A Specific Alpha Laboratory dedicated to Structural and Thermodynamic Studies on Actinide Complexes

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Abstract *– The main scope of the LN1 laboratory in Atalante facility is the chemical and physico-chemical study of transuranic samples to understand the behavior of compounds of actinide with selective ligands at a molecular scale. The main techniques implemented in this laboratory are the following ones: Nuclear Magnetic Resonance spectroscometer (400MHz shielded magnetic field), a four circle X-ray diffractometer for single crystals, a microcalorimeter to the measurement of low heats of reactions, a Time Resolved Laser-induced spectrofluorimeter, vibrational spectrometers: FTIR and Raman, an Electrospray Ionisation Mass spectrometer. Specific glove boxes have been built for each technique to work on radio elements with safety conditions and allow the analysis of samples in different states (aqueous and organic liquids, gels, solids…).*

INTRODUCTION

Basic research is necessary to explain specific macroscopic behavior in separation processes and to propose new processes in the future. The knowledge of structural and thermodynamic properties of actinide compounds in different media require dedicated equipments. The LN1 laboratory has been realized with the objective of centralizing selected techniques which allow to obtain structural information in solid and liquid state, speciation (identification of species) and thermodynamic properties (reaction constants for each chemical equilibrium and related heats of reaction.

CAPABILITIES OF THE LABORATORY

General Implementation

In the laboratory three specific premises where created for safety reasons :

- the N.M.R. spectrometry,
- the laser spectrometry,
- the X-diffractometer.

Four glove boxes are dedicated to classical chemical experiments, such dissolution, dilution, extraction, evaporation, centrifugation, essential to synthesize and purify specific actinide compounds (pure or in specific environment).

The nine others glove boxes are specific to prepare samples before the examination through the different techniques. To allow safe handling of the transuranium compounds, specific approach has been followed depending on the equipment: double encapsulation of the sample without modification of of the equiment (N.M.R. and X-diffractometer), addition of a specific sample device to allow the analysis (FTIR spectrometer), modification of the commercial equipment (microcalorimeter, electrospray-mass spectrometer) or transport of the beam through specific optic component like fibers (Raman spectrometer and Laser Induced Time Resolved Spectrometer).

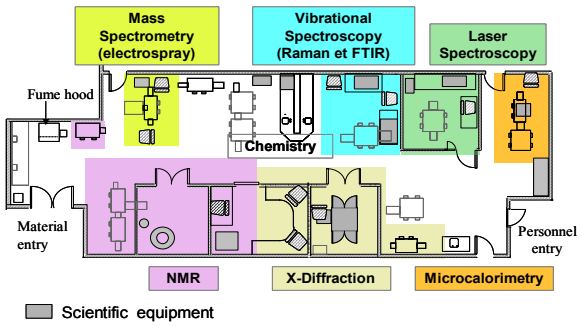

Fig. 1. Atalante LN1 laboratory

Description of Techniques

NMR spectrometer

The NMR spectrometer is a Varian INOVA 400MHz equipped with three channels, wave form generator, Z-gradient and a 100W proton amplifier for solid samples decoupling. The narrow bore magnet is located in a special room

separated from the electronic devices. Two glove boxes, next to the magnet room, are dedicated to prepare radioactive liquid samples in the NMR tubes. After an external absence of contamination check of the NMR tubes, they are easily handle from the glove box to the magnet room through a channel. The special feature of these glove boxes is to safely carry out radioactive experiments like any classical experiments. 5mm broad band and reverse commercial probes, both with Z-gradient, are used. Concerning NMR experiments with powder samples, such as MAS, a special probe head has to be designed and is under study.

Figure 2: Glove boxes dedicated to the preparation of NMR liquid samples

Single crystal X-diffractometer

Single crystal X-ray diffraction is the key tool in elucidating the geometric structure in the solid phase.

The diffractometer used is a Brucker ASX Kappa CCD (Nonius), allowing a fast data acquisition. The goniometer is equipped with a low temperature device (using liquid nitrogen) coupled with an air drying system.

A specific glove box allows the handling of the radioactive single crystal. An optical microscope equipped with a camera is used to fulfill the crystal selection and to introduce it in a quartz capillary.

The capillary used is protected in a sealed tube to avoid any external contamination during the crystal manipulation. The tube is then transported to the NMR glove box to add another encapsulation. After checking the absence of contamination the capillary will be mounted on the goniometer head.

Microcalorimeter

The Thermal Activity Monitor (TAM) microcalorimeter from Thermometric is a modular system with a highly stable (± 0.1 mK) temperature-controlled bath containing up to four calorimetry units. The sensor bulbs inserted in the units are capable of measuring heat flows in static or titration systems (Figure 2). Microcalorimetry, and calorimetric titration in particular, is a field in rapid expansion as a result of technical improvements in both hardware and software [1].

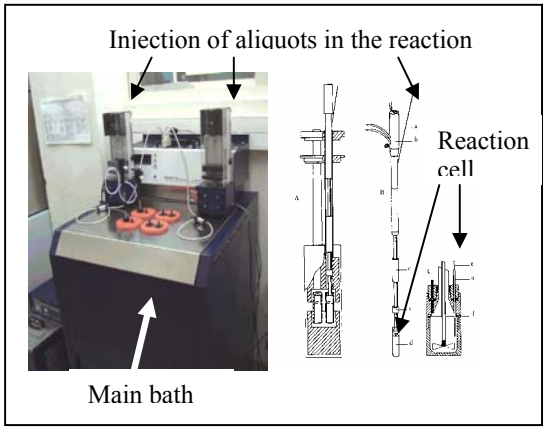

Figure 4: Microcalorimeter before implementation of glove box above

In the case of an equilibrium reaction, titration allows both $\Delta_r G$ and $\Delta_r H$ (and thus $\Delta_r S$) to be determined simultaneously. The technique has been optimized to allow to obtain the enthalpy variation related to the extraction of metals, cf. Figure 3.

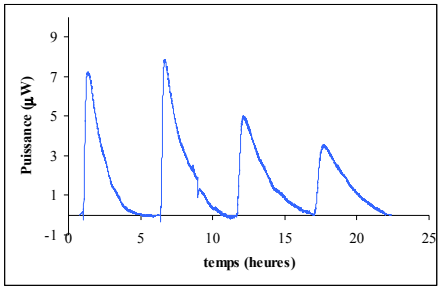

Figure 5: Example of a thermograme obtained with the extraction of Eu(III) by *i*PrBTP 0.03 mol.L^{-1} in *n*-octan-1-ol (25°C – [$NaNO_3$]=2.4 mol/L et $[Eu(III)]_{aq}^{init}$=0.01 mol.L^{-1})

Laser spectrometer

Laser spectrometries(Laurent Couston)

UV-visible-near IR molecular spectroscopy is both classical and reliable at the laboratory scale. Nevertheless, for some basic speciation studies or structural characterizations, they are not always sensitive enough, selective enough and not spatially localised.
For these three reasons, we were equipped with a special laser line using a pulsed Nd-Yag laser (PL8000, Excel Technology), an Optical Parametric Oscillator (Sunlite, Excel technology) and a light frequency doublers (FX1, Excel Technolgy). As a result, the exit beam of the laser line is adjustable from 220 to 1800 nm (energies varying from 3 to 20mJ) in an all solid state technology, easily nuclearized :

- ⇨ the strongly monochromatic laser beam improved the chemical selectivity,
- ⇨ the beam energy improved the measurements sensibility,
- ⇨ the optical characteristics of the beam make easier the image treatment, allowing a strongly located excitation.

Moreover, the pulsed emission , according to time resolved spectral detection (Princeton Instrument) strongly improved the selectivity, and make possible the molecular or atomic emission lifetime measurements taking place just after excitation.
Currently, this equipment is well adapted for a low detection level of fluorescent An (U^{VI}, Cm^{III} and Am^{III}) and Ln^{III} (EuIII in particular), making possible a sensitive quantitative analysis (below 10^{-10} mol.L) and speciation with little affined ligand (complexation constant below 1 $L.mol^{-1}$).
The third oxidation level gets a special spectroscopic property from the fluorescence lifetime : the hydration number of the first coordination shell, a fundamental data for a better understanding of the extraction process.

Beyond these current analytical results, the polyvalence of the spectroscopy unit make possible new instrumental development for a better knowledge of the physico-chemical process of the extraction at the interface scale, for fluorescing and non-fluorescing species

Vibrational spectrometer (FTIR and Raman)

Solid and liquid samples can be analyzed with the high performance FTIR spectrometer EQUINOX 55 from Bruker. Two detectors type have been installed: a classical DLATGS for medium infrared (400 to 4000 cm^{-1}) and a DTGS/PE for far infrared (80-450 cm^{-1}) in order to get direct information on metal-ligand vibrations. An additional sample compartment, connected to a glove box, has been developed on the right side to study radioactive compounds. This chamber is equipped with specific windows: ZnSe for mid infrared and silicium for far infrared

To perform Raman studies a LabRAM system from Dylor is installed.. The liquid radioactive compounds are introduced in a specific sample chamber (Super Head from Dylor) and the optical signal is transmetted through optical fibers. To complete the field of investigations an external continuous-wave 2W Nd-YAG laser, the millennia II, has been implemented.

The facility is well equipped to carry out Raman vibrational spectroscopy using continuous wave (cw) lasers

Mass spectrometer with Electrospray ionisation

The mass spectrometer is a Brucker Esquire-LC quadrupole ion trap equipped with an ESI (electrospray ionization) and an APCI (atmospheric pressure chemical ionization) interface (Figure 6). A positive or negative ionization mode can be used.

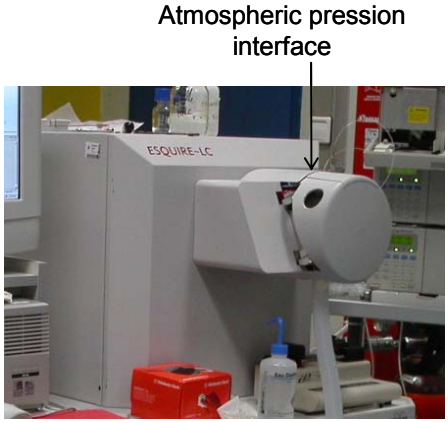

Fig. 6: Electrospray ionization mass spectrometer (Bruker Esquire LC) before implementation of a glove box.

The electrospray ionisation is useful for metal-ligand analysis (stoichiometry and stability) and the APCI allows a structural identification of

organic compounds. The figure 7 presents an example of the mass spectra of a metal-ligand complexe.

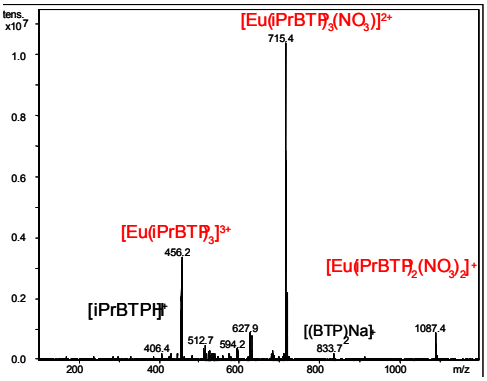

Fig. 6: Electrospray mass spectra of organic phase of iPrBTP after extraction of europium. (Organic phase. [iPr-BTP]= 2.10^{-2} mol.L^{-1} in n-octanol; aqueous phase. [$Eu(NO_3)_3$]= 2.10^{-2} mol.L-1, $NaNO_3$ 3 mol.L^{-1}; Dilution of organic phase 1/40^e in CH_3CN/H_2O mixture (1/1))

An ion trap system has been selected because its highly sensitivity and selectivity allow easier mass measurements on radioactive solutions.
The 'nuclearisation' strategy consists in a modification of the interface. The atmospheric pressure interface will be inside the glove box and the ions will be transferred into the external mass spectrometer through a specific interface.

Chemical glove boxes

An important basis for the experimental study is the preparation facilities. Specific glove boxes are dedicated to preparation in atmospheric or soon in inert conditions of actinide compounds: in solid state (powder or single crystals) or diluted in specific medium.

REFERENCES

[1] J.L.OSCARSON, R.M.IZATT, J.O.HILL, P.R. BROWN, "Continuous Titration Calorimetry" in *Solution Calorimetry - experimental Thermodynamics*, Ed., Blackwell Scientific, London, pp. 211-244 (1994).