Figures 1A_EA and 1B_EA show the stepwise experimental heats, \( Q_{\text{exp,j}} \), and the sum of the stepwise experimental heats, \( Q_{\text{exp,Tot}} \), measured for the five titrations with which \( \beta_1 \) and \( \Delta H_1 \) for the formation of Th(IV) nitrate complex were obtained. They are exothermic when the nitrate concentration in the cup solution is high, and decrease, becoming endothermic, when the nitrate concentration is lesser.

This trend has no immediate utility because it provides no information (proof) concerning the possible formation of nitrate complexes of Th(IV) in solution. It can only be explained as the result of multiple processes, exo- and endo-thermic, which occur simultaneously when the solution containing the metal cation is added to the solution in the calorimeter cell. Therefore, in order to rationalize the experimental data, it was necessary to identify each of these different processes.
In this part of the paper we describe how the stepwise experimental heat \((Q_{\text{exp},j})\) was corrected to obtain the stepwise net complexation heat \((Q_{\text{complex},j})\).

In our titrations, beside the heat due to the eventual formation of thorium nitrate complexes \((Q_{\text{complex},j})\), an important part of \(Q_{\text{exp},j}\) is due to the mixing of titrant with the cup solutions. In particular, when a definite volume of titrant is added to the cup solutions during metal-ligand titrations, some concentration changes occur which imply heat contributions and necessitate to be considered:

a) the concentration of \(\text{Na}^+\) and \(\text{Th}^{4+}\) passes from \(\sim 700\) and \(\sim 50\) mM, respectively, in the titrant, to \(\sim 900\) and \(\sim < 5\) mM, respectively, in the solution cell;

b) the concentration of perchlorate drastically decreases: from 1000 mM in the titrant, to \(\sim 100\) - \(\sim 625\) mM in the solution cell;

c) the concentration of nitrate in the titration cell (375, 500, 625, 750 and 900 mM) slightly decreases at each titrant addition.

In addition to the heat contributions due to the above concentration changes, indicated as \(Q_{\text{mix}1,j}\), \(Q_{\text{mix}2,j}\) and \(Q_{\text{cell}}\) (for a), b) and c), respectively), a constant “non chemical” heat \((Q_{\text{nc}})\), which probably arises from the friction of the titrant in the gold capillary tube, has been detected and had also to be taken into account.

| Scheme 1 Composition of the solutions employed, either as titrant or in the titration cell, in order to determine the different heat contributions. \(X = \sim 900, \sim 750, \sim 625, \sim 500, \sim 375\) mmol dm\(^{-3}\). |
|---|---|---|---|---|---|
| | \(Q_{\text{exp}}\) | \(Q_{\text{mix}1}\) | \(Q_{\text{mix}2}\) | \(Q_{\text{nc}}\) |
| | Titrant | Cell | Titrant | Cell | Titrant | Cell | Titrant | Cell |
| \([\text{H}^+]\) | \(\sim 100\) | \(\sim 100\) | \(\sim 100\) | \(\sim 100\) | \(\sim 100\) | \(\sim 100\) |
| \([\text{Na}^+]\) | \(\sim 700\) | \(\sim 900\) | \(\sim 700\) | \(\sim 900\) | \(\sim 900\) | \(\sim 900\) |
| \([\text{Th}^{4+}]\) | \(\sim 50\) | ---- | \(\sim 50\) | ---- | ---- | ---- |
| \([\text{ClO}_4^-]\) | 1000 | 1000 - \(X\) | 1000 | 1000 | 1000 - \(X\) | 1000 |
| \([\text{NO}_3^-]\) | ---- | \(X\) | ---- | \(X\) |
Separate experiments were carried out to determine $Q_{\text{mix1},j}$, $Q_{\text{mix2},j}$, $Q_{\text{cell}}$ and $Q_{\text{nc}}$ (See Scheme 1).

Measuring $Q_{\text{mix1},j}$ and $Q_{\text{mix2},j}$

$Q_{\text{mix1},j}$ and $Q_{\text{mix2},j}$ are functions of the cup composition and their values were obtained by interpolation of the experimental values.

Figure 2_EA, shows the experimental heats measured to evaluate $Q_{\text{mix1},j}$ (see details in Scheme 1) and the best fit line equation used to obtain the contributions of $Q_{\text{mix1},j}$ in equation (1).

$$Q_{\text{mix1},j} = -0.1528 + 5.58E-5 \times V_{\text{add}} \text{ mJ/10 \muL}$$
Figure 3A_EA shows the experimental heats and the linear best fits used to determine $Q_{\text{mix2},j}$ for the five nitrate concentrations used in the experiments. As it can be seen, in a single experiment the experimental heats decrease slightly with the increase of the volume added since nitrate concentrations decrease slightly along the titration. As expected, see Figure 3B_EA, the mixing effect is larger for the more concentrate nitrate solutions and decreases exponentially with the nitrate concentration.
Q_{nc} \text{ has been obtained averaging the values of } Q_{exp} \text{ for the mixing of two solutions with the same composition. (Scheme 1 and Figure 4_EA).}

Q_{cell}, the heat of dilution of nitrate during titrations, is included in Q_{mix2, j} \text{ and therefore neglected in the following computations.}

Having determined the above contributions, it was possible to estimate the heat due to the hypothesized formation of the Th(IV)–nitrate complexes (Q_{complex, j}) by the difference in eq. (1):

\[ Q_{complex, j} = (Q_{exp, j} - Q_{nc}) - (Q_{mix1, j} - Q_{nc}) - (Q_{mix2, j} - Q_{nc}) = Q_{exp, j} - Q_{mix1, j} - Q_{mix2, j} + Q_{nc} \quad (1) \]

The values of Q_{complex, j} \text{ so obtained for the five titrations (Figures 5A_EA and 5B_EA) establish that: a) the difference is not zero; which reflects interaction between Th(IV) and nitrate in solution; b) } Q_{complex, j} \text{ is negative (endothermic) and increase regularly with the concentration of nitrate in the cell, which is in agreement with the increase of complex formation in the more concentrate nitrate solutions.}
It is worth noting that the relative weight of thermal contributions which, subtracted to $Q_{\text{exp},i}$, allow the calculation of $Q_{\text{complex,Tot}}$ is quite different. In the Figure 6A_EA and 6B_EA we report, for example, the total heats of the different contributions for the titrations with maximum and minimum NO$_3^-$ concentration: 900 and 375 mM, respectively. The figures show clearly that $Q_{\text{complex}}$ for the more concentrate solution (red circles) is more negative (more endothermic) than that for the more diluted solution, notwithstanding $Q_{\text{exp,Tot}}$ is exothermic for [NO$_3^-$] ~ 900 and endothermic for [NO$_3^-$] ~ 375.

**Details on parameter optimization.**

In order to ensure that enthalpy and stability constant values reported in table 1 of the work reflect the true minimum, several runs of the minimization program, starting from initial
parameter values far from for the optimization values were made. To reach minimum, the program requires one or more runs but, always, it reaches the same minimum. Sometimes the values of $\beta_{\text{final}}$ and $\Delta H_{\text{final}}$ are insignificantly different (much less than $1\sigma$ reported by the program) from the values reported. From the fitting procedure it appears, as expected for very weak complexes, that $\Delta H$ and $\beta$ values are very correlated; the correlation coefficient is -0.9834.

The uncertainties obtained from the minimization program for $\beta$ (0.04, $3\sigma$) and $\Delta H$ (0.9 kJ mol$^{-1}$, $3\sigma$) do not reflect the possible uncertainties in the heat quantities used to correct $Q_{\text{exp}}$ ($Q_{\text{mix,1}}$, $Q_{\text{mix,2}}$, $Q_{\text{nc}}$) and so they are underestimated. The effect of introducing the uncertainties on $Q_{\text{mix,1}}$, $Q_{\text{mix,2}}$, and $Q_{\text{nc}}$ on the optimization procedure was estimated empirically by applying given perturbations to the heats of input ($Q_{\text{complex}}$). First, for each titration set, a value of the dispersion of the experimental heats (Fig. 3_EA) used to obtain $Q_{\text{mix,2}}$, the most relevant term in equation (1), was calculated. The estimated values for titrations 1-5 are 29.5, 25.2, 8.8, 13.5 and 5.5 μJ, respectively. Second, all $Q_{\text{complex,j}}$ for each data set were corrected in turn by adding or subtracting the corresponding dispersion value ($\delta$). Two new runs of the minimization program with such corrected data points gave the following $\beta$ and $\Delta H$ values:

when $\delta$ was added: \[ \beta = 0.13; \quad \Delta H = 8.76 \text{ kJ mol}^{-1} \]
when $\delta$ was subtracted: \[ \beta = 0.34; \quad \Delta H = 3.42 \text{ kJ mol}^{-1} \]

From the above values of $\beta$ and $\Delta H$, the following, more sound, values for the uncertainties on $\beta$ (0.11) and $\Delta H$ (2.7 kJ mol$^{-1}$) were calculated.