

Study of thorium hydrolysis species by electrospray-ionization mass spectrometry

C. Moulin^{a,*}, B. Amekraz^a, S. Hubert^b, V. Moulin^c

^a CEA-DEN/DPC/SCPA/LAS₂O, 91191 Gif sur Yvette Cedex, France

^b IPN-Groupe de Radiochimie, BP No. 1, 91406 Orsay, France

^c CEA-DEN/DDIN, 91191 Gif sur Yvette Cedex, France

Abstract

Electrospray-mass spectrometry (ES-MS) has been used for the first time to study the hydrolysis of thorium. Hence, important discrepancies exist in the literature concerning the appearance of the first hydroxo complex. By studying thorium species as a function of pH, it was possible to observe the appearance of the first thorium hydroxo complexes at pH 1 as well as the other hydroxo complexes at higher pH. By using MS/MS experiments, all thorium complexes corresponding to the different hydroxo thorium species, Th(OH)³⁺, Th(OH)₂²⁺, Th(OH)₃⁺ were attributed. Speciation of Th-hydrolyzed complexes obtained by ES-MS is compared to that obtained in the literature. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Reliable thermodynamic data are of prime importance to predict radionuclide speciation in natural environments, in particular for nuclear waste remediation purposes. In the particular case of actinides, a lot of studies have been carried out, and despite well-documented database and critical reviews [1–9], studies are still needed especially on actinides(IV) such as plutonium, neptunium, and thorium. Hence, for example Th⁴⁺, which is the least hydrolyzed tetrapositive ion, has a very complex chemistry in terms of hydrolysis. Aside from the presence of polymeric species, there are still discrepancies in the literature concerning the thorium hydrolysis speciation dia-

gram due to difference in stability constants of the hydrolyzed forms, in particular for the first hydrolyzed species Th(OH)³⁺.

Analytical methods used for these solution chemistry studies vary from spectrophotometry to potentiometry going through ultrafiltration and solvent extraction. Each of them possessing advantages and drawbacks, it seems valuable to evaluate the capacities of a new method based on electrospray-ionization tandem mass spectrometry experiments and to compare results with previously obtained data.

Electrospray ionization-mass spectrometry (ES-MS) was first developed for biological applications, since it allows very high mass to be reached by producing multiple protonated species and seems to be appropriate for speciation studies into solution due to its soft mode of ionization. The process can be divided in three steps: droplet formation, droplet shrinkage, and gaseous ion formation. Since the first coupling

* Corresponding author. Tel.: +33-1-6908-7751;

fax: +33-1-6908-5411.

E-mail address: cmoulin1@cea.fr (C. Moulin).

of ES to MS by Yamashita and Fenn [10], extensive studies have been devoted to mechanisms taking place in the source with the use of models, such as the single ion in droplet theory (SIDT) [11] and the ion evaporation theory (IET) [12], as well as the effect of operating conditions [13–17]. Conclusions from these studies emphasize on the complexity of mechanisms occurring into the source, the specificity of each system and special care that should be taken in terms of results interpretation. Hence, it is clear that many processes contribute to the ion abundance profiles in ES-MS: aqueous solution chemistry, kinetics of ion desorption, efficiency of gas phase ion formation, ion transmission into the vacuum, desolvation and declustering, and electrostatic optics/quadrupole mass filter transmission efficiencies.

Nevertheless, beside these processes that would introduce a bias in the resulting spectra, it has been stated that the ion abundance profile observed in the mass spectrum seems to retain the original abundance pattern imposed by aqueous solution chemistry. Aside from interesting reviews [18,19] and recent studies on metal speciation [20,21], it should be noted that very few studies have been carried out on the speciation of actinides/lanthanides by ES-MS, except one on lanthanides [22] and one on uranium [23]. Since, published results concerning thorium hydrolysis are rather diverse, it was decided to study by ES-MS hydroxo thorium species formation.

The purpose of this work is to evaluate the potential of ES-MS as a speciation tool for thorium and more particularly the formation of hydrolyzed species with a special emphasis on the pH occurrence of the first hydroxo complex $\text{Th}(\text{OH})^{3+}$.

2. Experimental

2.1. Materials

Standard solutions of thorium(IV) in perchloric acid were obtained at pH ranging from 0 to 3 by dissolving high-purity crystals of $\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$ ($M = 517.51$) in appropriate solution of perchloric acid (Fluka). The thorium concentration in perchloric acid was 5×10^{-4} M. Due to the hazardous properties of perchloric acid, this reaction was performed in a hood with absolutely no grease on the vessels.

All chemicals used were reagent grade and Millipore water was used throughout the procedure.

2.2. Instrumentation: MS apparatus and conditions

The mass spectrometric measurements were recorded in positive ion mode using a Quattro II tandem quadrupole mass spectrometer (Micromass, Manchester, England) equipped with an electrospray ionization source. The spray needle voltage was set to 3.6 kV and nitrogen operating at 250 l h^{-1} was employed as both the drying and nebulizing gas. Freshly prepared sample were injected into the spectrometer at a flow rate of $10 \mu\text{l min}^{-1}$ using a syringe infusion pump (Harvard Apparatus, Cambridge, MA). The source temperature was set to 80°C and the cone voltage was maintained at 45 V. Spectra were acquired at 6 s per scan over a mass range of $m/z = 50\text{--}1000$ with an acquisition time of 3 min. The resolution of the quadrupole mass selector allows the observation of the isotopic mass distribution, which arises from the thorium–chloride complex. Chloride complexes are seen in their natural abundances, i.e. 76% ^{35}Cl and 24% ^{37}Cl . For clarity, mass spectra are shown between 250 and 690 mass units, since no relevant peaks were observed below and above these values.

For MS/MS measurements, collision-induced dissociation was performed with argon, the collision gas pressure being 2×10^{-3} mbar. Spectra were obtained at different collision energies ranging from 20 to 40 eV.

2.3. Measurement procedure

The pH of the solution was measured with a conventional pH meter (Model PHN 81, Tacussel) equipped with a subminiature combined electrode (Model PH C3359-9). No correction for ionic strength was performed. Thorium solutions were introduced in the spectrometer both in increasing order of pH and randomly. Between each pH, the instrument was rinsed with dilute perchloric acid (1×10^{-3} M).

3. Results and discussion

Thorium hydrolysis (neglecting polymeric species as will be seen later on under our chemical

Table 1
Formation constants for thorium hydroxides at $I = 0$ and 25°C^a

Reaction	Baes and Mesmer [1]	Grenthe and Lagerman [5]	Ekberg et al. [9]	Moon [6]	Robouch [7]
$\text{Th}^{4+} + \text{H}_2\text{O} \rightarrow \text{Th}(\text{OH})^{3+} + \text{H}^+$	-3.22	-3.15	-2.75	-0.95	0.05
$\text{Th}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{Th}(\text{OH})_2^{2+} + 2\text{H}^+$	-6.94	-	-7.5	-4.5	-0.59
$\text{Th}^{4+} + 3\text{H}_2\text{O} \rightarrow \text{Th}(\text{OH})_3^+ + 3\text{H}^+$	-11.7	-9.08	-12.9	-6.4	-3.78
$\text{Th}^{4+} + 4\text{H}_2\text{O} \rightarrow \text{Th}(\text{OH})_4 + 4\text{H}^+$	-15.87	-13.87	-18.1	-12.1	-8.66

^a All data have been normalized to ionic strength = 0 using the extended Davies equation.

conditions) can schematically be described by the following reaction:

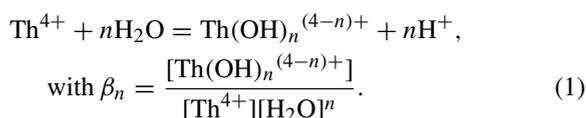


Table 1 summarizes the different formation constants (β) reported in the literature. The thorium hydroxide formation constants that are usually taken into account are the one by Baes and Mesmer [1], but other studies present alternative data that can be quite different, as seen in Table 1. The speciation diagrams associated with three sets of data (representing the main differences observed) are presented in Fig. 1, which shows the differences in terms of β values for thorium species as a function of pH. Hence, between the lower and higher dataset, the appearance of species can be shifted by more than 3 pH units, and for example the presence of the first hydrolyzed species ($\text{Th}(\text{OH})^{3+}$) is a maximum at pH 0 in the latter case [7] (Fig. 1c), and only appears significantly (>10%) above pH 2.5 for the former case [1] (Fig. 1a).

In order to study the thorium hydrolysis by ES-MS, special care should be taken in terms of possible matrix effects that could affect or even inhibit data acquisition. Hence, as previously observed [23], the use of sodium perchlorate to fix the ionic strength gives rise in ES-MS to important signals due to sodium adducts that do not allow the observation of species of interest. It was decided in a first approach to directly perform experiments in perchloric acid with the ionic strength fixed mainly by the perchloric acid and thorium concentrations. For thorium-hydrolyzed species studies, the ionic strength variation of only one order of magnitude (from 0.1 M ($[\text{HClO}_4] = 0.1 \text{ M}$, $[\text{Th}] = 1 \times 10^{-3} \text{ M}$) to 10^{-2} M ($[\text{Th}] = 1 \times 10^{-3} \text{ M}$,

$[\text{HClO}_4] = 0.001 \text{ M}$) was considered to have little effect on pH measurements as well as the appearance of hydroxo species.

The experiments were carried out at four different pH values starting from 0 to 3 by simply varying the perchloric acid concentration (1, 0.1, 0.01, 0.001 M) with a constant thorium concentration fixed at $1 \times 10^{-3} \text{ M}$. At this concentration and in this pH range, polymerization is very unlikely to occur. Hence, considering a solubility product (K_s) [24] for the solid thorium hydrous oxide ($\text{ThO}_2 \cdot x\text{H}_2\text{O}$) equal to 10^{-46} , the thorium concentration at pH 3 (the most limiting pH) is one order of magnitude below the solubility limit.

It is important to note that each data acquisition was carried out three times, varying the order of solution introduction in order to estimate the reproducibility and potential memory effects. The conclusions are that the experiments are reproducible to within 5% and no memory effects occur. The experiments were then repeated over a duration of 2 months. During this time, the relative abundance of ions within the spectra were observed to be independent of mass spectrometer operating conditions.

One main concern in ES-MS speciation studies is to be sure of the non-intrusivity of the process and above all to possible changes in the pH of the solution due to inherent electrolytic processes of the electrospray ion source [25]. In order to avoid possible pH changes (mainly decrease in ES+), special care was taken in terms of limiting water oxidation. Therefore, an EC capillary in stainless steel (rather than a platinum capillary) was used in order to favor relative electrolytic corrosion of the stainless steel [26] rather than the oxidation of water. The flow rate used ($10 \mu\text{l min}^{-1}$) was important, since the magnitude of the expected pH decrease is inversely related to the solution flow rate [25]. Moreover, it is important to note that pH

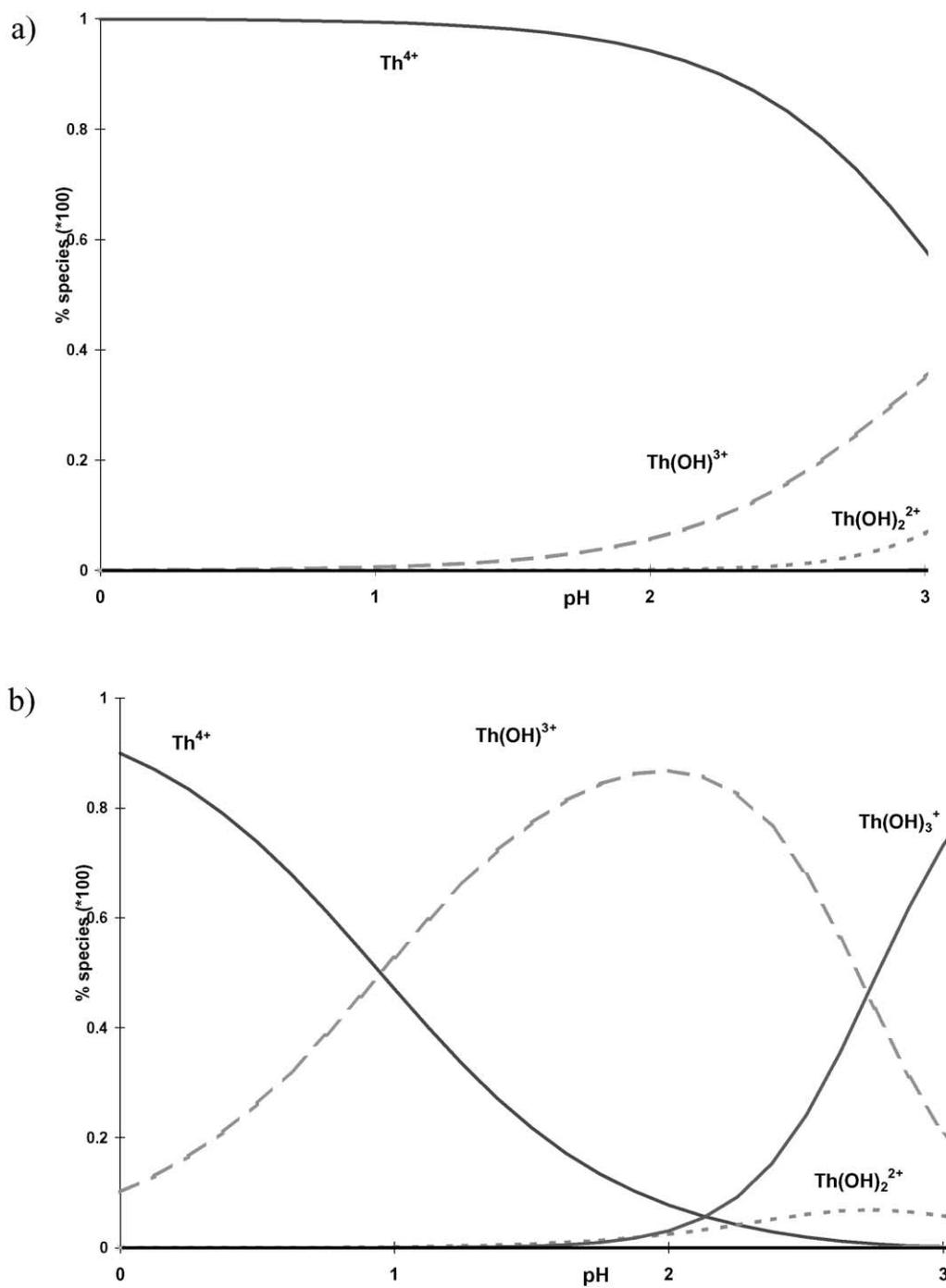


Fig. 1. Speciation diagram of thorium according to literature data: (a) Baes and Mesmer [1]; (b) Moon [6]; (c) Robouch [7] (see Table 1).

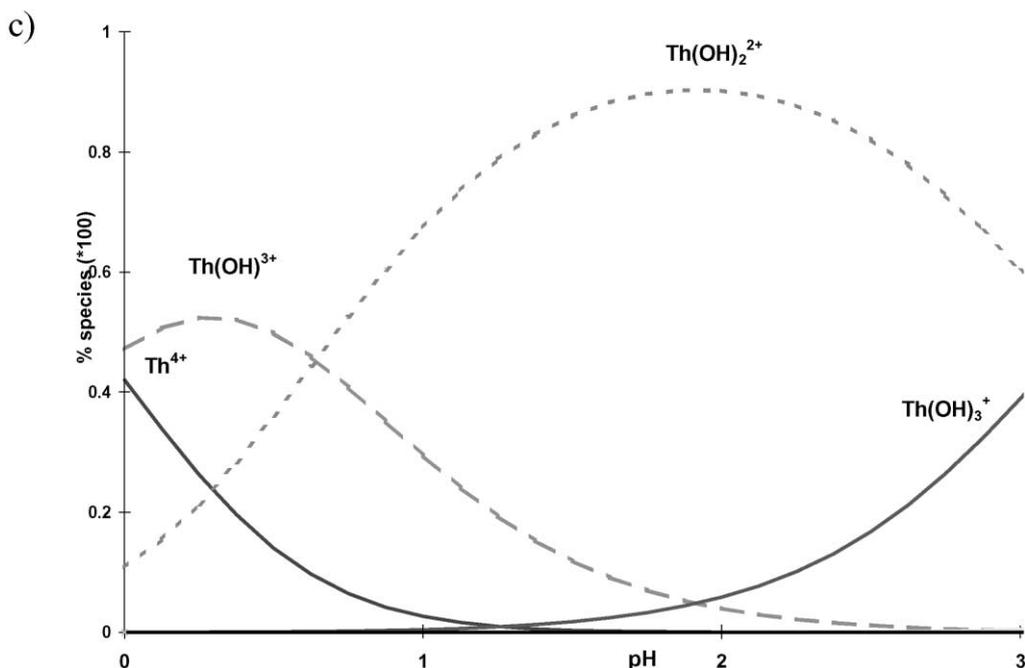


Fig. 1. (Continued).

changes are more drastic near neutral pH and that for strongly acidic solutions, the pH change due to electrolytically produced protons is negligible. Consequently, thorium solutions in the pH range 0–3 were studied with previously quoted parameters by ES-MS.

The evolution of the ES-mass spectra as a function of pH from 0 to 3 in the mass range 250–700 (no significant peaks were observed outside this range) obtained with the same operating conditions are shown in Fig. 2. Only hydrated singly charged complexes having a metal-perchlorate core are observed with over four water molecules attached, and can be rapidly analyzed by ES-MS for size distribution and composition (thanks to Cl isotope distribution) by observation of the parent ion in positive mode.

Several comments can be made. At pH 0, the main peak observed at m/z 583 corresponds to $[\text{Th}(\text{ClO}_4)_3(\text{H}_2\text{O})_3]^+$ as further identified by MS/MS (see Fig. 3). The other peaks attributed to thorium complexes are very weak and arise from the loss or gain of water molecules (m/z 565 ($-\text{H}_2\text{O}$), m/z 547 ($-2\text{H}_2\text{O}$), m/z 601 ($+\text{H}_2\text{O}$)). In Fig. 3a, the tandem mass spectrum of the peak at m/z 583 provides direct composition information of the

complex, with a sequential loss of one, two, and three water molecules ($m/z = 565, 547, \text{ and } 529$, respectively). The other fragment observed (m/z 465) is likely to be $[\text{Th}(\text{OH})(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}]^+$ produced by desolvation.

It is also interesting to observe that for thorium (Th^{4+}), the main limiting thorium complexes (in terms of the positively charged ion) observed by ES-MS is $[\text{Th}(\text{ClO}_4)_3(\text{H}_2\text{O})_3]^+$, as compared with europium (Eu^{3+}), a triply charged lanthanide where the main limiting europium complex [27] is $[\text{Eu}(\text{ClO}_4)_2(\text{H}_2\text{O})_4]^+$ as also observed by FT-IR [28] for the number of perchlorate ions and with uranium (UO_2^{2+}) as an actinide(VI) where the limiting uranium complex [23] observed is $[\text{UO}_2(\text{ClO}_4)(\text{H}_2\text{O})_3]^+$. In each case, direct analysis by ES-MS of actinides/lanthanides speciation produces a singly charged complex having metal-perchlorate cores with three to four water molecules in the first coordination sphere. Interestingly, actinides/lanthanides species hydrate nearly identically when formed by the electrospray ionization method. This would suggest that the number of water molecules attached is likely to be dependent on the charge state and it might be an

ES-MS analysis, Quattro II / LASO

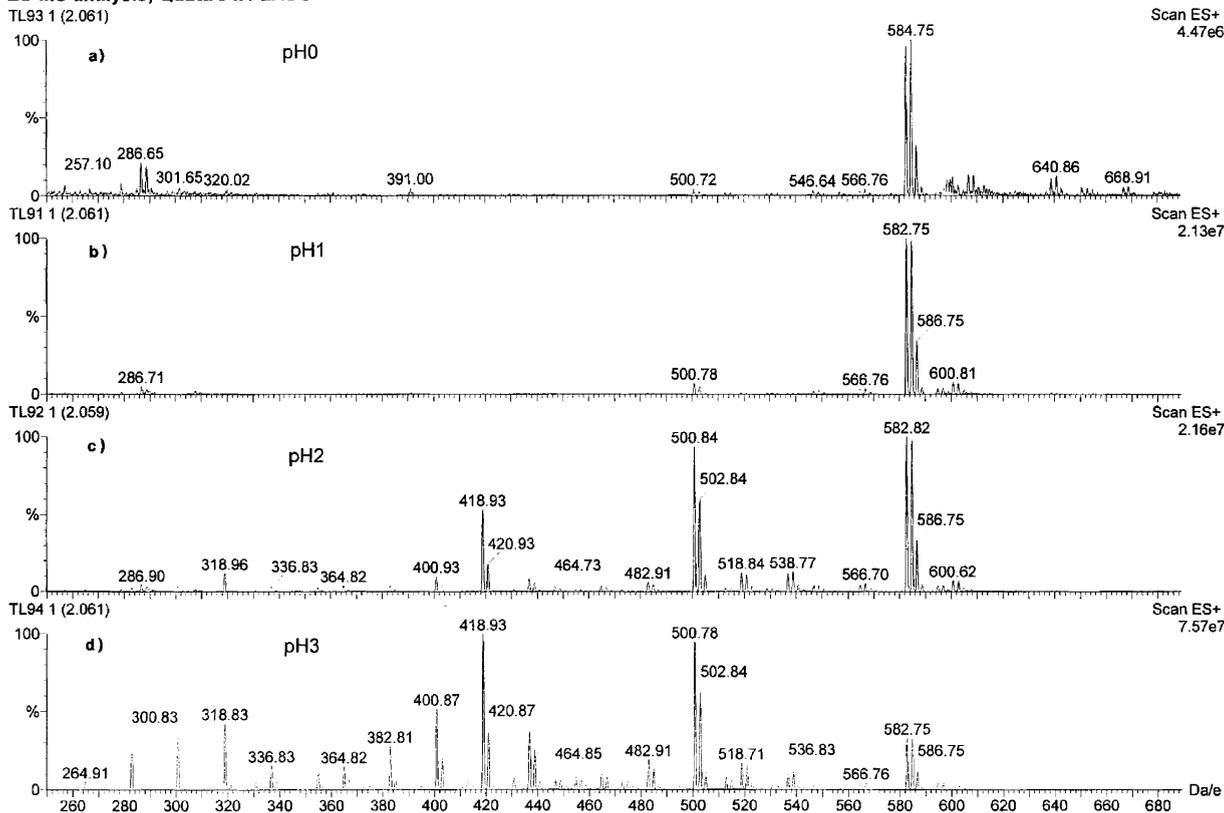


Fig. 2. ES-mass spectra of thorium at 1×10^{-3} M: (a) pH 0, (b) pH 1, (c) pH 2, and (d) pH 3 in perchloric acid.

indication that the extent of intramolecular charge solvation in the singly charged actinides/lanthanides perchlorates complex is similar.

At pH 1, $[\text{Th}(\text{ClO}_4)_3(\text{H}_2\text{O})_3]^+$ still gives the most intense peaks in the mass spectra. The $[\text{Th}(\text{ClO}_4)_3(\text{H}_2\text{O})_n]^+$, $n = 1-4$ complexes have the same distribution ratio at pH 0 and 1. The only difference is that the peak at m/z 501 is only very weakly observed at pH 0, but increases in intensity at pH 1. The isotopic mass distribution suggests that these species are likely to be $[\text{ThOH}(\text{ClO}_4)_2(\text{H}_2\text{O})_3]^+$. MS/MS measurements at higher pH result in confirmation of this assignment.

At pH 2, the mass spectrum is more complex (11 main peaks) with still the previously observed $[\text{Th}(\text{ClO}_4)_3(\text{H}_2\text{O})_n]^+$, $n = 1-4$ complex distribution but also the peak at m/z 501 for $[\text{Th}(\text{OH})(\text{ClO}_4)_2(\text{H}_2\text{O})_3]^+$ which is becoming

much more important. This complex is attributed to $\text{Th}(\text{OH})^{3+}$. The tandem mass spectrum relative to the ion at m/z 501 (Fig. 3b) presents again successive loss of water molecules ($m/z = 483, 465, \text{ and } 447$). More precisely, for $\text{Th}(\text{OH})^{3+}$, a series of multicharged ions corresponding to $[\text{Th}(\text{OH})(\text{ClO}_4)_2(\text{H}_2\text{O})_n]^+$, $n = 0-3$ is observed together with the association with chloride ($m/z = 519$ and 537). Moreover, unlike pH 1, a new peak around 419 is observed (Fig. 2c) and identified as $[\text{Th}(\text{OH})_2(\text{ClO}_4)(\text{H}_2\text{O})_3]^+$. This complex is attributed to $\text{Th}(\text{OH})_2^{2+}$.

At pH 3, the mass spectrum is very complex (15 main peaks) with all the peaks previously seen at lower pH ($m/z = 583, 501, 419$), but now the main distribution observed is centered around m/z 419 and can be related to $[\text{Th}(\text{OH})_2(\text{ClO}_4)(\text{H}_2\text{O})_n]^+$, $n = 0-3$. Moreover, peaks hardly seen at pH 2, between 283 and 355, clearly increase and correspond to the following

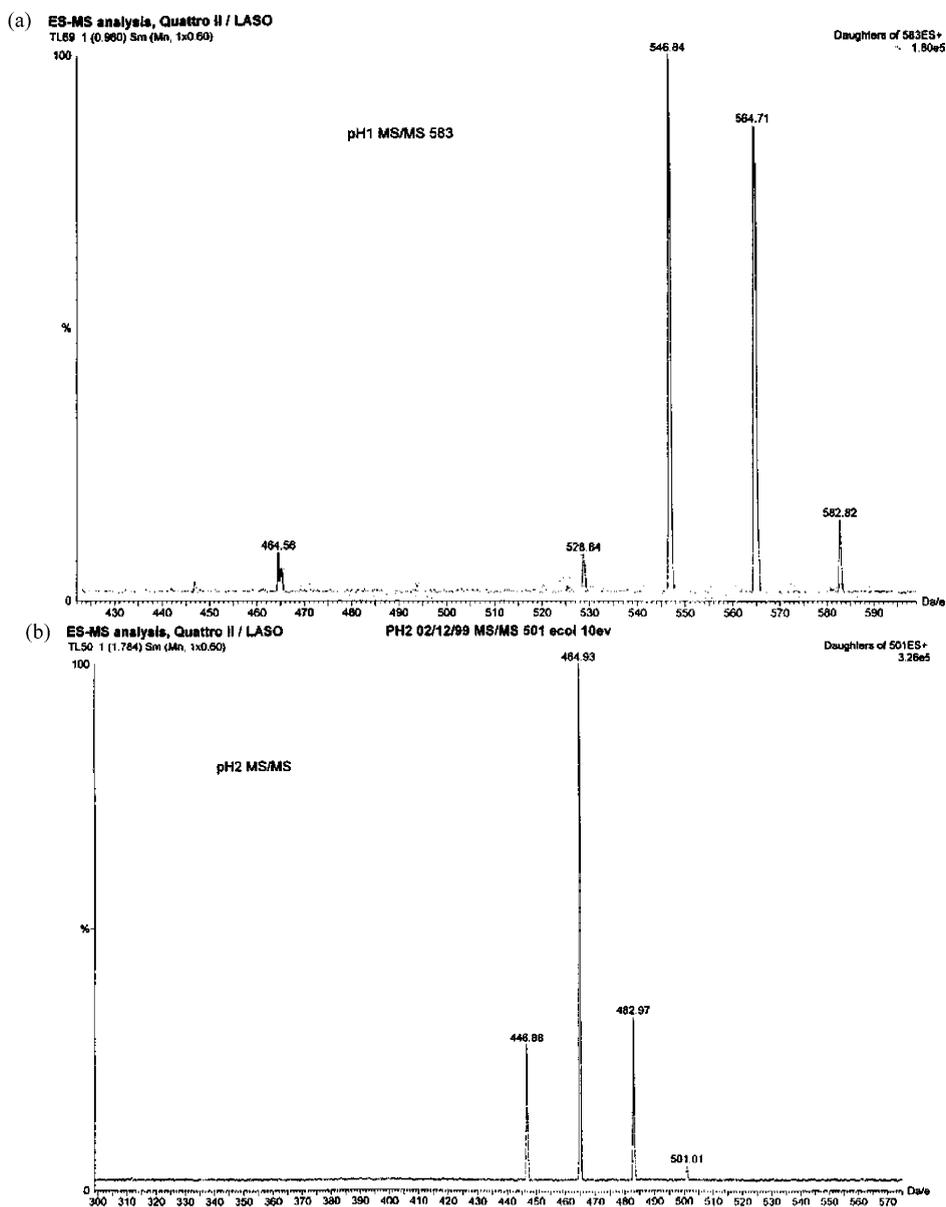


Fig. 3. Th complexes MS/MS identification at: (a) $m/z = 583$ (pH 1); (b) $m/z = 501$ (pH 2).

distribution $[\text{Th}(\text{OH})_3(\text{H}_2\text{O})_n]^+$, $n = 0-4$. These complexes are attributed to $\text{Th}(\text{OH})_3^+$.

All the different peaks observed in these spectra have been fully identified by MS/MS and the main ones are presented in Table 2 together with the daughter ions and the corresponding loss. It is very important

to note that all the thorium and thorium-hydrolyzed species identified are singly charged with mainly perchlorate and water molecules. Moreover, no reduction of thorium is observed, since the IV state is the only stable one [2] contrary to studies on other actinides such as uranium (as UO_2^{2+}) [23] or on lanthanides,

Table 2
Thorium complexes characterization by MS/MS

Thorium complexes	<i>m/z</i>	Daughter ions <i>m/z</i>	Loss
pH = 0			
[Th(ClO ₄) ₃ (H ₂ O) ₃] ⁺	583 (³⁵ Cl)	565	H ₂ O
[Th(ClO ₄) ₃ (H ₂ O) ₃] ⁺	583 (³⁵ Cl)	547	2H ₂ O
[Th(ClO ₄) ₃ (H ₂ O) ₃] ⁺	583 (³⁵ Cl)	529	3H ₂ O
[Th(ClO ₄) ₃ (H ₂ O) ₃] ⁺	583 (³⁵ Cl)	465	H ₂ O + HClO ₄
pH = 2			
[Th(ClO ₄) ₃ (H ₂ O) ₃] ⁺	583 (³⁵ Cl)	565	H ₂ O
[Th(ClO ₄) ₃ (H ₂ O) ₃] ⁺	583 (³⁵ Cl)	547	2H ₂ O
[Th(ClO ₄) ₃ (H ₂ O) ₃] ⁺	583 (³⁵ Cl)	529	3H ₂ O
[Th(OH)(ClO ₄) ₂ (H ₂ O) ₂] ⁺	483 (³⁵ Cl)	465	H ₂ O
[Th(OH)(ClO ₄) ₂ (H ₂ O) ₂] ⁺	483 (³⁵ Cl)	447	2H ₂ O
[Th(OH)(ClO ₄) ₂ (H ₂ O) ₃] ⁺	501 (³⁵ Cl)	483	H ₂ O
[Th(OH)(ClO ₄) ₂ (H ₂ O) ₃] ⁺	501 (³⁵ Cl)	465	2H ₂ O
[Th(OH)(ClO ₄) ₂ (H ₂ O) ₃] ⁺	501 (³⁵ Cl)	447	3H ₂ O
pH = 3			
[Th(OH) ₂ (ClO ₄)(H ₂ O)] ⁺	383 (³⁵ Cl)	365	H ₂ O
[Th(OH) ₂ (ClO ₄)(H ₂ O)] ⁺	383 (³⁵ Cl)	347	2H ₂ O
[Th(OH) ₂ (ClO ₄)(H ₂ O)] ⁺	383 (³⁵ Cl)	280	103
[Th(OH) ₂ (ClO ₄)(H ₂ O)] ⁺	383 (³⁵ Cl)	265	HClO ₄ + H ₂ O
[Th(OH) ₂ (ClO ₄)(H ₂ O) ₂] ⁺	401 (³⁵ Cl)	383	H ₂ O
[Th(OH) ₂ (ClO ₄)(H ₂ O) ₂] ⁺	401 (³⁵ Cl)	365	2H ₂ O

such as europium (as Eu³⁺) [22], where oxidation state modifications have been observed leading to reduced species, such as UO₂⁺ and Eu²⁺.

These different observations for thorium (similar chemical species, no reduction) are very important for the rest of the study, since it is likely that the desorption of the different thorium species from the surface of the droplet in the ion source at atmospheric pressure will be restricted, and consequently they will have a very similar behavior as they are detected in the gas phase. This assumption is crucial and is very difficult to assess experimentally in going from the liquid to the gas phase, explaining the number of studies in ES-MS devoted to such purposes in order to evaluate potentialities and limitations for speciation studies.

Hence, in the framework of thorium speciation studies, the challenge is not only to identify the different complexes but to be able to quantify the percentage of the different thorium species, i.e. Th⁴⁺, Th(OH)³⁺, Th(OH)₂²⁺, Th(OH)₃⁺ in order to obtain complexation constants. Therefore, in order to go further and with the assumption previously made, it

was possible by integrating all the different thorium complexes at each pH to obtain percentages of the four thorium species. The thorium species together with the thorium complexes observed by MS with their relative percentages are reported as a function of pH in Table 3. As previously mentioned, the thorium complexes observed involve water molecules and perchlorate ions, but one can also observe three minor thorium adducts with HCl at *m/z* = 437, 537, 519 coming from the dissolution of the starting material (ThCl₄·8H₂O).

All the ions shown in Table 3 have a mass to charge ratio < 600 and the ion distribution in each pH value does not span over 300 *m/z* units. It is reasonable to expect that these conditions minimize the influence of quadrupole mass spectrometer “roll-off”, i.e. decrease in ion transmission at increasing *m/z* values that may cause discrimination against high mass ions. Hence, if present, a mass spectrometer roll-off function will introduce a bias, increasing the relative abundance of Th(OH)₃⁺ complexes, which is in contradiction with the relatively low calculated ratio compared with other complexes at pH < 2.

Table 3
Thorium species quantification

Thorium complexes	<i>m/z</i>	Thorium species (%)
pH = 0		
[Th(ClO ₄) ₃ (H ₂ O) ₃] ⁺	583	100 (<i>Th</i> ⁴⁺)
pH = 1		
[Th(ClO ₄) ₃ (H ₂ O) ₂] ⁺	565	3
[Th(ClO ₄) ₃ (H ₂ O) ₃] ⁺	583	86
[Th(ClO ₄) ₃ (H ₂ O) ₄] ⁺	601	6
[Th(OH)(ClO ₄) ₂ (H ₂ O) ₃] ⁺	501	95 (<i>Th</i> ⁴⁺) 5 (<i>Th(OH)</i> ³⁺)
pH = 2		
[Th(ClO ₄) ₃ (H ₂ O) ₂] ⁺	565	2
[Th(ClO ₄) ₃ (H ₂ O) ₃] ⁺	583	37
[Th(ClO ₄) ₃ (H ₂ O) ₄] ⁺	601	3
[Th(OH)(ClO ₄) ₂ (H ₂ O) ₂] ⁺	483	42 (<i>Th</i> ⁴⁺) 2
[Th(OH)(ClO ₄) ₂ (H ₂ O) ₃] ⁺	501	26
[Th(OH)(ClO ₄) ₂ (H ₂ O) ₂ HCl] ⁺	519	4
[Th(OH)(ClO ₄) ₂ (H ₂ O) ₃ HCl] ⁺	537	5
[Th(OH) ₂ (ClO ₄)(H ₂ O) ₂] ⁺	401	37 (<i>Th(OH)</i> ³⁺) 4
[Th(OH) ₂ (ClO ₄)(H ₂ O) ₃] ⁺	419	11
[Th(OH) ₂ (ClO ₄)(H ₂ O) ₂ HCl] ⁺	437	3
[Th(OH) ₃ (H ₂ O) ₂] ⁺	319	18 (<i>Th(OH)</i> ₂ ²⁺) 3 (<i>Th(OH)</i> ₃ ⁺)
pH = 3		
[Th(ClO ₄) ₃ (H ₂ O) ₃] ⁺	583	10 (<i>Th</i> ⁴⁺)
[Th(OH)(ClO ₄) ₂ (H ₂ O) ₂] ⁺	483	5
[Th(OH)(ClO ₄) ₂ (H ₂ O) ₃] ⁺	501	21
[Th(OH)(ClO ₄) ₂ (H ₂ O) ₂ HCl] ⁺	519	5
[Th(OH)(ClO ₄) ₂ (H ₂ O) ₃ HCl] ⁺	537	4
[Th(OH) ₂ (ClO ₄) ₂] ⁺	365	35 (<i>Th(OH)</i> ³⁺) 2
[Th(OH) ₂ (ClO ₄)(H ₂ O)] ⁺	383	5
[Th(OH) ₂ (ClO ₄)(H ₂ O) ₂] ⁺	401	8
[Th(OH) ₂ (ClO ₄)(H ₂ O) ₃] ⁺	419	17
[Th(OH) ₂ (ClO ₄)(H ₂ O) ₂ HCl] ⁺	437	8
[Th(OH) ₃] ⁺	283	40 (<i>Th(OH)</i> ₂ ²⁺) 3
[Th(OH) ₃ (H ₂ O)] ⁺	301	4
[Th(OH) ₃ (H ₂ O) ₂] ⁺	319	5
[Th(OH) ₃ (H ₂ O) ₃] ⁺	337	2
[Th(OH) ₃ (H ₂ O) ₄] ⁺	355	1
		15 (<i>Th(OH)</i> ₂ ⁺)

It is also very important to note that virtually no change in the relative abundance of the different thorium hydroxo species is observed when modifying the inlet capillary position or the solution flow rate. If the electrolytic reactions are promoting hydroxo ions by

ESI, then the intensities of these species are likely to be modified as the residence time for the ions in the ESI source varies.

Finally, if the response of the thorium hydroxo species, in particular the first thorium hydroxo complexes, is caused by electrolytic reactions occurring in the gas phase, then the relative abundance of *Th(OH)*³⁺ species should be more important at pH 0–1, and this process is expected to produce a quasi-continuous steady-state intensity as the pH is increased. The data in Fig. 2 show a severe decrease in *Th(OH)*³⁺ species intensity.

These different observations support the hypothesis that an equilibrium distribution of hydroxo thorium species is mainly responsible for the final ion abundance profile observed in the ESI-mass spectra and that thorium speciation is possible by ES-MS.

By using the percentages obtained in Table 3 for the different thorium hydroxo complexes and at the different pH values (except pH 0 where only *Th*⁴⁺ is present), it is possible to calculate the complexation constants presented in Eq. (1). For example, at pH 3, $\beta_1 = (35/10) \times 10^{-3} \Rightarrow \log \beta_1 = -2.5$, $\beta_2 = (40/10) \times (10^{-3})^2 \Rightarrow \log \beta_2 = -5.4$, $\beta_3 = (15/10) \times (10^{-3})^3 \Rightarrow \log \beta_3 = -8.8$. However, in order to compare them with published data, it is mandatory to correct for the difference in ionic strength throughout the study. By using the extended Davies equation, it is therefore possible to calculate the complexation constant at zero ionic strength for the different equilibria. By doing so, it was possible to calculate the complexation constants at zero ionic strength for the three first equilibria, $\log \beta_1^0 = -2.0 \pm 0.2$, $\log \beta_2^0 = -4.5 \pm 0.5$, and $\log \beta_3^0 = -7.5 \pm 1$, and to compare them with literature data. In fact, for the first thorium hydroxo complexes these data lie between the data of Ekberg et al. [9] and Moon [6], and for the two other complexes (to be taken with caution since they are based on few data) closer to the data of the latter. Fig. 4 presents thorium hydrolysis speciation from ES-MS data measurements, where it can be seen that the first thorium hydroxo complex appears only above pH 1 and is maximum at pH 2.

The possibility to access the equilibrium constants of thorium hydroxo complexes shows the potential of ES-MS for such studies. Furthermore, the possibility to work at lower concentrations will allow the study

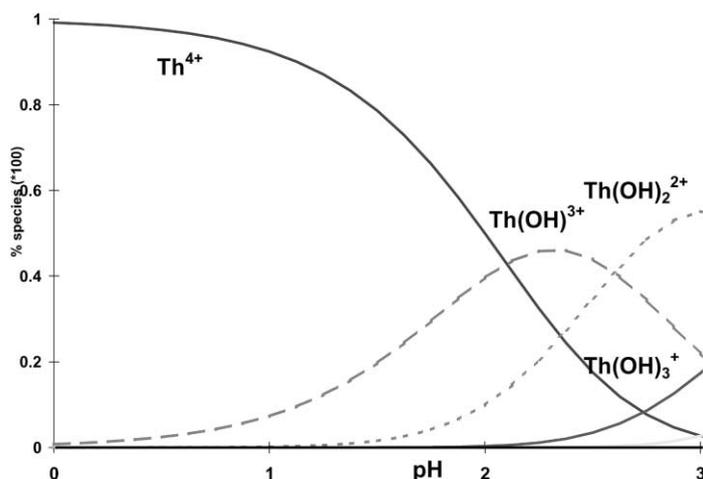


Fig. 4. ES-MS hydroxo thorium speciation ($[Th] = 1 \times 10^{-3}$ M).

of the other thorium species at higher pH. It is for the first time to our knowledge that an actinide(IV) that is of great interest in the nuclear fuel cycle has been studied by ES-MS. If special care is taken in terms of interpretation, since data obtained from the gas phase should reflect the equilibrium in liquid phase, it opens a new field of investigation for other actinides such as plutonium and neptunium.

4. Conclusions

Electrospray-mass spectrometry has been successfully applied for the investigation of thorium hydrolysis. By varying pH and using MS/MS experiments, it was possible to completely identify the different thorium complexes together with their corresponding hydrolysis species. The appearance of the thorium hydrolysis species is not likely to be caused by reactions occurring in the gas phase. It is most likely that the electrospray ionization process does not modify the ion abundance distribution. By using the percentages obtained for the different thorium hydroxo complexes, complexation constants have been estimated and are in fair agreement with literature data.

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