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Electrospray mass spectrometry for actinides and lanthanide speciation

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Abstract

Electrospray mass spectrometry (ES-MS) is a new speciation technique that has the great interest to be able to probe the element, the ligand and the complex in order to reach the speciation. This paper will focus on the use of ES-MS for the speciation of actinides/lanthanides on several systems of interest in various fields such as the interaction between DTPA (decorporant) and europium, HEBP and uranium, BTP (new extracting agent) and lanthanides with comparison with known chemistry as well as whenever possible with other speciation techniques.

Keywords: Actinide; Lanthanide; Fluorescence; Speciation; Electrospray mass spectrometry

1. Introduction

The determination of the different species present in solution is a key point to reach the speciation and to understand the behavior of element of interest in fields such as biology, environment or industrial processes. This requires being able to determine the oxidation state, complex species than can be neutral, charged or polymeric as well as the stoichiometry, complexing constants and thermodynamical parameters.

Electrospray mass spectrometry (ES-MS) has opened the field of macromolecules (Fenn and Yamashita, Chemistry Nobel prize 2002) [1] due to the fact that multicharged species are created within the source and are analyzed by a quadripole. Hence, a macromolecule of 100 000 atomic mass unit with a charge of 100 will be detected at 1000 m/z. It is also the first time that it is possible to directly couple a liquid at atmospheric pressure to a mass spectrometer via a soft ionization mode. The process can be divided into three steps: droplet formation, droplet shrinkage and gaseous ion formation. It can be used basically in two different ways, each giving access to a different kind of information. (i) Full scan simple MS spectra can be recorded with soft conditions to detect the complexes that are present in the infused solution. (ii) Once the complexes of interest are isolated in the gas phase, the structural information (without any influence of the solvent) can be obtained. The advantages are its capacity to perform speciation studies since it is possible to observe the complex as well as the ligand and the metal, to have access to the isotopy and above all to be multielementary. Direct speciation of dissolved metals [2–4], actinides (U, Th) [5,6], and fission products [7,8] has already been achieved by this technique. This presentation will focus on several systems such as nuclear toxicology (Eu-DTPA, U-HEDP) and nuclear waste partitioning (DATP-Ln) with comparison with a well-known speciation technique, which is time resolved laser induced fluorescence (TRLIF).

2. Experimental

2.1. Electrospray mass spectrometry

The mass spectrometric measurements were recorded either in ± ion mode using a Quattro II triple-quadrupole spectrometer (Micromass, Manchester, UK). The spray needle voltage was set to 3.5 kV and nitrogen operating at 300 L/h was employed as both the drying and nebulizing gas. Samples were introduced using a 50-μL glass syringe with a

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stainless steel needle (Hamilton Co.). The source temperature was set to 80 °C and the sample cone voltage varied between 20 and 60 V. Spectra were acquired at 6 s/scan over a mass range of *m/z* 50–1800 with an acquisition time of 3 min.

2.2. Time-resolved laser-induced fluorescence

A laser (Nd-YAG (Continuum)) operating at 266 nm delivering about 2 mJ of energy in a 4 ns pulse with a repetition about 10 Hz was used as the excitation source. The laser beam was directed into the 4 mL quartz cell of the spectrofluorometer "FLUO2001" (Dilor) with a measurement range of 200 nm into the visible spectrum with a resolution of 1 nm. The detection was performed by an intensified photodiode (1024) array cooled by the Peltier effect with integration time (1–99s), determined time delay (0.1–999 μs) and during a determined aperture time (0.5–999 μs).

3. Results and discussion

Potential or accidental human exposure to radionuclides is a relevant topic in the nuclear industry: in case of inhalation or wound contamination, the rapid use of a strong chelating agent is required for decorporation since complexation has been demonstrated as the way to enhanced mobility of toxic metals.

3.1. Diethylenetriaminepentaacetic acid (DTPA) –Eu

The DTPA ligand has five carboxylic groups (pK_a 2.6, 2.0, 1.6, 0.7, −0.1) and three nitrogen (pK_a 10.5, 8.6, 4.3) that can easily be protonated [9]. Between pH 5 and 8, the main form is H_2L^{3-}. Fig. 1 presents the Eu-DTPA (10^{-4} M for each) ES-MS spectra in negative mode at pH 6.5. The main complex observed is the expected $[EuDTPA]^{2-}$ at 270 atomic mass unit (amu). It was also possible to show (see inset) that the ion signal of this complex (and its lower homologous $[Sr\text{-}EDTA]^{2-}$ taken as a reference) observed in gas phase by ES-MS has the same trend as chemical equilibria (plain curves) in solution. Fig. 1b show the drastic difference in the TRLIF spectra going from free europium with a symmetric environment with nine water molecules to the Eu-DTPA complex that lead to a very dissymmetric environment with the characteristic inversion at the hypersensitive transitions at 618 nm and only one water molecule left has shown by lifetime measurements (free Eu 110 μs, Eu-DTPA

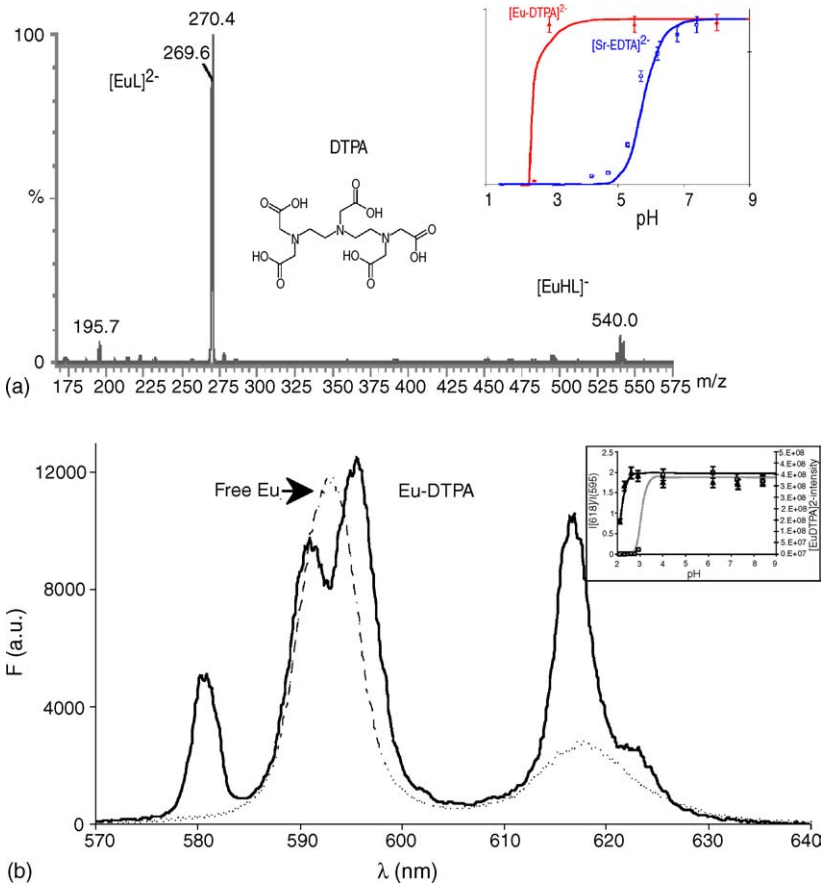

Fig. 1. (a) DTPA ES-MS spectra (- ion mode). Inset: Ion signal together with chemical equilibria. (b) TRLIF spectra of free europium and Eu-DTPA. Inset: I_{fluo} and ES-MS evolution as a function of pH.

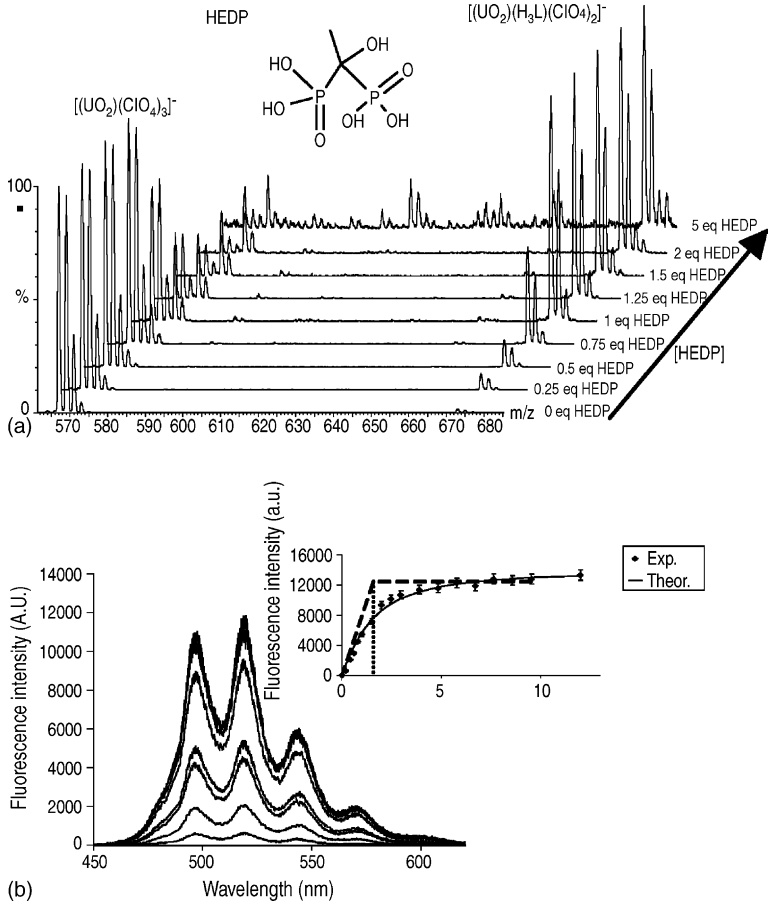

Fig. 2. (a) U – HEDP ES-MS spectrum. (2) TRLIF spectra of U with addition of HEDP. Inset: fluorescence titration curve.

550 μs) with applying the formula $n_{H_2O} = (1.05/\tau - 0.44)$. The inset of Fig. 1b shows the good correlation obtained with the two techniques while comparing fluorescence ratio and $[EuDTPA]^{2-}$ as a function of pH.

3.2. 1-Hydroxyethane-1,1′-diphosphonic acid (HEDP) – uranium(VI)

Bisphosphonates such as HEDP are known to reduce the rate of bone turnover [10]. Fig. 2a shows the ES-MS spectra evolution as a function of addition of HEDP where there is progressive disappearance of free uranyl (observed as the adduct $[UO_2(ClO_4)_3]^-$) at 570 amu leading to the formation of the UO_2-HEDP complex observed as $[UO_2(HEDP)(ClO_4)_2]^-$ at 675 amu. It was possible to determine the complexing constant $\log \beta = 4.2 \pm 0.5$ for this 1–1 complex. By the same token, Fig. 2b shows the evolution of the uranyl fluorescence spectrum as a function of HEDP together with the associated titration curve (inset) leading to the formation of a 1–1 complex with a $\log \beta = 4.7 \pm 0.5$ in good agreement with the one obtained by ES-MS.

In the framework of nuclear waste partitioning process, 2,6-bis (5,6-dialkyl-1,2,4-triazin-3yl)pyridines (DATPs) (see Fig. 3a inset) belong to a new family of extracting agents that exhibit exceptional properties to separate actinides (III) from lanthanides (III) in nitric acid.

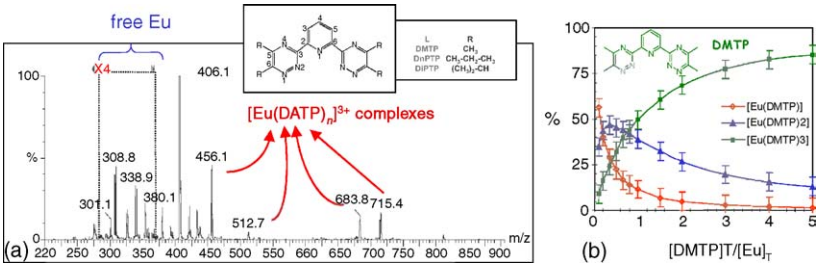

Fig. 3. (a) DATP – Eu ES-MS spectrum. (b) Speciation diagram for DMTP-Eu.

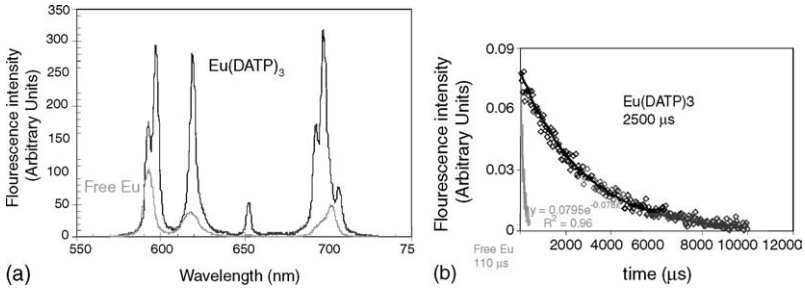

Fig. 4. (a) Free Eu and DATP – Eu fluorescence spectra. (b) Free Eu and DATP-Eu lifetimes.

3.3. DATP-Ln(III)

Fig. 3a presents a typical ES-MS spectrum for [Eu] 10^{-4} M and [DiPTP] 10^{-4} M where free europium, free DiPTP at 406 amu and complex $[Eu(DiPTP)_3]^{3+}$ at 456 amu with their adducts (nitrate) can be observed [11,12]. In this particular case (DiPTP) and surprisingly enough only 1–3 complex are observed. In the case of DMTP and DnPTP, it is possible to observe 1–1 and 1–2 complex together with the 1–3 complex and to determine the speciation diagram (Fig. 3b). Fig. 4a shows the evolution of the fluorescence spectrum of free europium to the $Eu(DiPTP)_3$ confirming the absence of 1–1 and 1–2 complex. Moreover, the fluorescence lifetime observed for the complex of 2500 μs (110 μs for free europium) confirms the complete disappearance of all the water molecules (9) in the europium inner sphere as observed by ES-MS. The different values obtained for the different complexing constants by both methods are in perfect agreement. It has also been shown that the stability constants for the Ln-DiPTP increase regularly within the Ln series (La: $\log\beta$ 11.7 to Lu: $\log\beta$ 16.7).

4. Conclusions

The examples presented here on several radionuclides-ligands systems allowing comparison with a reference speciation technique (i.e. TRLIF) show that ES-MS is a very powerful technique for radionuclides speciation. Hence, it was shown that results obtained in gas phase are very close to the one obtained in liquid phase allowing to work on non fluorescent radionuclides such as Th, Tc, Pu and Np.

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