + 7\text{H}^+ = \text{HW}_6\text{O}_2\text{I}_5^- + 3\text{H}_2\text{O} \quad \text{(fast)} \quad (1)
\]

\[
2\text{HW}_6\text{O}_2\text{I}_5^- = \text{W}_{12}\text{O}_{41}^{10^-} + \text{H}_2\text{O} \quad \text{(slow)} \quad (2)
\]

Figure 1. pH and conductometric titrations of 25 
ml of M/100 N₂WO₄ with M/10 HNO₃.

**Table 3. Summary of analytical results of the lanthanum tungstate precipitates.**

<table>
<thead>
<tr>
<th>Proposed formula of the compound</th>
<th>Mode of synthesis</th>
<th>Analysis %: Found (Calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>La</td>
</tr>
<tr>
<td>Analysis of the normal-tungstate precipitates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La₂O₃.3WO₃</td>
<td>Direct*</td>
<td>27.17(27.20)</td>
</tr>
<tr>
<td></td>
<td>Reverse*</td>
<td>27.24</td>
</tr>
<tr>
<td>Analysis of the para-tungstate precipitates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5La₂O₃.36WO₃</td>
<td>Direct</td>
<td>13.92(13.93)</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>13.95</td>
</tr>
<tr>
<td>Analysis of the meta-tungstate precipitates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La₂O₃.12WO₃</td>
<td>Direct</td>
<td>8.92(8.94)</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>8.96</td>
</tr>
</tbody>
</table>

*Direct – Lanthanum nitrate solution added to sodium tungstate solution.
*Reverse – Sodium tungstate solution added to lanthanum nitrate solution.

During the region of the second inflection 
in the titration curves, corresponding to the for-
mation of metatungstate isopolyanions, the ten-
dency to increase the pH value on waiting was 
again observed, leading to a conclusion that the 
formation of the final metatungstate species, 
W₁₂O₃₉⁶⁻, is also a slow process and should be 
preceded by the formation of an unstable species 
HW₆O₂₀³⁻, pseudo-metatungstate [5,6]. The two 
stage reaction may be represented as follows:

\[
6\text{WO}_4^{2-} + 9\text{H}^+ = \text{HW}_6\text{O}_2\text{O}_2^{3-} + 4\text{H}_2\text{O} \quad \text{(fast)} \quad (3)
\]

\[
2\text{HW}_6\text{O}_2\text{O}_2^{3-} = \text{W}_{12}\text{O}_{39}^{6^-} + \text{H}_2\text{O} \quad \text{(slow)} \quad (4)
\]
It was observed that after passing the second inflection the pH value got stabilized and did not give any more inflection even with an addition of a lot excess of the acid (H+:WO₄²⁻ : 10:1) and hence not confirming the formation of the tungstic acid [2b].

Conductometric titrations between HNO₃ and Na₂WO₄ were also carried out employing the same concentrations of the reactants as in pH titrations for the sake of comparison of the results. The plots (Fig. 1, curve 3) of corrected conductance as a function of the volume of titrant yielded two well-defined breaks at the ratio H+:WO₄²⁻ as 7:6 and 9:6 corresponding to the formation of paratungstate and metatungstate, respectively, as suggested by the preceding pH study. In all these titrations the break corresponding to the addition of 1.5 equivalents of the acid per Na₂WO₄ is strongly defined, followed by a sharp rise in conductance which was determined to be the same as expected for the addition of free acid to the system.

When a basic tungstate solution containing WO₄²⁻ and Na⁺ is acidified, the tungstate ions have been found to condense in definite steps, as evidenced by the foregoing electrometric experiments, to form different isopolytungstate anions. The overall condensation process may be considered formally at least to begin with partial neutralization of the tungstate ions, and then expanding its coordination sphere from four to six by water molecules followed by the formation of a highly aggregated isopolyanion at lower pH value.

\[
\begin{align*}
\text{WO}_4^{2-} + \text{H}^+ & = \text{HWO}_4^- \\
\text{HWO}_4^- + 2\text{H}_2\text{O} & = [\text{WO(OH)}_3]^- \\
6[\text{WO(OH)}_3]^- + \text{H}^+ & = \text{HW}_6\text{O}_{21}^{5-} + 15\text{H}_2\text{O}
\end{align*}
\]

The condensation process may be represented by the following general equation, which is almost similar to the one proposed by MacInnis and Kim [15]:

\[
a\text{H}^+ + b\text{WO}_4^{2-} = c\text{W}_x\text{O}_y\text{H}_z^{n-} + d\text{H}_2\text{O}
\]

with the values for a and b as represented in Table 4.

It is quite probable that the highly charged species given in Table 4 may be hydrated; e.g., W₁₂O₄₁₀⁻ as H₁₀W₁₂O₄₆₁₀⁻, and W₁₂O₃₉₆⁻ as H₂W₁₂O₄₀₆⁻ as suggested by Cotton and Wilkinson [6] or W₁₂O₄₁₀⁻ as W₁₂O₄₀(OH)₂₆⁻ [16] and W₁₂O₃₉₆⁻ as W₁₂O₃₈(OH)₂₆⁻ as recently reported by Rozantsev and Sazonova [17].

The results of a careful pH and conductometric study on the acid tungstate system provided definite evidence for the formation of para-W₁₂O₄₁₀⁻ (via HW₆O₂₁⁵⁻) and meta-W₁₂O₃₉₆⁻ (via HW₆O₂₀³⁻) in the pH ranges 5.7-6.0 and 3.6-4.1, respectively. The observation of MacInnis and Kim [15] about the formation of W₁₂O₄₆₂₀⁻, W₃O₁₁₄⁻ and WO₃·H₂O, of Meier and Schwarzenbach [18] about H₅W₄O₁₆³⁻, of Simons [19] about W₂O₇²⁻ and of Timofeeva et al. [20] about W₇O₂₄⁶⁻ could not be confirmed by the study.

**Formation of lanthanum tungstates**

The above studies show that the addition of acid to Na₂WO₄ solution under suitable condition causes the formation of paratungstate W₁₂O₄₁₀⁻ and metatungstate W₁₂O₃₉₆⁻ anions. Hence it was considered of interest to ascertain whether similar salts of heavy metals may be precipitated as a result of double decomposition. The reaction between lanthanum nitrate and different alkali tungstates has therefore been studied by means of pH and conductometric titrations. The solution of Na₂WO₄ was prepared in deionized distilled water. The solutions of sodium para- and meta-tungstates were prepared by adding 7 and 9 mol of HNO₃ to 6 mol of Na₂WO₄.

\[
12\text{Na}_2\text{WO}_4 + 14\text{HNO}_3 = \text{Na}_{10}\text{W}_{12}\text{O}_{41} + 14\text{NaNO}_3 + 7\text{H}_2\text{O}
\]

**Table 4: Summary of isopolytungstate ions represented by equation 8**

<table>
<thead>
<tr>
<th>H⁺:WO₄²⁻</th>
<th>a</th>
<th>b</th>
<th>pH range</th>
<th>polytungstate</th>
<th>common name</th>
<th>rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>7:6</td>
<td>7</td>
<td>6</td>
<td>5.5-6.0</td>
<td>HW₆O₂₁⁵⁻</td>
<td>Paratungstate A</td>
<td>Fast</td>
</tr>
<tr>
<td>7:6</td>
<td>14</td>
<td>12</td>
<td>5.7-6.0</td>
<td>W₁₂O₄₁₀⁻</td>
<td>Paratungstate Z</td>
<td>Slow</td>
</tr>
<tr>
<td>9:6</td>
<td>9</td>
<td>6</td>
<td>3.5-4.1</td>
<td>HW₆O₂₀³⁻</td>
<td>Pseudo-metatungstate</td>
<td>Fast</td>
</tr>
<tr>
<td>9:6</td>
<td>18</td>
<td>12</td>
<td>3.6-4.1</td>
<td>W₁₂O₃₉⁶⁻</td>
<td>Metatungstate</td>
<td>Slow</td>
</tr>
</tbody>
</table>

12Na₂WO₄ + 18HNO₃ = Na₆W₁₂O₃₉ + 18NaNO₃ + 9H₂O  \( \text{(10)} \)

**Lanthanum normal tungstate**

Figure 2 illustrates the curves of the pH and conductometric titrations performed between the solutions of the normal tungstate and lanthanum nitrate. In direct titrations (curve 1), when La(NO₃)₃ solution (pH 4.3) was added to the Na₂WO₄ solution (pH 8.0) a sharp fall in pH was noted with an inflection at molar ratio of \( \text{La}^{3+}:\text{WO}_4^{2-} \) as 2:3 in the vicinity of pH 6.3, corresponding to the stoichiometry for the formation of lanthanum tungstate, \( \text{La}_2\text{O}_3\cdot3\text{WO}_3 \). This sharp fall in pH occurs because of the presence of unreacted acidic (pH 4.3) La(NO₃)₃ in the cell just after completion of precipitation of lanthanum tungstate. In reverse titrations (curve 3), when Na₂WO₄ solution was added to the lanthanum 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:

\[
2\text{La(NO}_3\text{)}_3 + 3\text{Na}_2\text{WO}_4 = \text{La}_2\text{O}_3\cdot3\text{WO}_3 + 6\text{NaNO}_3 \quad \text{(11)}
\]

Employing similar concentrations of the reactants, both direct (curve 2) and reverse (curve 3) conductometric titrations between the solutions of La(NO₃)₃ and Na₂WO₄ gave well-defined breaks at 2:3 molar ratio of \( \text{La}^{3+}:\text{WO}_4^{2-} \), confirming the stoichiometry for formation of the cerium tungstate \( \text{La}_2\text{O}_3\cdot3\text{WO}_3 \), as suggested by the pH study.

**Lanthanum paratungstate**

The solution of sodium paratungstate, \( \text{Na}_{10}\text{W}_{12}\text{O}_{41} \), was prepared by addition of nitric acid to Na₂WO₄ in the molar ratio 7:6. Figure 3 illustrates the changes occurring in pH and conductance when La(NO₃)₃ solution (pH 4.3) is treated with \( \text{Na}_{10}\text{W}_{12}\text{O}_{41} \) solution (pH 5.9). In direct titrations (curve 1) when La(NO₃)₃ solution was added from microburette to \( \text{Na}_{10}\text{W}_{12}\text{O}_{41} \) solution, a gradual change in pH was noted with the inflection corresponding to the molar ratio of \( \text{La}^{3+}:\text{W}_{12}\text{O}_{41}^{10-} \) as 10:3, suggesting the formation of lanthanum paratungstate \( 5\text{La}_2\text{O}_3\cdot36\text{WO}_3 \) in the vicinity of pH 5.0. In case of reverse titrations (curve 3) the first addition of \( \text{Na}_{10}\text{W}_{12}\text{O}_{41} \) solution to La(NO₃)₃ caused a slight decrease in pH till about half the volume of titrant required for the precipitation of lanthanum paratungstate was added. This initial lowering in pH value was due to the presence of hydrolyzed acid from the lanthanum 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 lanthanum paratungstate. Employing similar concentrations of the reactants a series of direct (curve 2) and reverse (curve 4) conductometric titrations were performed between the solutions of La(NO₃)₃ and \( \text{Na}_{10}\text{W}_{12}\text{O}_{41} \). The titration curves provide well-defined breaks at a point where the molar ratio of \( \text{La}^{3+}:\text{W}_{12}\text{O}_{41}^{10-} \) is 10:3 (Table 2), thus confirming formation of the paratungstate as suggested by the pH study. The

![Figure 2. Normal-tungstate direct (1 and 2) and reverse (3 and 4) titrations. 1, 2: 25 mL of M/250 Na₂WO₄ titrated with M/30 La(NO₃)₃. 3, 4: 25 mL of M/375 La(NO₃)₃ titrated with M/20 Na₂WO₄](image-url)
formation of the paratungstate can be represented as follows:

$$10\text{La(NO}_3\text{)}_3 + 3\text{Na}_{10}\text{W}_{12}\text{O}_{41} = (5\text{La}_2\text{O}_3.36\text{WO}_3) + 3\text{NaNO}_3 \quad (12)$$

Lanthanum metatungstate

Sodium metatungstate, $\text{Na}_6\text{W}_{12}\text{O}_{39}$, solution was prepared by addition of nitric acid to $\text{Na}_2\text{WO}_4$ in the molar ratio 3H:2W. Using different concentrations of the solutions of $\text{La(NO}_3\text{)}_3$ and $\text{Na}_6\text{W}_{12}\text{O}_{39}$, a series of direct and reverse conductometric titrations was carried out. The nature of these titration curves (Figure 4) is similar to those of the paratungstate. The curves provide breaks at molar ratio 2:1 of $\text{La}^{3+}$$\text{W}_{12}\text{O}_{39}^{6-}$ corresponding to the stoichiometry for formation of lanthanum metatungstate $\text{La}_2\text{O}_3.12\text{WO}_3$ in the vicinity of pH 4.2, according to the reaction:

$$2\text{La(NO}_3\text{)}_3 + \text{Na}_6\text{W}_{12}\text{O}_{39} = \text{La}_2\text{O}_3.12\text{WO}_3 + 6\text{NaNO}_3 \quad (13)$$

The pH titrations of this system did not provide reliable results for the formation of lanthanum metatungstate, which may be ascribed to very close pH values of the reactants involved.

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.

Conclusions

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 3).

The present electrometric and analytical investigations confirm the formation and precipitation of three lanthanum tungstates, viz. normal-$\text{La}_2\text{O}_3.3\text{WO}_3$, para-$5\text{La}_2\text{O}_3.36\text{WO}_3$ and

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Figure 3. Para-tungstate direct (1 and 2) and reverse (3 and 4) titrations. 1, 2: 25 mL of $\text{M/1200 Na}_{10}\text{W}_{12}\text{O}_{41}$ titrated with $\text{M/30 La(NO}_3\text{)}_3$. 3, 4: 25 mL of $\text{M/900 La(NO}_3\text{)}_3$ titrated with $\text{M/240 Na}_{10}\text{W}_{12}\text{O}_{41}$

Figure 4. Meta-tungstate direct (1) and reverse (2) titrations. 1: 25 mL of $\text{M/750 Na}_6\text{W}_{12}\text{O}_{39}$ titrated with $\text{M/30 La(NO}_3\text{)}_3$. 2: 25 mL of $\text{M/1500 La(NO}_3\text{)}_3$ titrated with $\text{M/240 Na}_6\text{W}_{12}\text{O}_{39}$
meta-La$_2$O$_3$.12WO$_3$ in the vicinity of pH 6.3, 5.0 and 4.2, respectively. The pH values reported correspond to the 20% ethanol medium. As structure of these compounds is not known they are represented as double oxides, the manner which is usually adopted for such compounds [21].

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Resumo: A estequiometria de poliánions formados pela ação do ácido nítrico sobre a solução de tungstato de sódio (≤ 0,01M) foi estudada por meio de técnicas eletrométricas envolvendo titulações potenciométricas e condutométricas. As inflexões e degraus bem definidas nas curvas de titulações forneceram evidências convincentes pela existência de poliánions, para-W$_{12}$O$_{41}^{10-}$ e meta-W$_{12}$O$_{39}^{6-}$ nas faixas do pH 5,7-6,0 e 3,6-4,1; correspondendo a razão H$^+$:WO$_4^{2-}$ como 7:6 e 9:6, respectivamente. A interação entre soluções de nitrato de lantânio e tungstato de sódio a especificos níveis de pH 8,0; 5,9 e 4,0 também foi estudada por titulações potenciométricas e condutométricas, nos meios aquoso e etanólico, com cada reagente usado alternadamente como titulante. Os experimentos eletrométricos forneceram evidências incontestáveis sobre a formação de tungstatos normal-La$_2$O$_3$.3WO$_3$, para-5La$_2$O$_3$.36WO$_3$ e meta-La$_2$O$_3$.12WO$_3$ nas proximidades de valores de pH 6,3; 5,0 e 4,2; respectivamente. Investigações analíticas sobre os precipitados formados confirmam os resultados do estudo eletrométrico.

Palavras-chave: isopolitungstatos; lantânio; eletrometria.

References