

## Report:

XAS measurements have been carried out at Ruthenium K edge in presence of various ligands at both liquid (aqueous and organic media) and solid state. The main goal of the proposal was to identify the extracted species of ruthenium including redox state and molecular structure. This experiment is the first structural studies undertaken using x-ray measurements on ruthenium in liquid-liquid extraction. Another aim was to gain information on the controversial Ruthenium nitrosyl redox state using XANES spectrum.

The samples selected are:

- 1- Reference samples for Ruthenium chloride and Ruthenium nitrosyl with chloride and nitrate ligands.
- 2- Stock 1M nitrate ruthenium solution
- 3- Ruthenium in liquid-liquid extraction process by tributylphosphate 30% and 80%.
- 4- Ruthenium in liquid-liquid extraction process by two types of monoamide and 2 acidic conditions (HNO<sub>3</sub> 1m and 5M).
- 5- Aged Ruthenium in liquid-liquid extraction process.

## XANES analysis:

Commercial precursor Ruthenium Nitrosyl Nitrate and analogous chloride were first studied together with Ru(II) and Ru(III) chloride in order to calibrate the XANES energy relatively to a ruthenium metal foil (Ru Kedge). As presented figure 1, an energy shift is observed for the edge, the white line position and the first EXAFS oscillation when the ruthenium is oxidized from +II to +III.

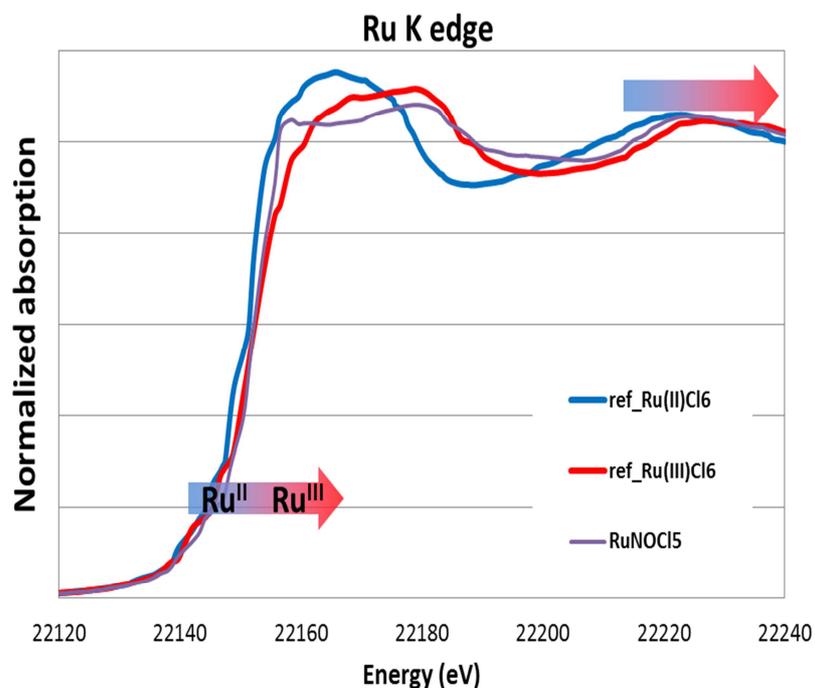


Figure 1: XANES spectra of Ru(II) and Ru(III) chloride (blue and red) and nitrosyl chloride sample.

The presence of the nitrosyl group (Figure 1: violet line) in the ruthenium coordination sphere is known to modify the ruthenium electronic structure by sigma donation and pi back bonding. Also, the Oh symmetry of ruthenium chloride is distorted by the short NO bonds. Consequently the WL splits into two peaks and the first EXAFS oscillation is intermediate between RuII and RuIII references. At the absorption edge (derivative first maximum) the nitrosyl sample appears at the same energy as the Ru(III) chloride (+III atomic charge).

On Figure 2 and 3 the normalized XANES spectrum obtained from ruthenium in aqueous nitrate solution (1M) and extracted ruthenium by TBP and monoamide (in light red on Figure 2 and 3 respectively) are compared to the chloride references Ru(II) and Ru(III) (blue and red respectively). As for the ruthenium nitrosyl chloride complex, the WL splits into two peaks but the first EXAFS oscillation is closer to the Ru(III) chloride one. Ru absorption edges observed for nitric acid, TBP and monoamide solutions are observed at the same or higher energy than the Ru(III) chloride. It indicates first that the Ru point group is a distorted from Oh.

According to the first EXAFS oscillation, the averaged Ru first shell distances in nitrate systems are shorter than in the chloride ones.

Comparing the edge energy to chloride references, it is also clear that no redox reaction occurs during the liquid-liquid extraction process and, as demonstrated with the aged samples, by aging organic solution. It also reveals a very close speciation for the two studied monoamide ligands and no significant differences in between TBP30% and TBP80%.

By comparison to the aqueous HNO<sub>3</sub> 1M solution, XANES spectrum for ruthenium in TBP are very close to the one observed in the aqueous phase. On the contrary in the monoamide system, the intensity of the first WL peak is decreasing in the organic phase whereas the second peak intensity is rising.

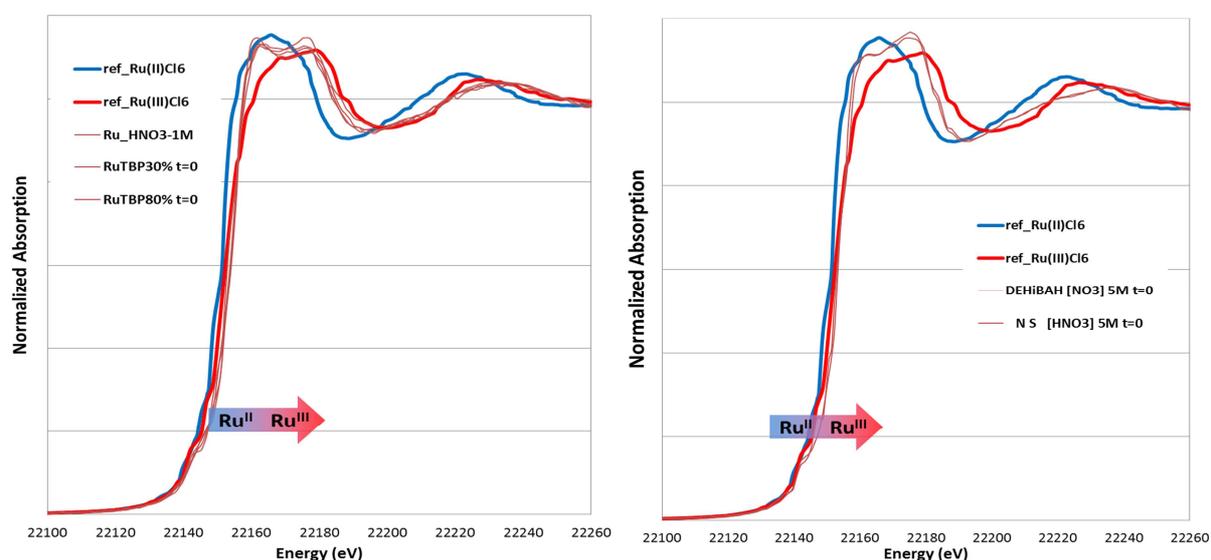


Figure 2 and 3: XANES spectra of Ru(II) and Ru(III) chloride (blue and red) compared to ruthenium in nitric acid, in TBP 30% and 80% and to monamides sample.

### EXAFS analysis:

The EXAFS spectra were extracted from the absorption spectrum using a spline function implemented in the Athena code. Hereafter is presented the modulus of Experimental FT's obtained for  $k^3$  weighted spectrum.

By direct reading of the FT the EXAFS spectrum confirms that, at the very beginning of the liquid-liquid extraction, the ruthenium coordination sphere in the organic phase is very similar to the ruthenium in the aqueous phase (see Figure 4). After 48 hours, the spectrum still exhibits the same features in the first and second coordination sphere.

After 10 days the same organic solution spectrum differs from the first  $t=0$  spectrum and it became completely different after a month with shorter distances in the second coordination sphere.

This evolution concerns mostly the second coordination sphere which is mostly dependent on the nitrate coordination mode and to ligand alignment through multiple scattering effects. Fitting with hypothetical models is necessary for a more advanced interpretation. DFT calculation on ruthenium coordination is under process to understand this evolution in terms of coordination number ( $H_2O$ ,  $HNO_3$ ,  $OH^-$ , TBP and nitrate coordination mode).

Some authors also proposed TBP coordination in the a first shell of ruthenium, no evidence of a phosphorous back-scatterer expected at  $3.5 \text{ \AA}$  was found during this experiment but simulation should help to determine this point more accurately.

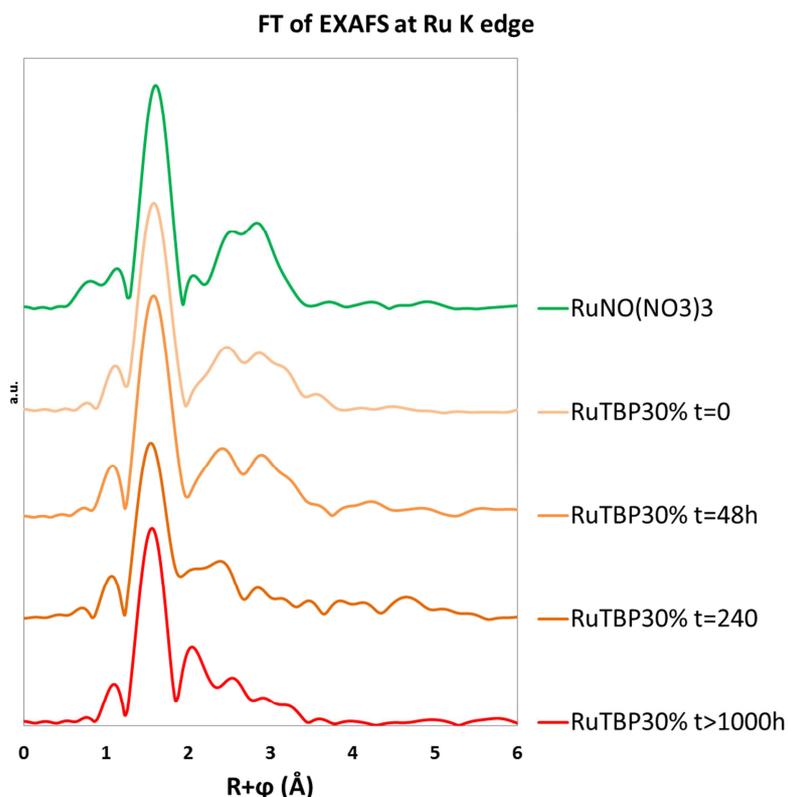


Figure 4: Experimental EXAFS spectra for Ru in nitric acid conditions and aging of the organic phase (TBP 30% vol./TPH).

For the monoamide samples, it was observed on XANES spectrum that the monoamides behave the same in terms of ruthenium extraction and coordination. The exact same conclusion is given by the EXAFS FT which are strictly identical for the two extracting agent. Moreover the peaks intensity in the second coordination sphere could be again associated to nitrate groups in the Ru coordination sphere. Concerning a coordination by the monoamide itself is hard to confirm if its in the coordination shell or not.

EXAFS spectra observed at  $t=0$  after the extraction and after 3 weeks of aging doesn't exhibit the same evolution than with TBP solvent. In term of solvent aging it could be interpreted by the low water content in monoamide organic phases. Ligand exchange in solution was found to be driven by water exchange in the ruthenium coordination sphere. In TBP the water content in organic phases is very high on the contrary to the monoamide systems.

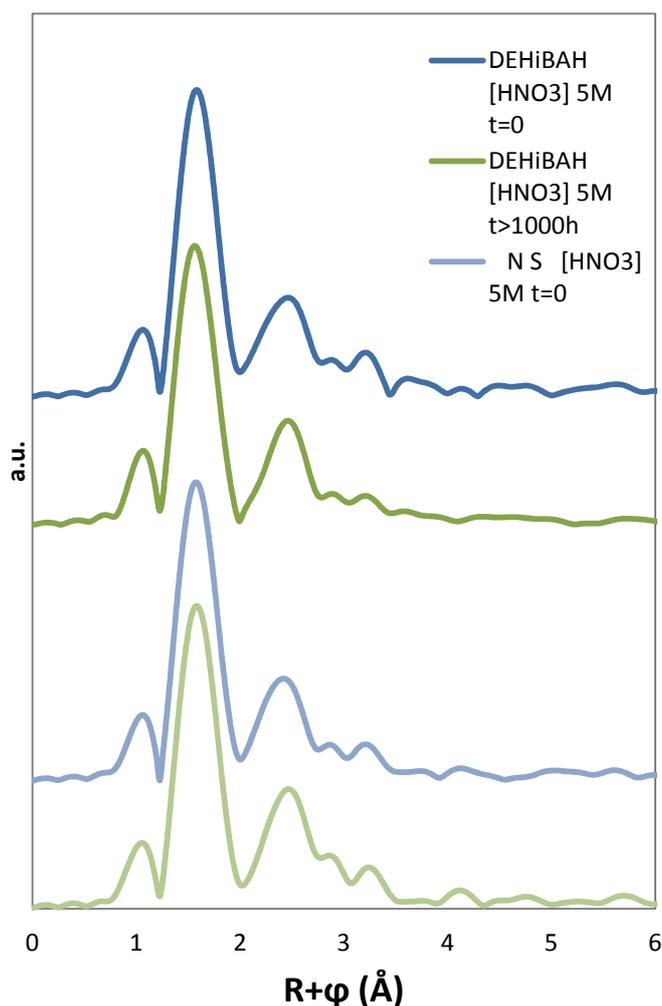


Figure 5: Experimental EXAFS spectra for Ru in nitric acid conditions and aging of the organic phase (TBP 30% vol./TPH).

#### **EXAFS simulations (first attempts):**

In order to determine the ruthenium coordination sphere in solution several model concerning octahedral and pseudo-octahedral Ru structure were built and used to simulate EXAFS spectrum. By

varying  $x$ ,  $y$ ,  $z$  in  $\text{RuNO}_z(\text{NO}_3)_y(\text{H}_2\text{O})_x$  the EXFAS spectrum evolves mostly in terms of second coordination sphere. Simulated spectra are presented Figures 6 in comparison to experimental Ruthenium nitosyl nitrate system (concentrated solution, 1M nitric acid and the commercial solid  $\text{RuNO}(\text{NO}_3)_3$ ). The simulation demonstrate how the second coordination sphere evolute over the all range of experimental condition and how the ruthenium speciation is difficult to access only using the EXAFS spectrum due to similarity in the expected species.

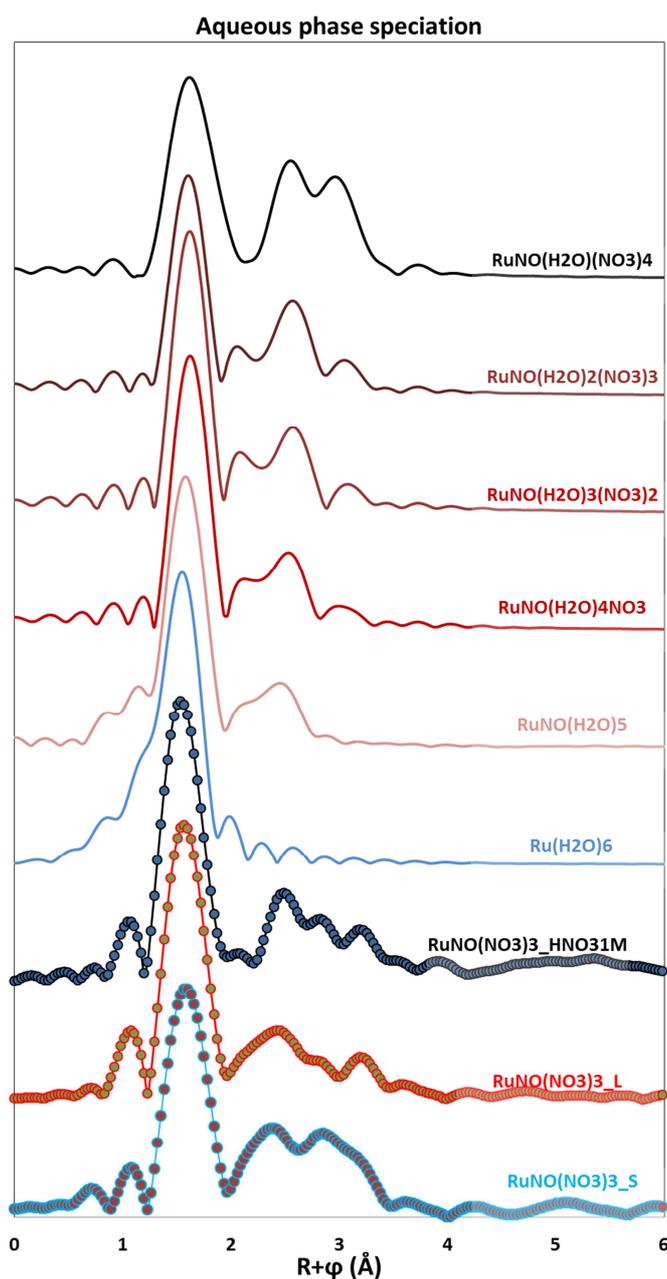


Figure 6: simulated EXAFS spectrum for the ruthenium-aquo-nitrosyl-nitrate system and comparison to experimental Ruthenium nitosyl nitrate system (concentrated solution, 1M nitric acid and the commercial solid  $\text{RuNO}(\text{NO}_3)_3$ ).