Interest of NMR in the field of radioactive environments Examples and limits.

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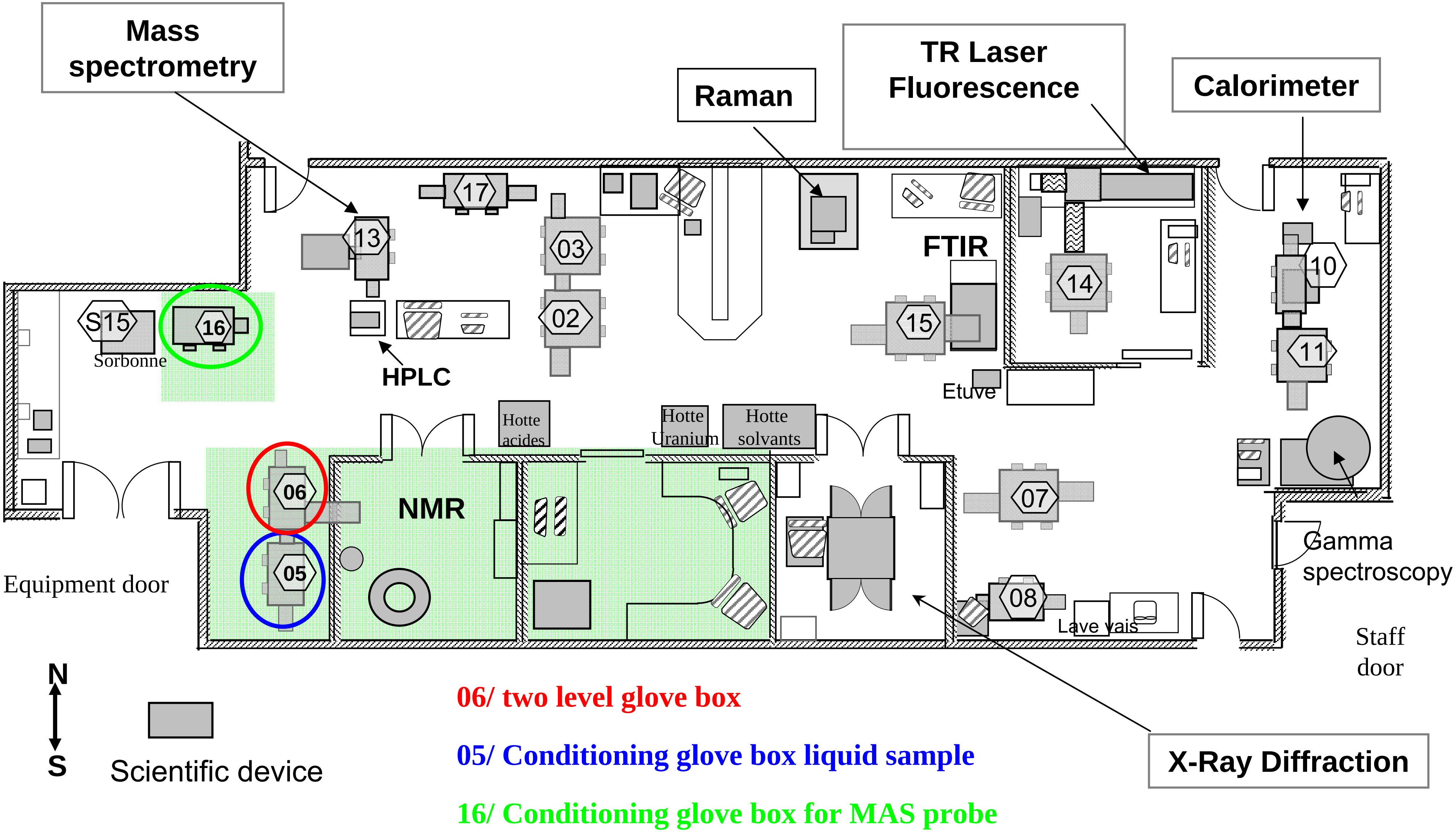
EURACT-NMR Workshop

Karlsruhe, Germany

overview

- NMR facilities to handle radioactive samples
- Liquid state analysis example
  - Radiolysis study
  - Characterization of metallic complexes
  - Conformational study (paramagnetic probe)
  - Diffusion and localized spectroscopy
- Solid state analysis
  - U Aluminate, Pu-doped glasses, ashes… same problem.
- Conclusion



Mass spectrometry
Raman
TR Laser Fluorescence
Calorimeter
17
13
03
02
FTIR
14
10
S15
16
Sorbonne
HPLC
15
11
Etuve
Hotte acides
Hotte Uranium
Hotte solvants
06
NMR
07
05
Equipment door
08
Lave vais
Gamma spectroscopy
Staff door
N
S
Scientific device
06/ two level glove box
05/ Conditioning glove box liquid sample
16/ Conditioning glove box for MAS probe
X-Ray Diffraction

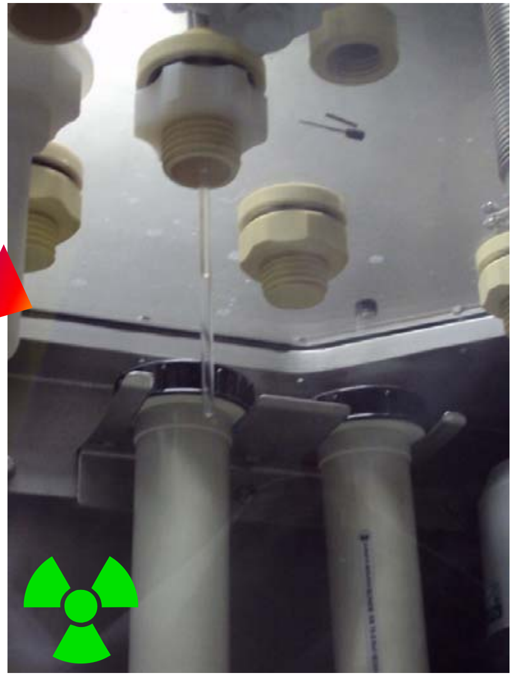
Radioactive samples and NMR

The two level glove box is linked to a normal glove box for the teflon tube conditioning.

Magnet room of the 400MHz spectrometer

The two level glove box:

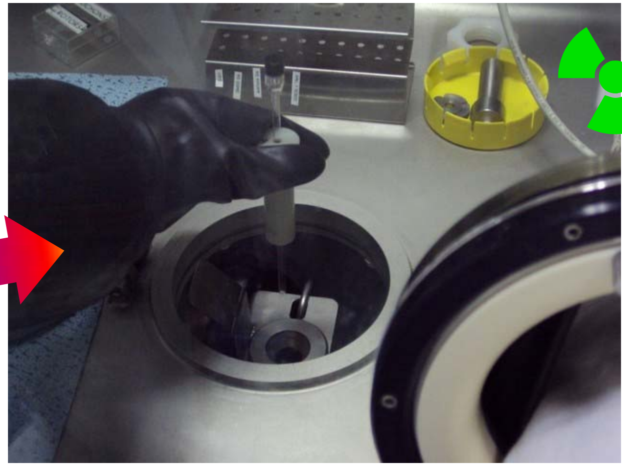
Liquid state sample management



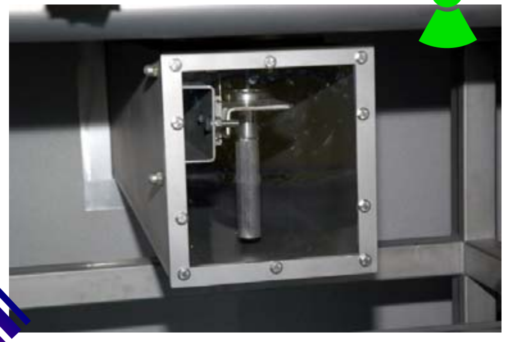
Teflon and glass tubes
are commercial items

Safe and reliable management of radioactive liquid samples in use in Atalante lab.

Checking of the NMR tube exterior before…



it leaves the glove box and…

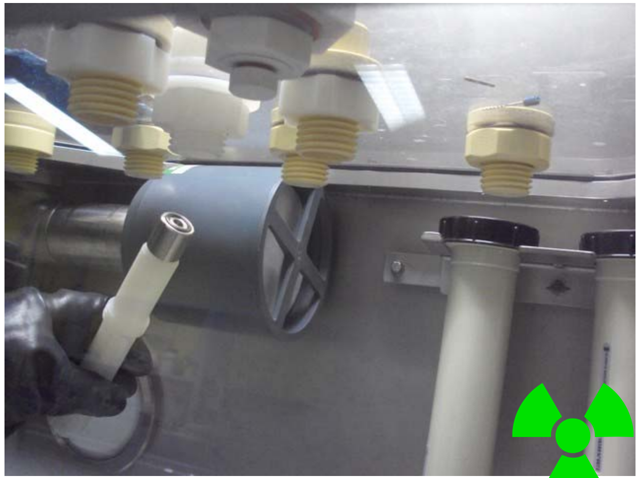


…is inserted into the magnet.

The two level glove box:

Solid state sample management

Commercial insert manage
through a screw
(drilled at the bottom)



Tool designed to handle rotor
and…
to plug the cap safely.

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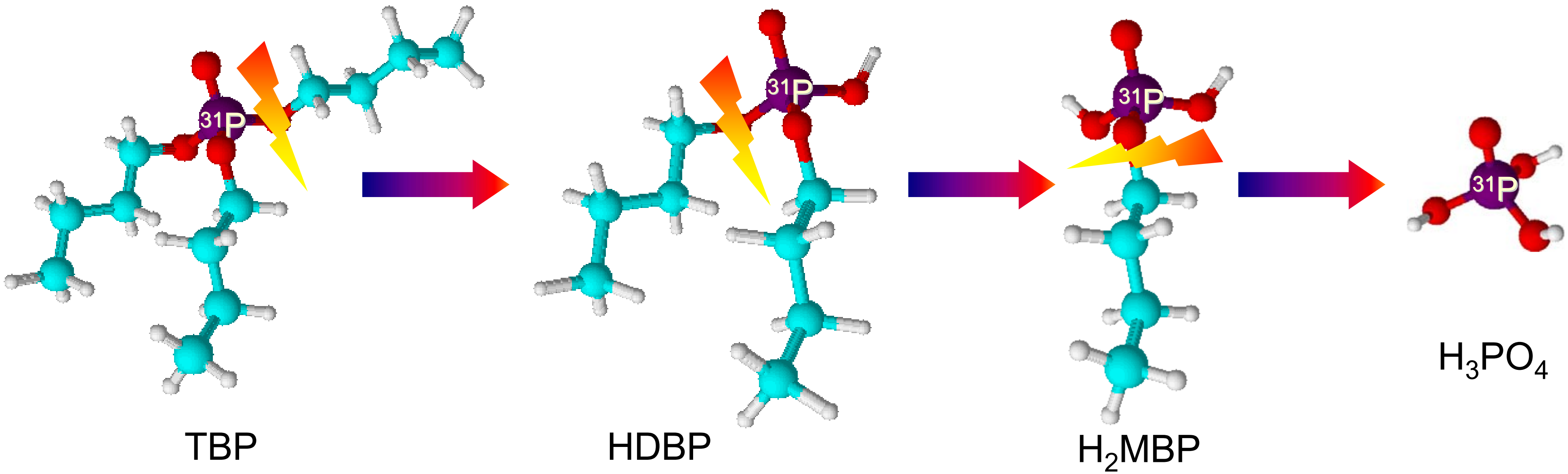
α radiolysis studies

- TBP (Tributyl Phosphate) degradation mechanism:



TBP radiolysis in organic phase (30% in TPH).

Purpose: Find a model to quantify degradation products depending on:

α radiation $^{238}Pu/^{239}Pu$, hydrolysis: $[Pu^{4+}]$, $[HNO_3]$ and temperature effects.

Degradation products have specific ^{31}P NMR signal.

$I_{P31}=1/2$; 100% natural abundant → sensitive signal.

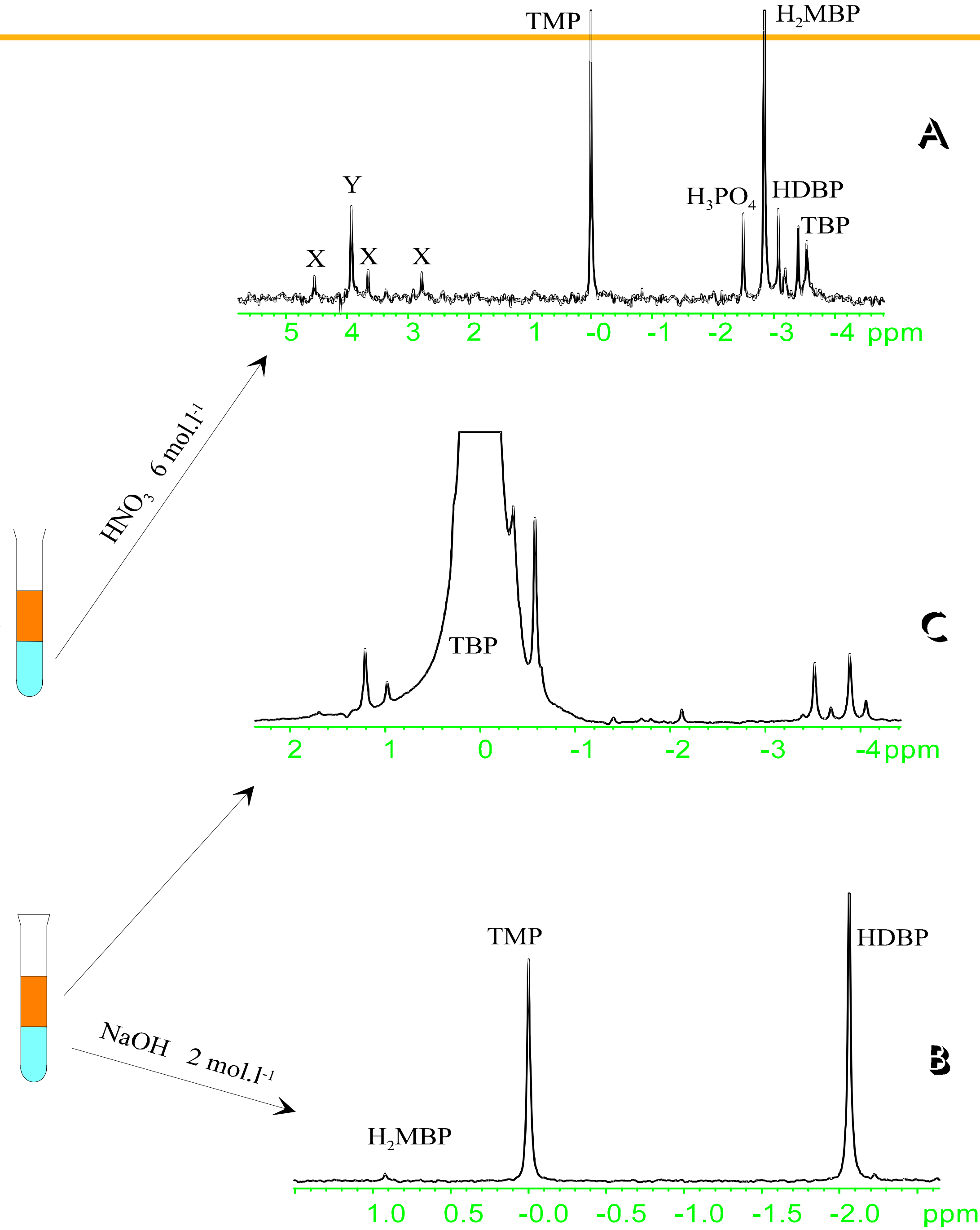
⚠ paramagnetic element must be removed before analysis.

After Pu(IV) extraction:
phase separation and organic phase left.

Preparation stage:

the organic phase is washed:

- to remove Pu(IV),
- to separate organic compounds.



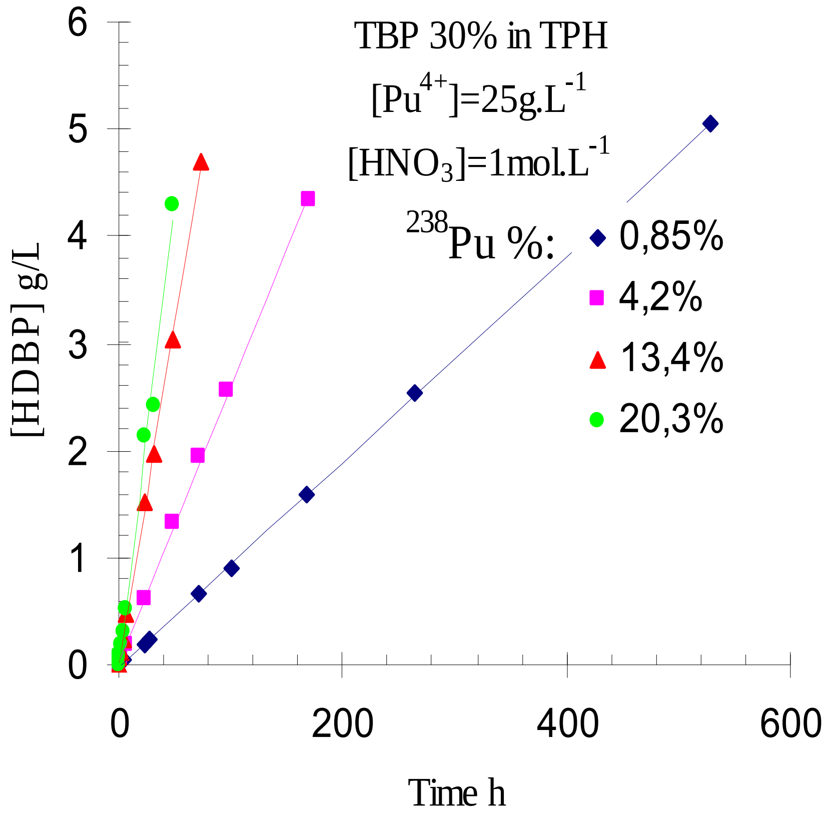
Wide experimental conditions:

- $0{,}5M<[HNO_3]_{aq}<6M$
- Pu isotope: 0,65% $<^{238}Pu<$ 20%
- Pu concentrations: $0{,}4mM<[Pu]_{org}<0{,}1M$ ($25g.L^{-1}$)
- experiments lasted up to 7000hours

No problem of concentration from a radiological point of view (mainly α emitters)

(TBP experiences < $2{,}7W.L^{-1}$)

Example of HDBP formation



Results:

Linear variation of the concentrations with plutonium contact time:

zero-order apparent reaction.

Kinetic constants k_i depend on some parameters which can be expressed in this empirical equation:

hydrolysis effect

α radiolysis effect

$$k_i = \underbrace{k_{io} + \overbrace{k_{iH^+}[H^+]}^{\text{nitric acid}} + \overbrace{k_{iPu^{4+}}\frac{[Pu^{4+}]}{239}}^{\text{plutonium}}}_{\text{can be neglected other } 500\text{mW.L}^{-1}\text{.}} + k_{i\dot{D}}\dot{D}$$

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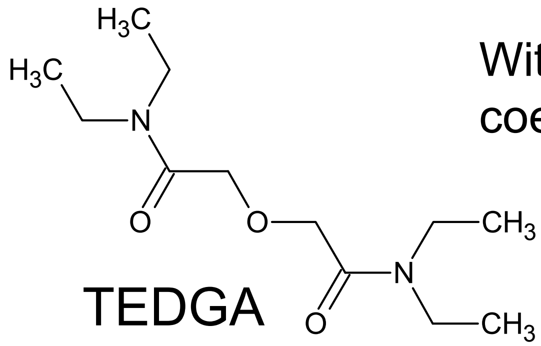
Characterization of metallic diglycolamide complexes in aqueous phase.



TEDGA

With longer alkyl chains diglycolamide are promising extractants for coextraction of An(III) and Ln(III).

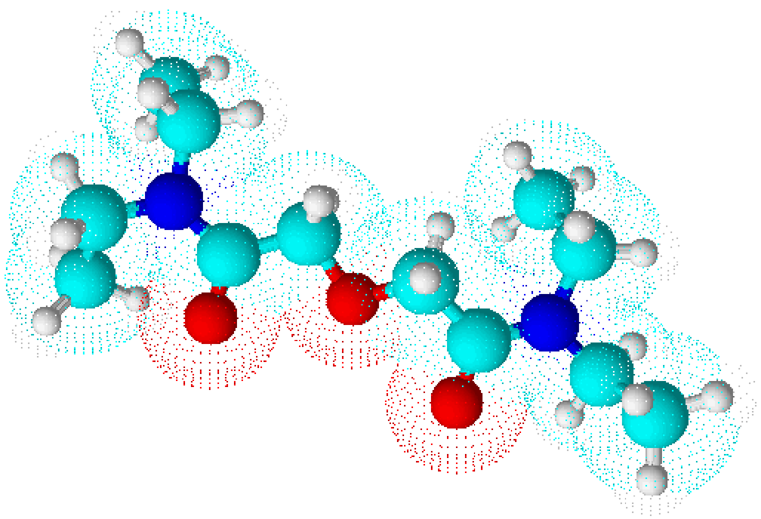
Aim of the study:

- Characterization of metallic complexes formed.
- Determination of the constant formation.

$$Nd(III) + nTEDGA \xrightarrow{\beta_{1n}} Nd(TEDGA)_n$$

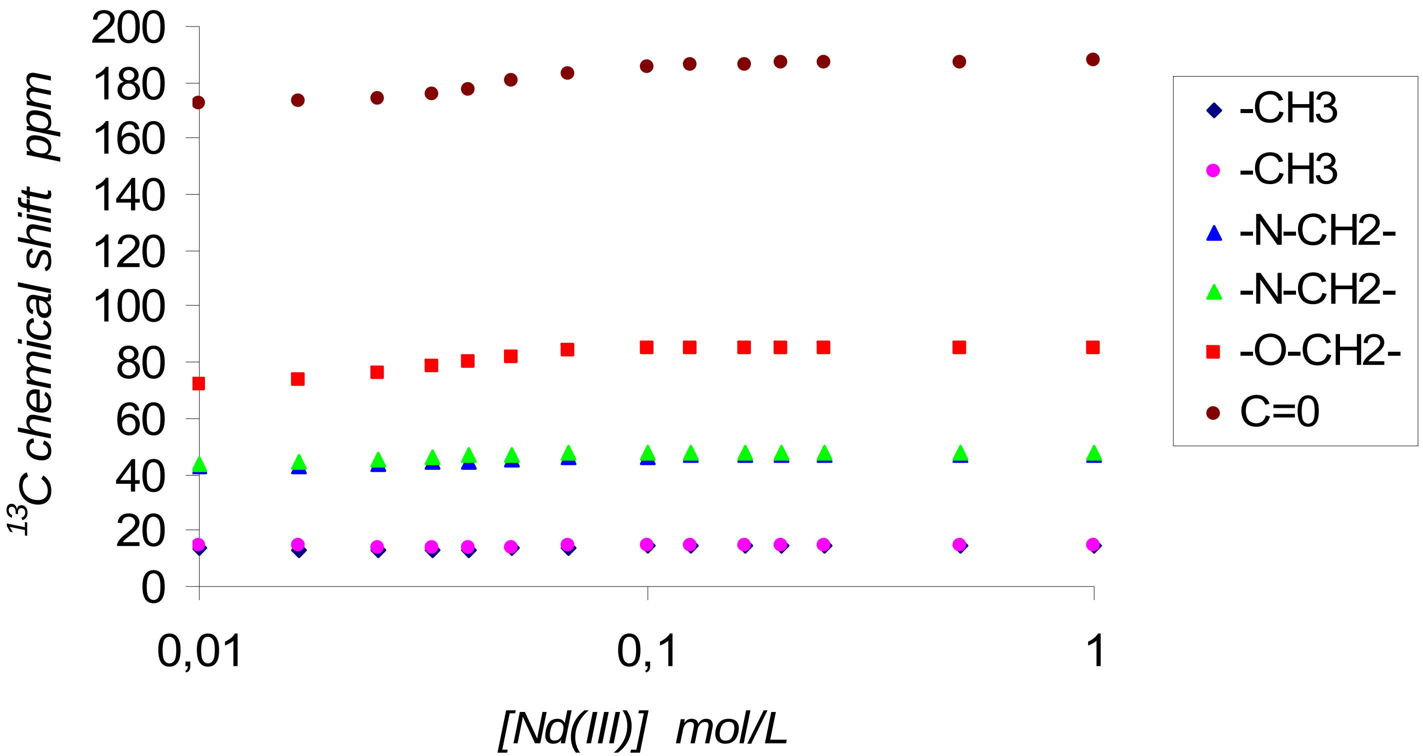
n=? β_{1n}=?

Nd(III) and Am(III)



Monitoring chemical shift of TEDGA solutions according to different ratios:

$$0{,}1 < \frac{[TEDGA]}{[Nd(III)]} < 10$$



^{13}C chemical shift vs [Nd(III)] [TEDGA]=0,1M at 25°C Ionic Strengh: $NaNO_3$=1; pH=2

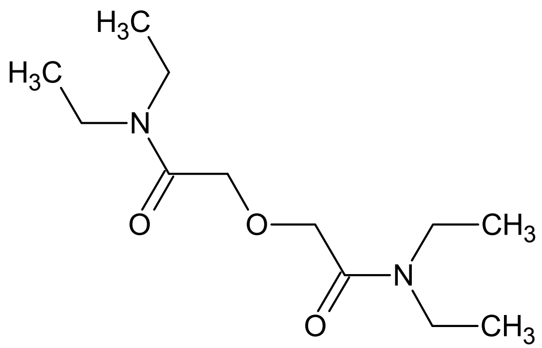
Fast chemical exchange at room temperature ⇒ *HypNMR software*

$$Nd(III) + TEDGA \xrightarrow{\beta_{11}} Nd(TEDGA) \qquad Log\beta_{11} = 1{,}9 \pm 0{,}1$$

$$Nd(III) + 2TEDGA \xrightarrow{\beta_{12}} Nd(TEDGA)_2 \qquad Log\beta_{12} = 4{,}4 \pm 0{,}1$$

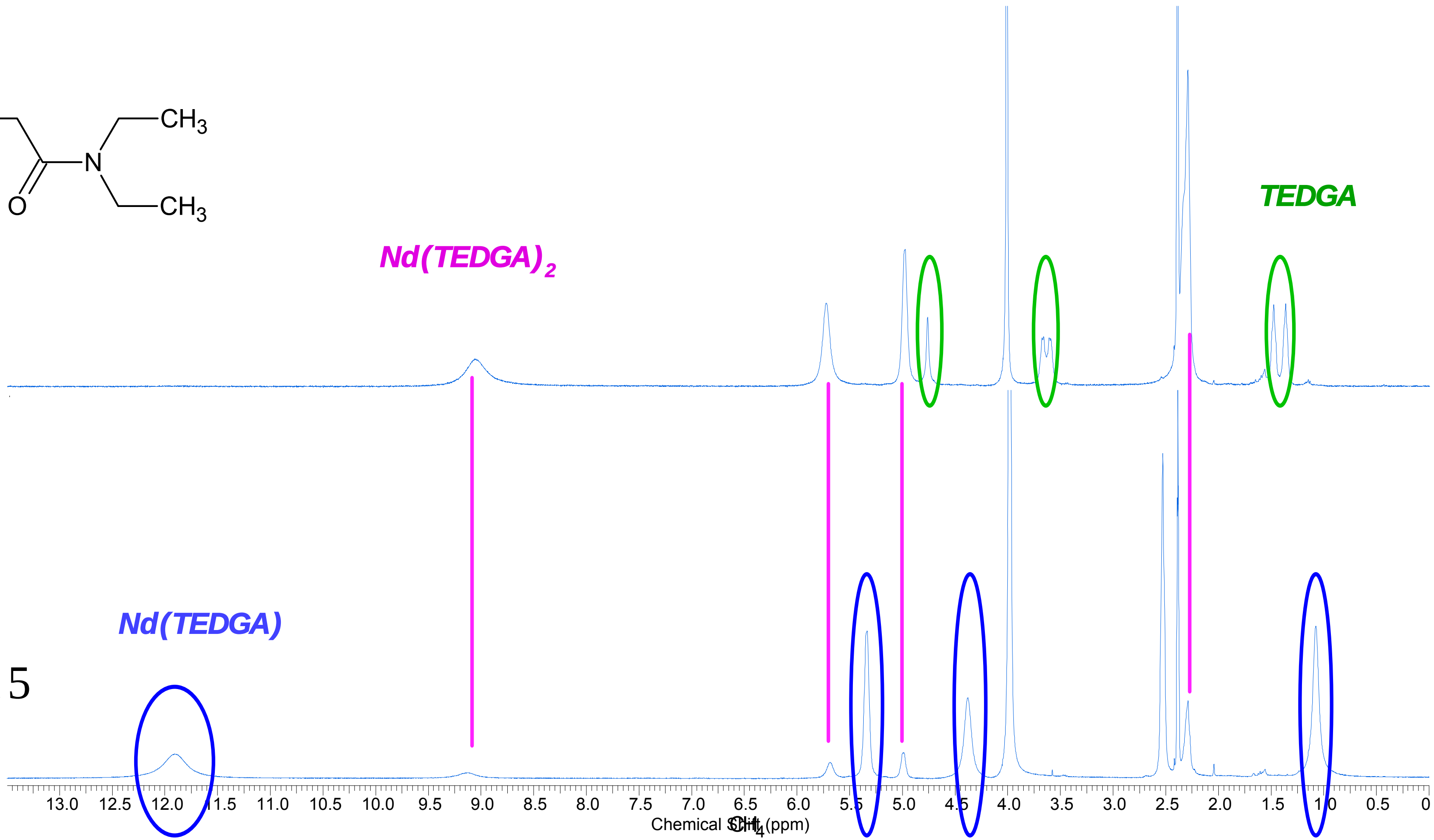
Do these species really exist?

Characterization of complexes by slowing down chemical exchange (Temperature)



$$\frac{[TEDGA]}{[Nd(III)]} = 2$$

$$\frac{[TEDGA]}{[Nd(III)]} = 0,5$$



^{1}H spectra: TEDGA/Nd(III) 1% in acetoneD6 T=-50°C ([TEDGA]=1mM)

^{13}C spectra: more difficult to get at such TEDGA concentration

What about the same study with Am(III)?

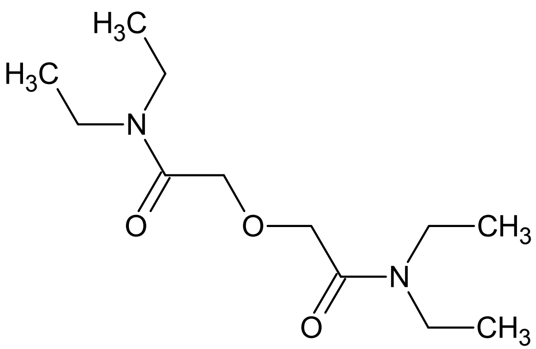
$1{,}5.10^{-2}$ mol/L of Am(III) in nitric solution → 400µGy/h contact

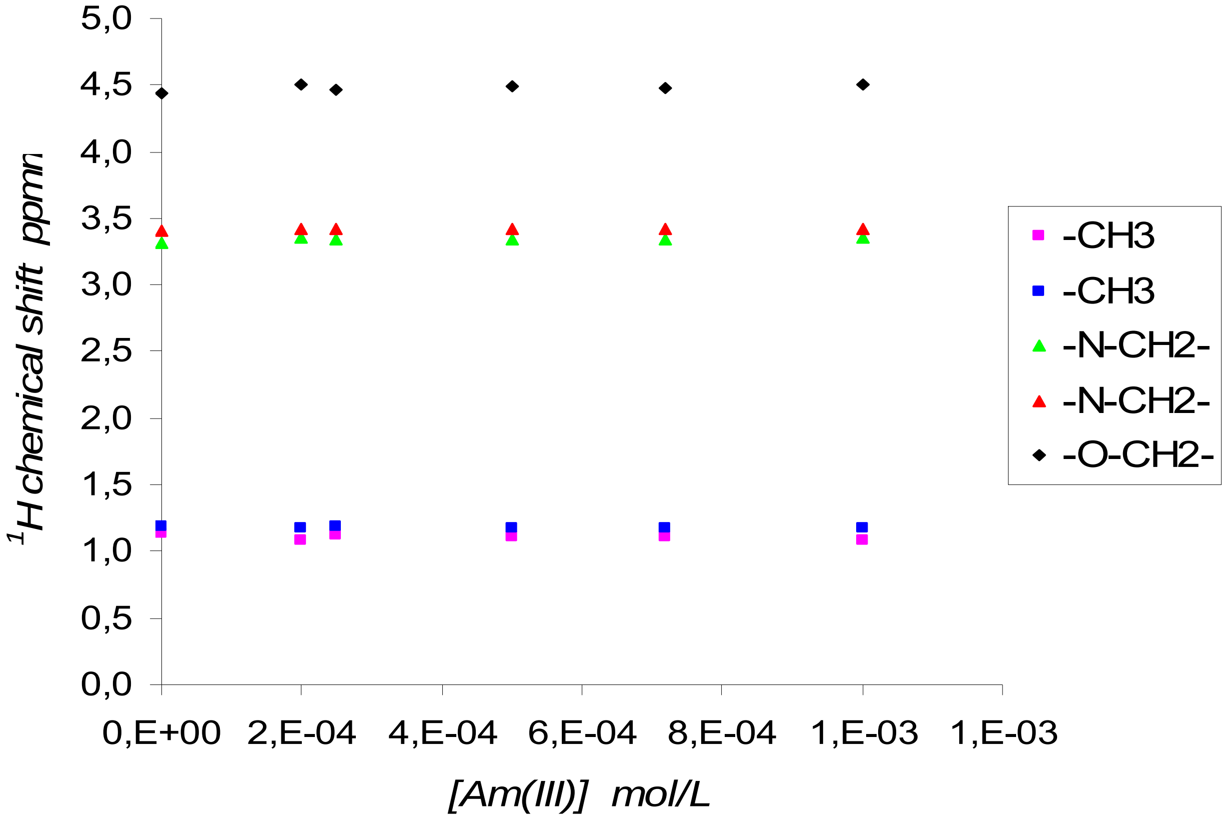
100µGy/h body

Safety radioprotection involves experimental concentrations and monitoring:

[Am(III)] used lower than those of Nd[III] [TEDGA]=10^{-2} mol/L

^{1}H spectra





^{1}H chemical shift vs [Am(III)]
[TEDGA]=10^{-2}M at 25°C
Ionic Strengh: $NaNO_3$ = 0,6

HypNMR software calculation:

$$Am(III) + TEDGA \xrightarrow{\beta_{11}} Am(TEDGA) \qquad Log\beta_{11} = 3{,}9 \pm 1$$

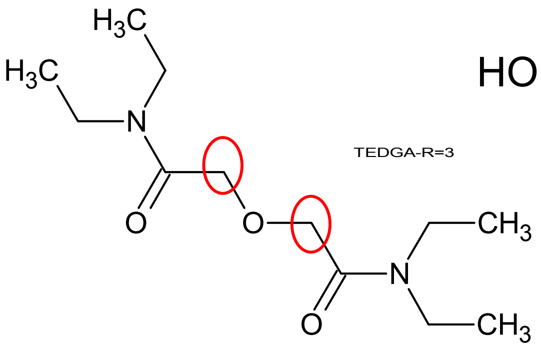
$$Am(III) + 2TEDGA \xrightarrow{\beta_{12}} Am(TEDGA)_2 \qquad Log\beta_{12} = 7{,}8 \pm 1$$

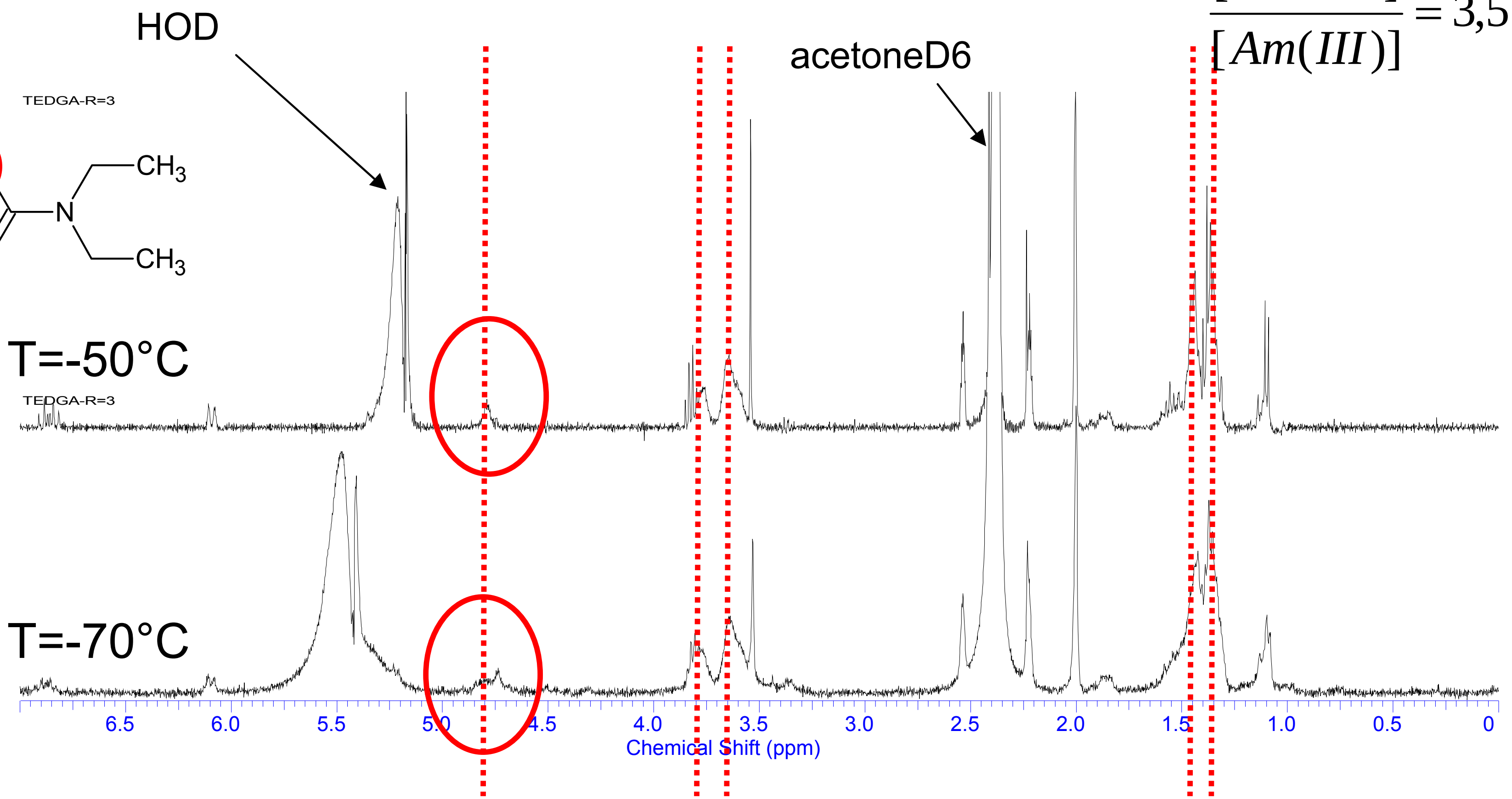
Characterization of Am(III) complexes by slowing down chemical exchange

1% dilution: [TEDGA]=0,1 mmol/L too low to be detected with a standard reverse probe.

10% to much water. → Slow exchange not reached before freezing

$$\frac{[TEDGA]}{[Am(III)]} = 3,5$$





^1H spectra: TEDGA/Am(III) 10% in acetoneD6 ([TEDGA]=1mM)

Cryogenic probe useful for ^{13}C chemical shift monitoring and ^1H spectra at low temperature.

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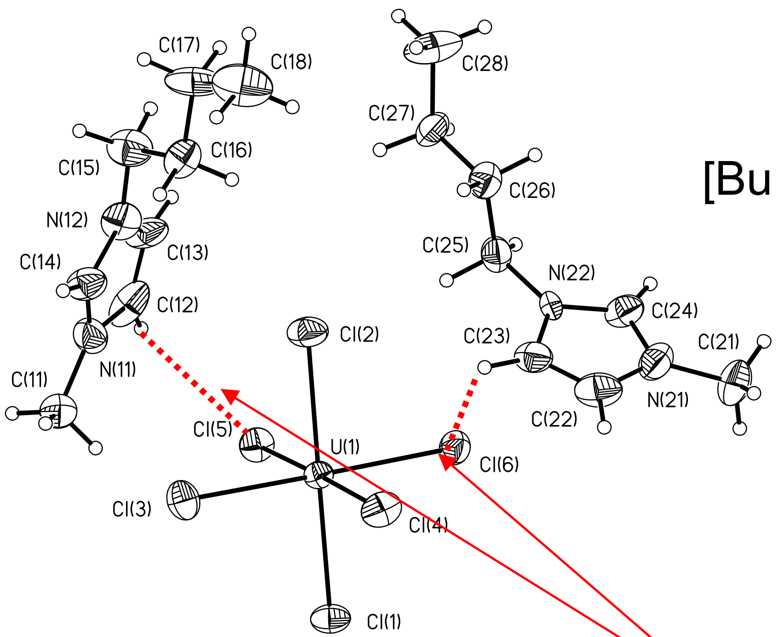
Conformational studies

Room temperature ionic liquid (RTIL) are potential solvent to develop new processes for recovery and purification of actinides.

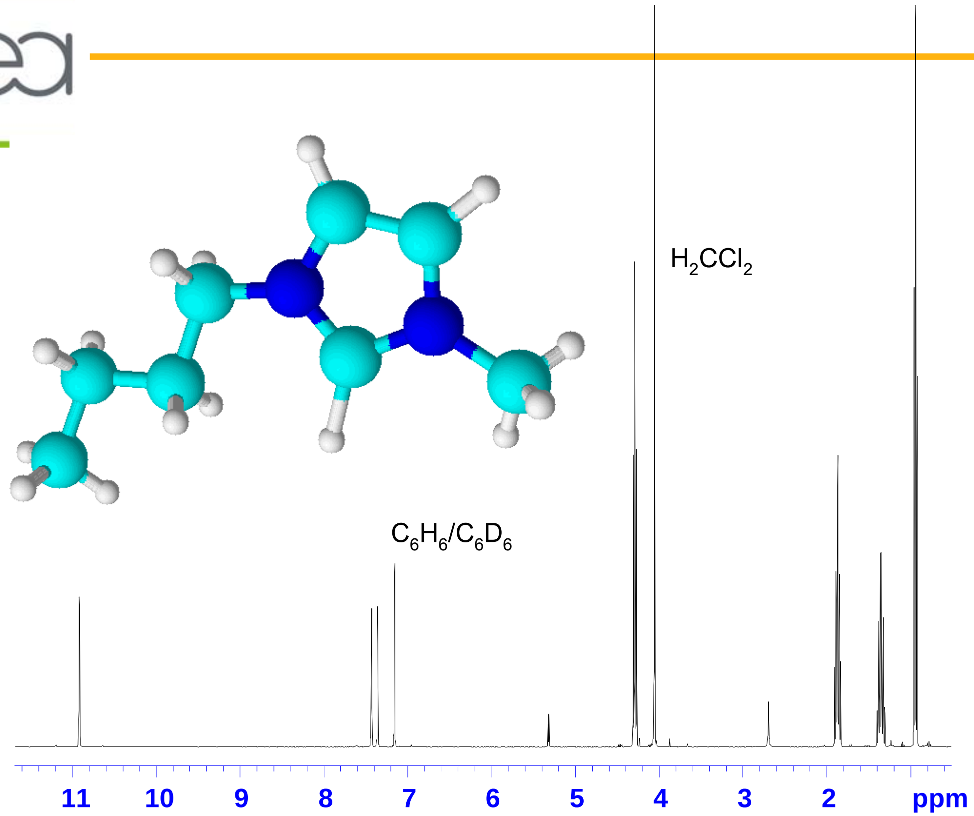


[BuMeIm]$_2$[UCl$_6$]

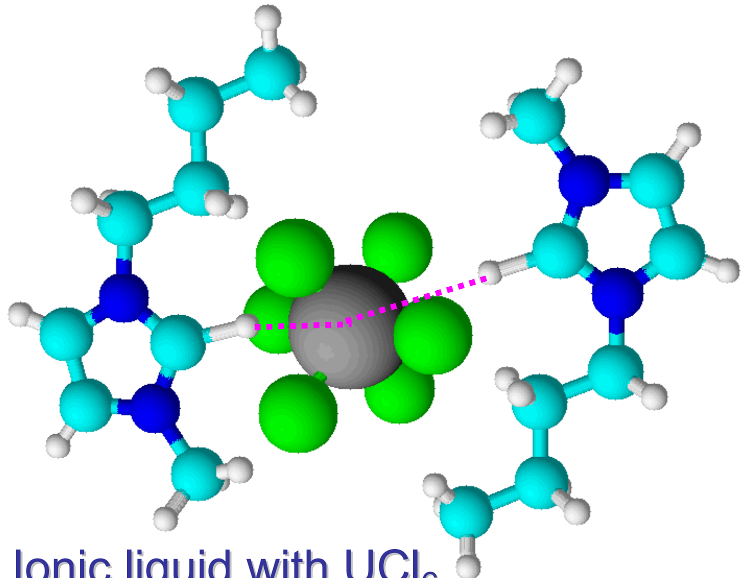
X-Ray data for [BuMeIm]$_2$UCl$_6$ → hydrogen bonding between the chlorine and the proton of the imidazolium moity.

Purpose: What about the structure in solution (dichloro methane) ?

S. Nikitenko and al.; *Polyhedron,* Vol26 p3136-3142 (2007)

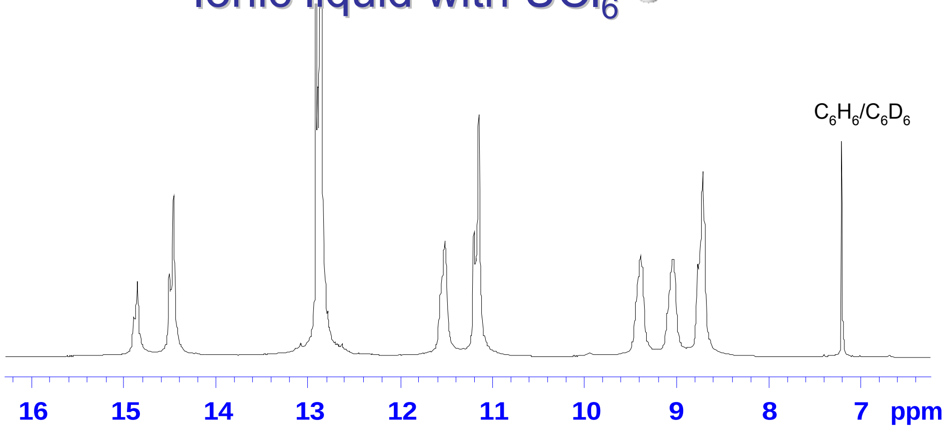


H[1] NMR spectrum of $[BuMeIm^+][Cl^-]$ in H_2CCl_2

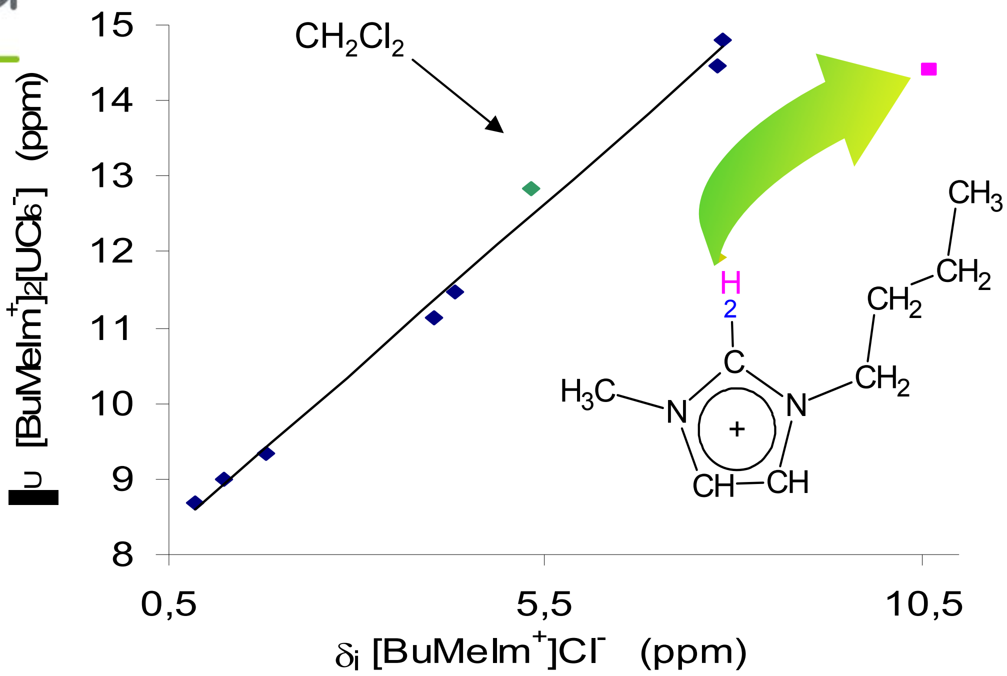


Ionic liquid with UCl_6

U(IV) paramagnetic behavior: lines are broadened and shifted:



H[1] NMR spectrum of $[BuMeIm^+]_2[UCl_6^-]$ in H_2CCl_2



Chemical shift changes on NMR spectra are well described through equations:

$$\Delta\delta_i = \Delta\delta_{cont} + \Delta\delta_{dip}$$

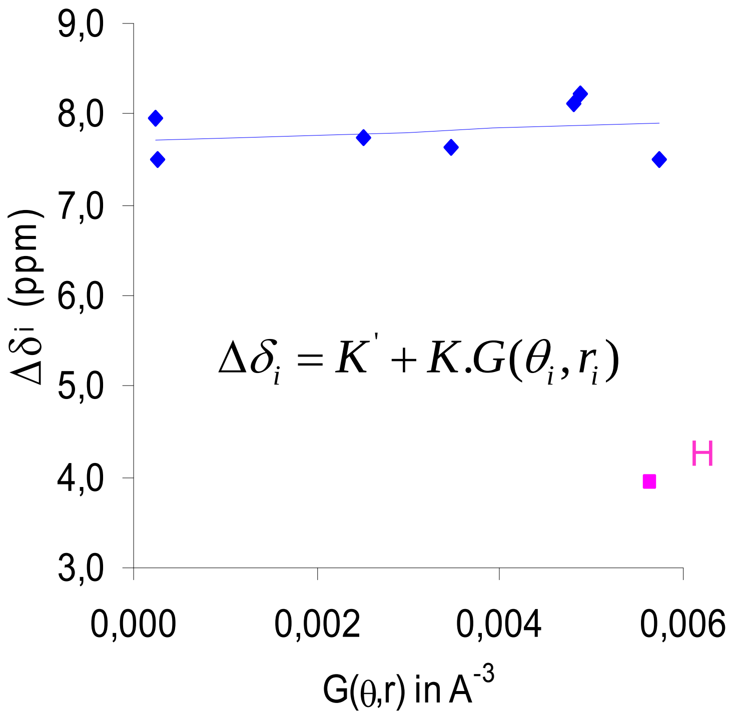
$$C^D G$$

Contact term:
electron-nucleus coupling

Dipolar term:
geometric factors θ ,*r*.

$$\Delta\delta_i = \underbrace{\langle S_Z \rangle F}_{} + \underbrace{\frac{g^2\beta^2 S(S+1)}{3kT} \cdot \left(\frac{3\cos^2\theta_i - 1}{r_i^3} \right)}_{C^D G}$$

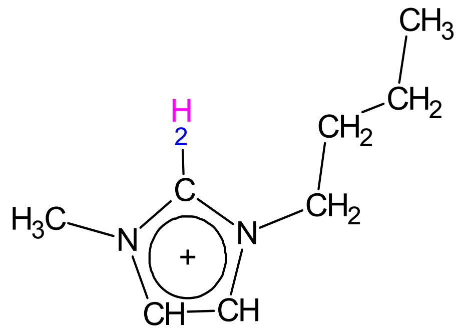
From XRD structural data it has been possible to calculate the geometric (or dipolar) contribution in the U(IV) induced shift.



$$\Delta\delta_i = \Delta\delta_{cont} + \Delta\delta_{dip}$$

$$C^D G$$

$$\Delta\delta_i = \langle S_Z \rangle F + \frac{g^2\beta^2 S(S+1)}{3kT} \cdot \left(\frac{3\cos^2\theta_i - 1}{r_i^3} \right)$$



The contact term of the H2 chemical shift proves the hydrogen bonding in solution.

Simple structural study thanks to available XRay data, but ….

•Relaxation time measurements: (Solomon-Bloembergen equation)

$$\frac{1}{T_{1p}} = \underbrace{\frac{2}{15}(\gamma_I \gamma_J \hbar)^2 \frac{J(J+1)}{r_{IJ}^6}\left[\frac{3\tau_{c1}}{1+(\omega_I \tau_{c1})^2} + \frac{7\tau_{c2}}{1+(\omega_J \tau_{c2})^2}\right]}_{\text{dipolar term}} + \underbrace{\frac{2}{3}J(J+1)\left(\frac{A}{\hbar}\right)^2 \frac{\tau_{e2}}{1+(\omega_J \tau_{e2})^2}}_{\text{contact term}}$$

•Chemical shifts:

$$\Delta\delta_{IS} = \overbrace{D_1 \frac{3\cos^2\theta - 1}{r^3} + D_2 \frac{\sin^2\theta\cos\theta - 1}{r^3}}^{\text{dipolar term}} + \overbrace{\langle S_z \rangle \frac{\beta}{3kT\gamma_I}\frac{A}{\hbar}}^{\text{contact term}}$$

$$\Delta\delta_{IS} = C^D G + \langle S_Z \rangle F$$

C^D and $\langle S_Z \rangle$ are characteristic of the cation, independent of the ligand.

Since the seventies, C^D ,$\langle S_Z \rangle$ have been determined and calculated for Ln(III).

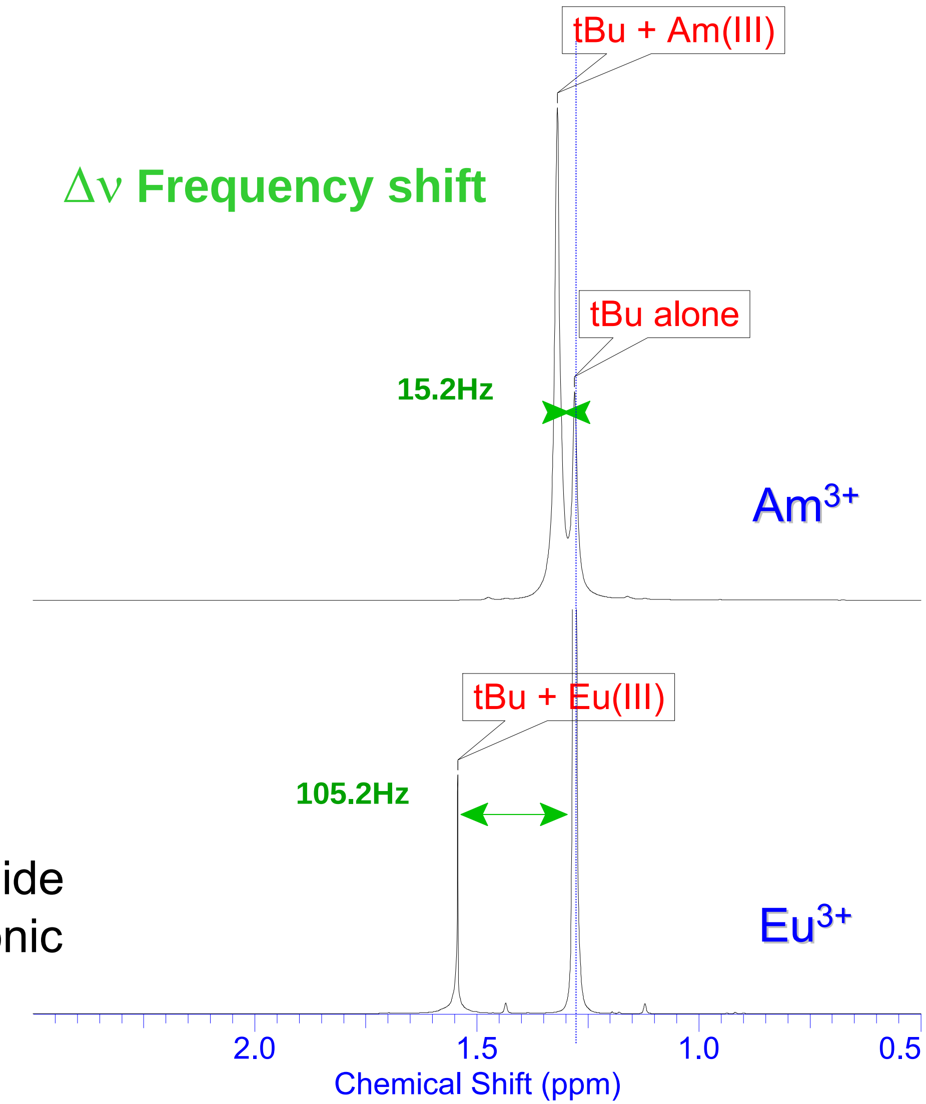
Very few studies have been published dealing with Actinides' C^D or $\langle S_z \rangle$.

Despite isoelectronic configuration between 4f and 5f ions paramagnetic behavior are different.

Example: $f^{\,6}$

Magnetic susceptibility measurements from ^{1}H NMR spectra according to Evans' method for the $7F^0$ electronic configuration of Eu^{3+} and Am^{3+}:

$$\mu_{eff} = f(\Delta\nu, m, MW)$$



Outlook: Ph D student (Steve JAN) to look at actinide paramagnetic behavior and correlation with electronic configuration.

Use of NMRD thanks to J. F. DESREUX.

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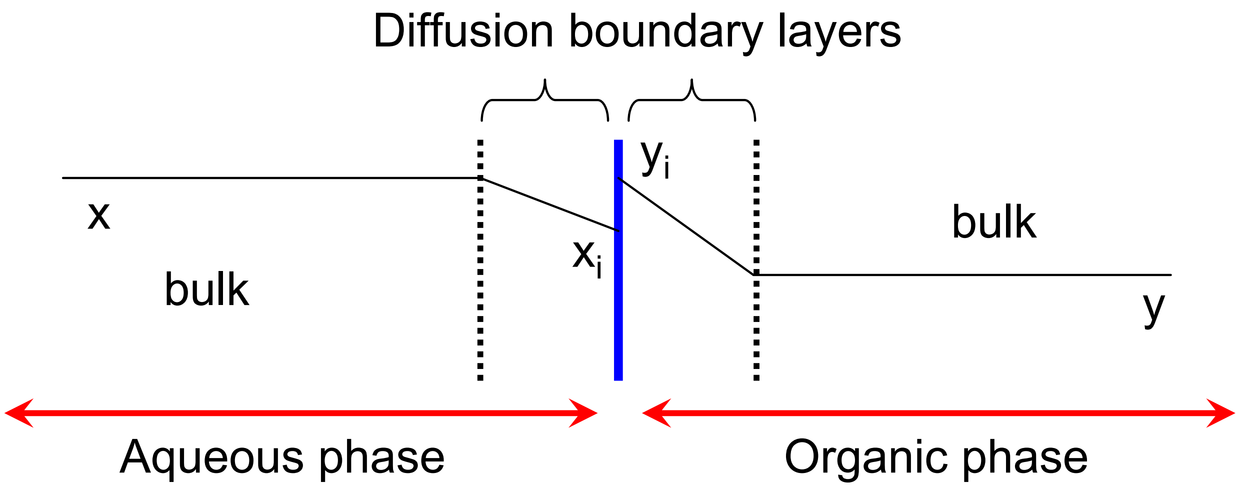
Diffusion and localized spectroscopy

NMR can help to understand what happens in a biphasic system:

- chemical reaction at the interface: thermodynamic and kinetic phenomena.
- transfer in the aqueous and organic phase: diffusion

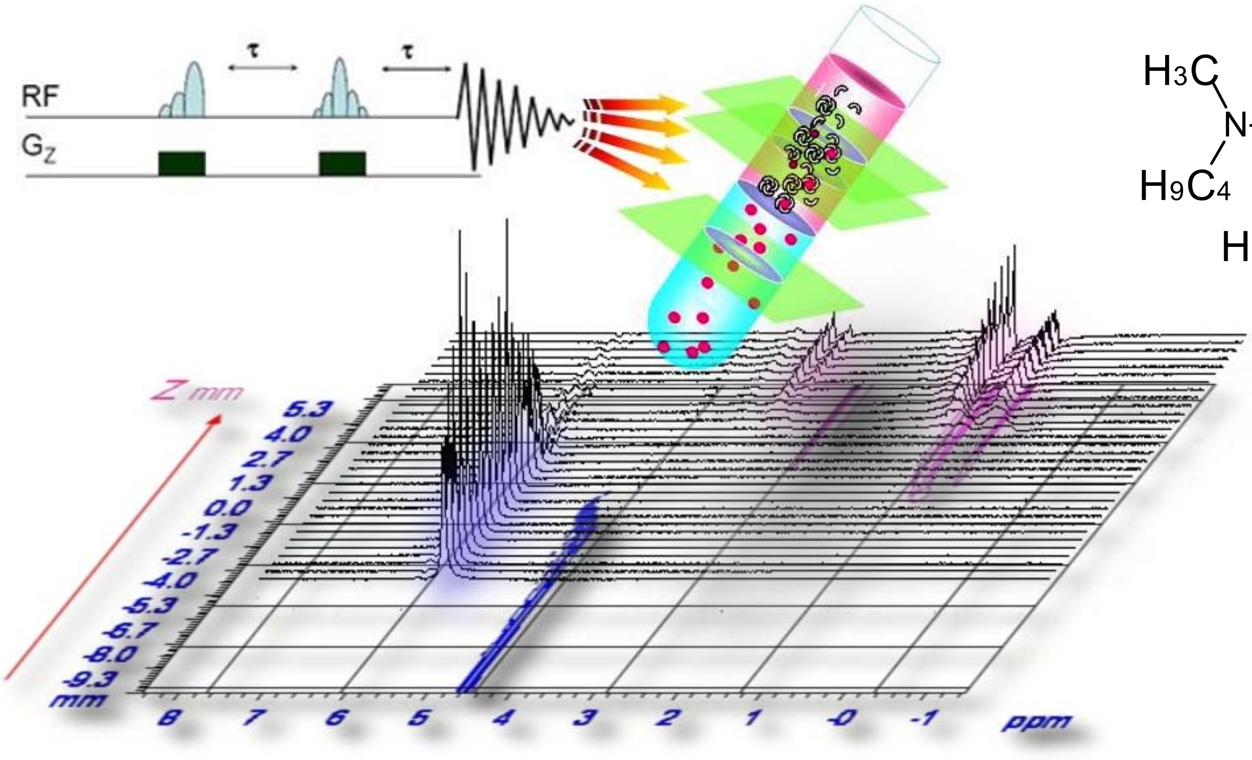


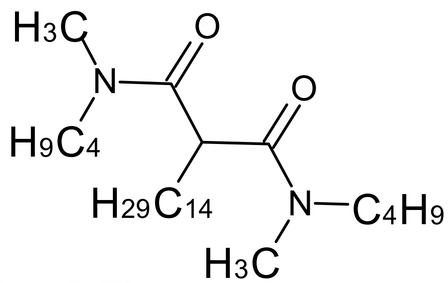
Imagine you can get a spectrum from a slice perpendicularly to an NMR tube….

Concentration profile from the interface to the bulk ⇒ Diffusion coefficient (≠ self diffusion)

Look at new species formed next to the interface.

LOCSY pulse sequence developed with M. BARDET, S. HEDIGER (CEA-Grenoble team) and C. MANTEL (Post-doc). Implemented for standard probe with z-gradient.





[1]H spectra of a biphasic system:

malonamide (DMDBTDMA) brings into contact with an aqueous phase.

Slice thickness= 68μm

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Solid state analysis

Story started 5 years ago with ^{11}B NMR to study borosilicate glass doped with Pu.

The main problem: get high resolution → High spinning speed of the samples *(not only)*.

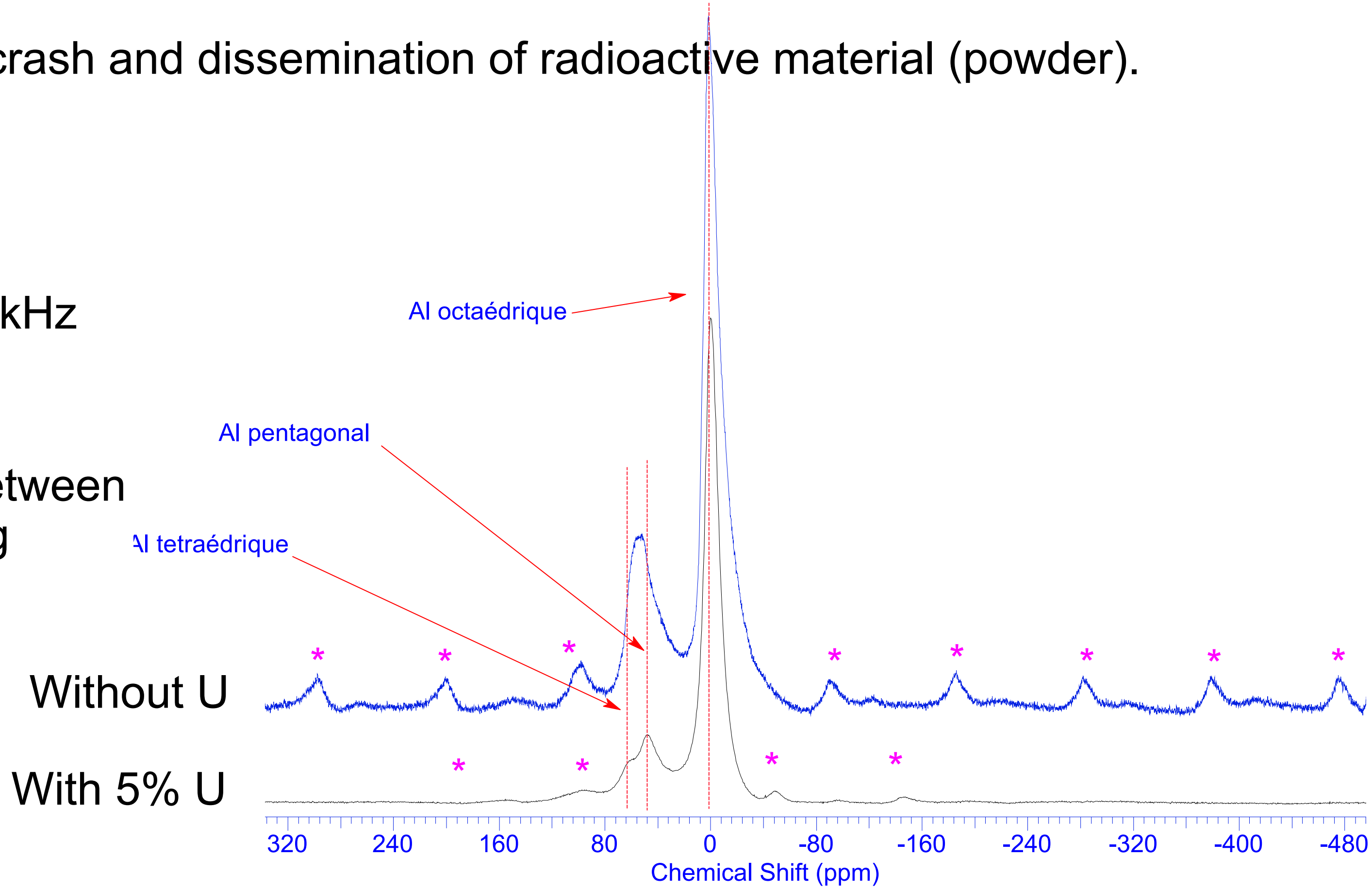
Safety problem: crash and dissemination of radioactive material (powder).

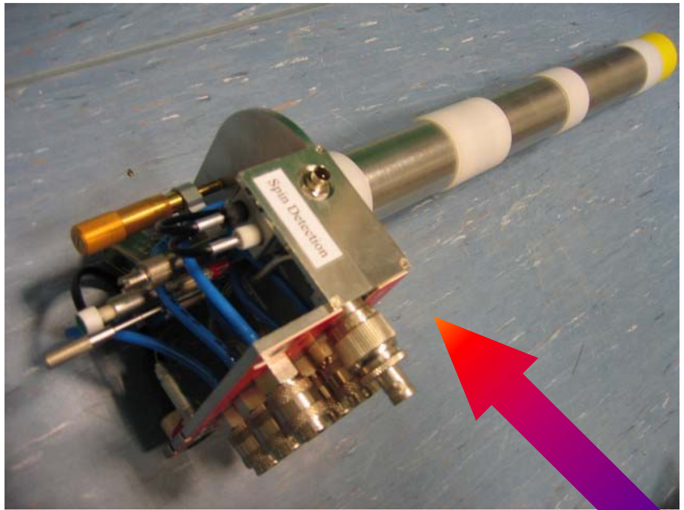
^{27}Al spectrum 7mm probe 5kHz

And use of insert

Still difficult to distinguish between isotropic peaks and spinning sidebands

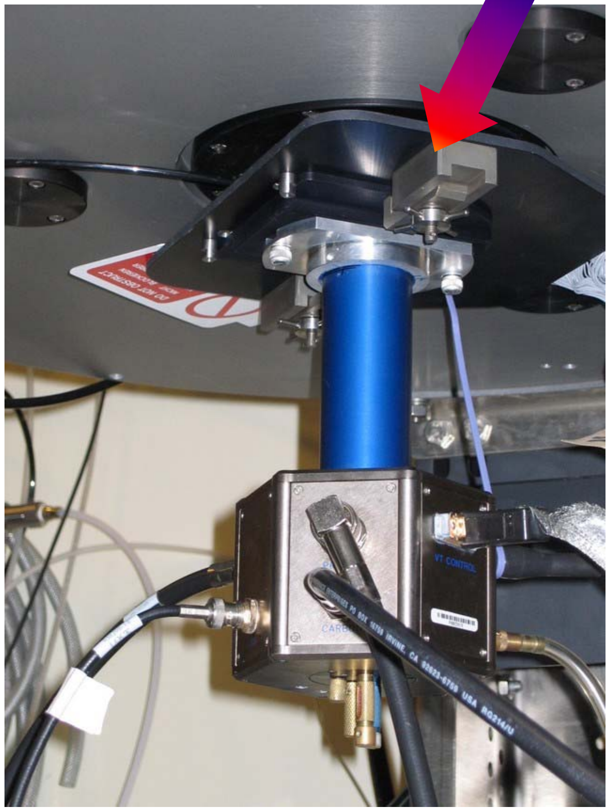
S. NIKITENKO aluminates





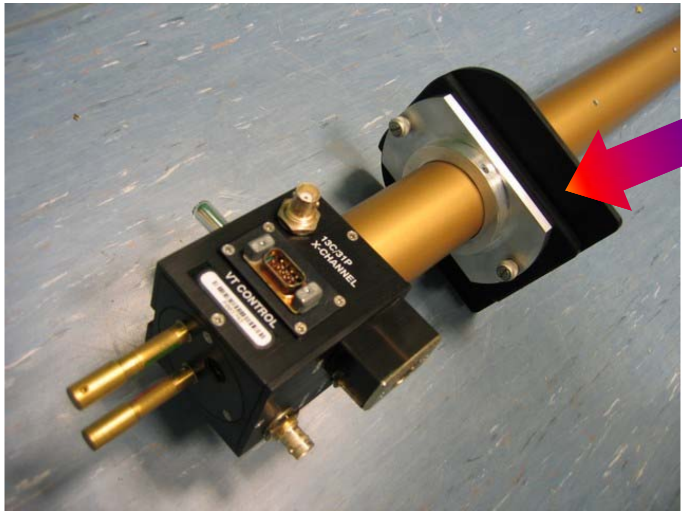
7mm CP/MAS Bruker probe

new design of the cover shim coil with locking parts



5mm Varian probe in a Varian narrow bore + adaptation for Bruker probes.

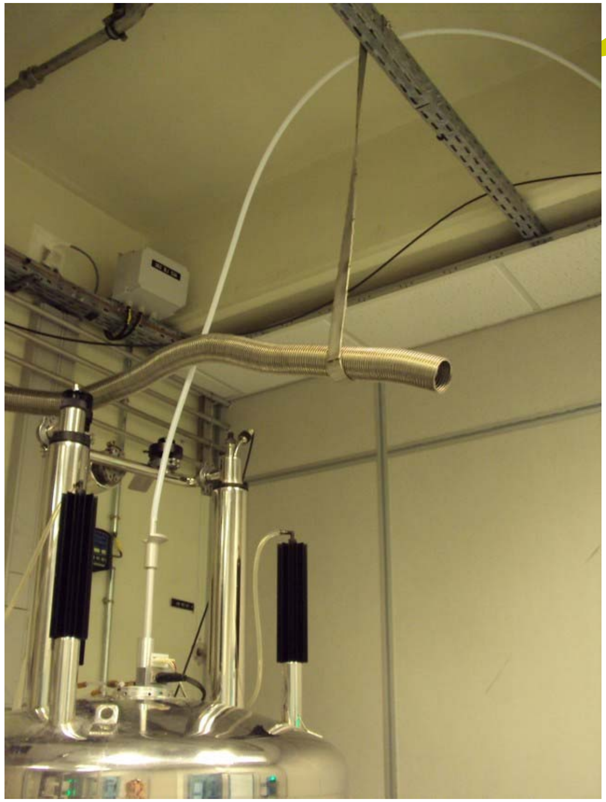
adaptation part looks like Bruker top probe.

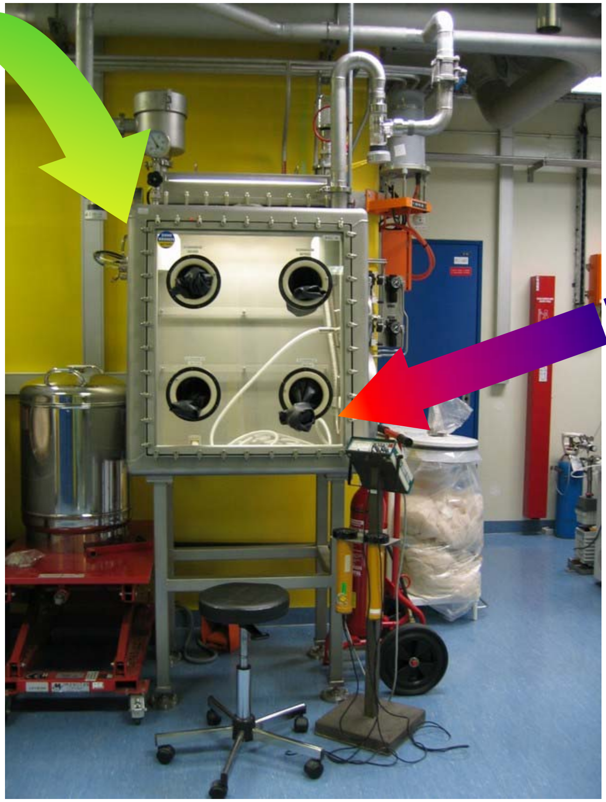


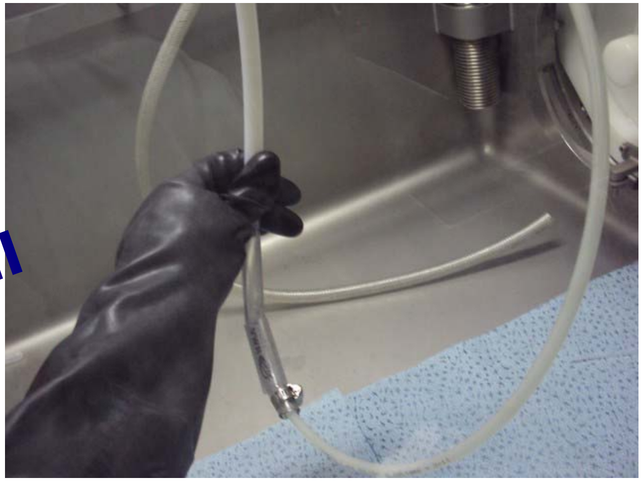
5mm Varian probe + adaptation part

Alternative: no spinning speed limit → probe head nuclearization

1. To insure confinement of the stator.
2. Link to a glove box thanks to a MASII Bruker device

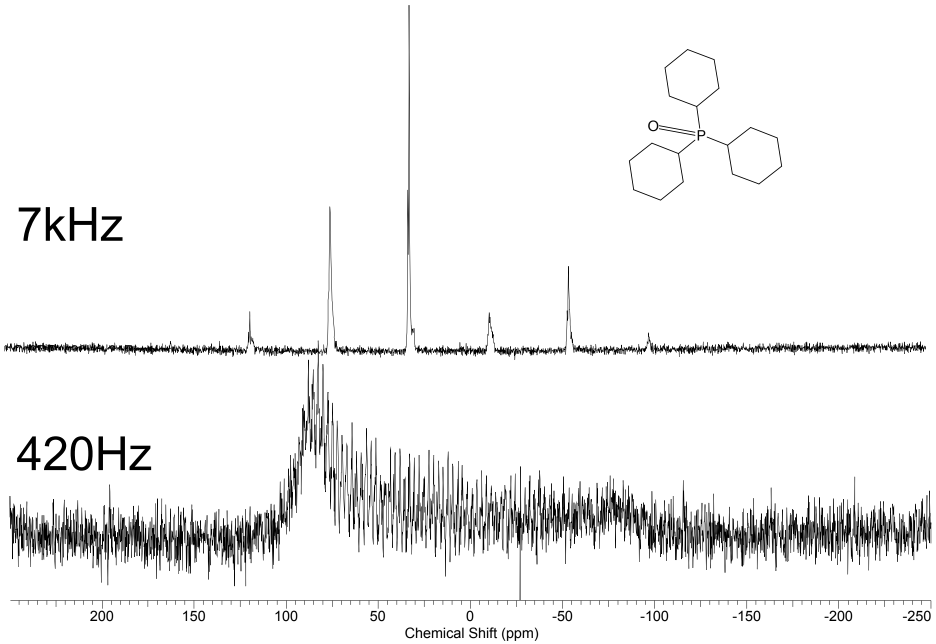






Case of ½ spin: ^{31}P
CP/MAS 7mm probe

TOPO solid state

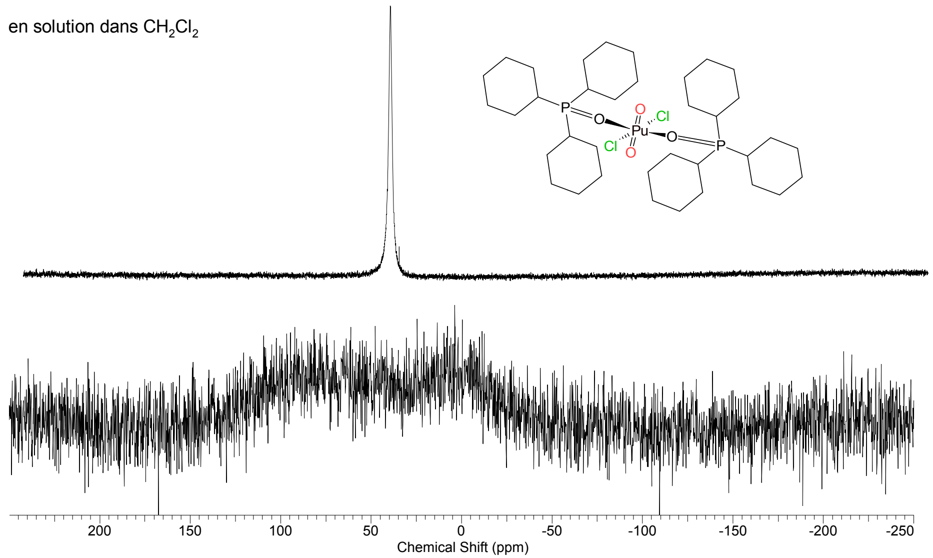


in D_2CCl_2

$(TOPO)_2PuO_2Cl_2$

Broadening paramagnetic effect

Solid state 420Hz

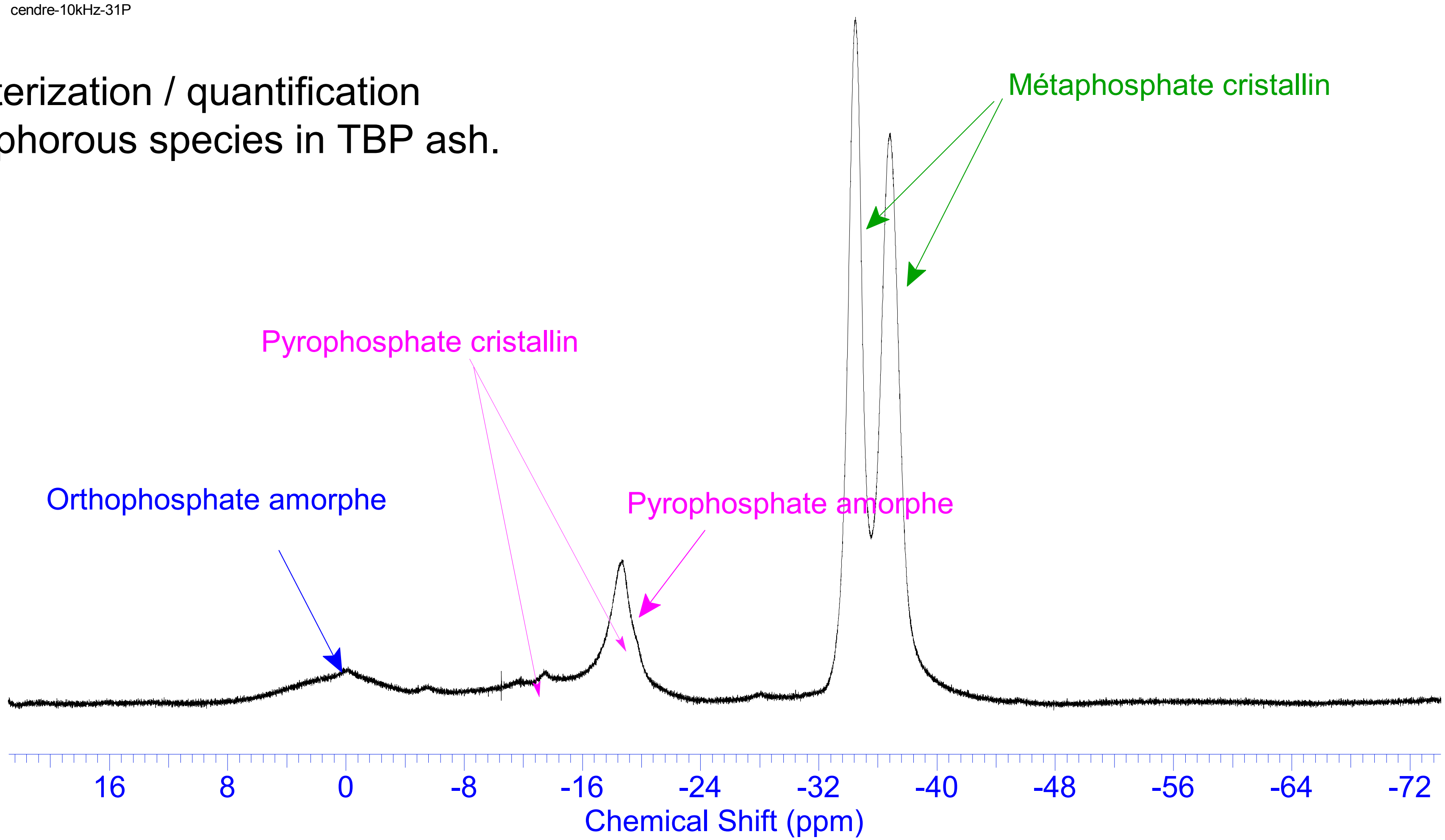


Prepared by S. CORNET (Post-Doc Atalante)

Before starting irreversible modifications of the probe …

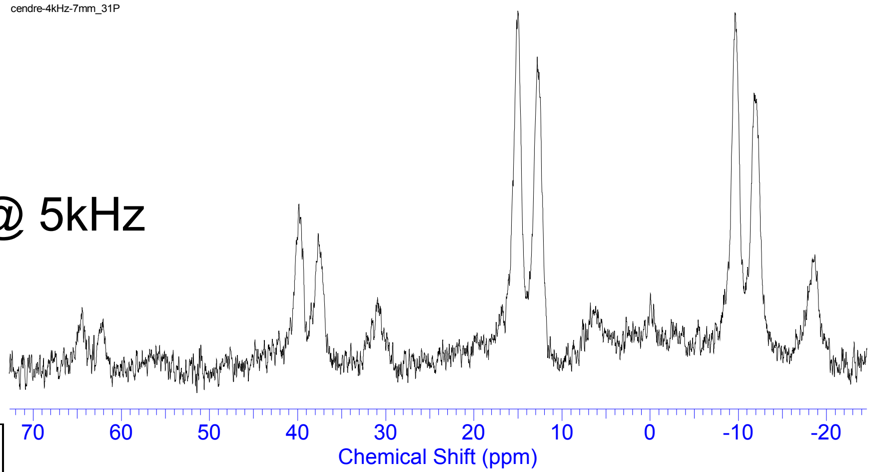
Assumption: spinning speed < 1KHz no hazard

Characterization / quantification of phosphorous species in TBP ash.

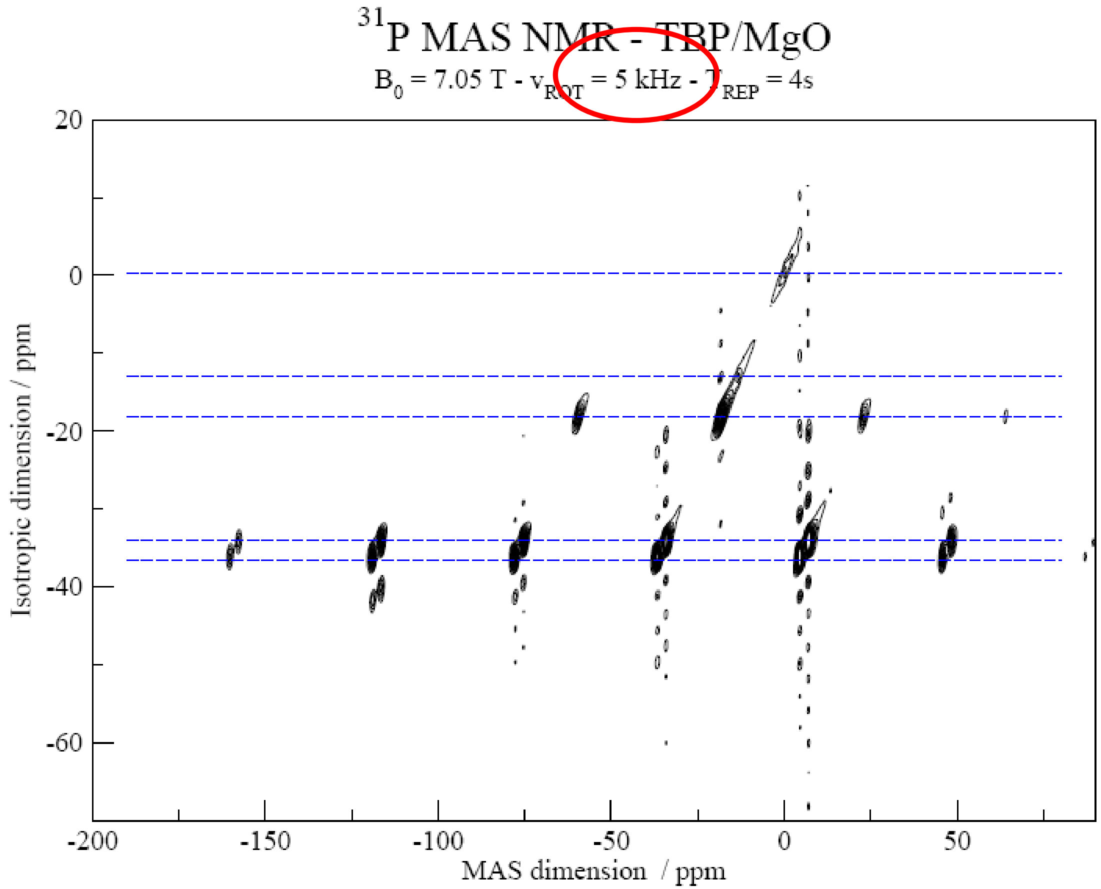


^{31}P MAS spectrum about inactive ash 5mm probe 10kHz

Double conditioning within 7mm rotor through insert (inactive powder).



^{31}P MAS spectrum @ 5kHz



MAT pulse sequence @ 5kHz
T. CHARPENTIER

Outlook: to keep on decreasing spinning speed until 1kHz

Conclusion and outlooks

The applications of NMR in the field of nuclear material are:

- Extremely wide
- Fascinating: even standard experiments have something new
- Challenging

To go further:

- Cryogenic liquid probe (^{13}C, ^{1}H)
- Confined CP/MAS probe designed to radioactive solid state samples.