



# *Microbobines et RMN en phase solide*

G. LAURENT<sup>a</sup>, C. BONHOMME<sup>a</sup>,  
D. SAKELLARIOU<sup>b</sup>

a Sorbonne Universités, UPMC Univ Paris 06, CNRS,  
Collège de France, UMR 7574, Laboratoire de Chimie de la  
Matière Condensée de Paris, F-75005, Paris, France

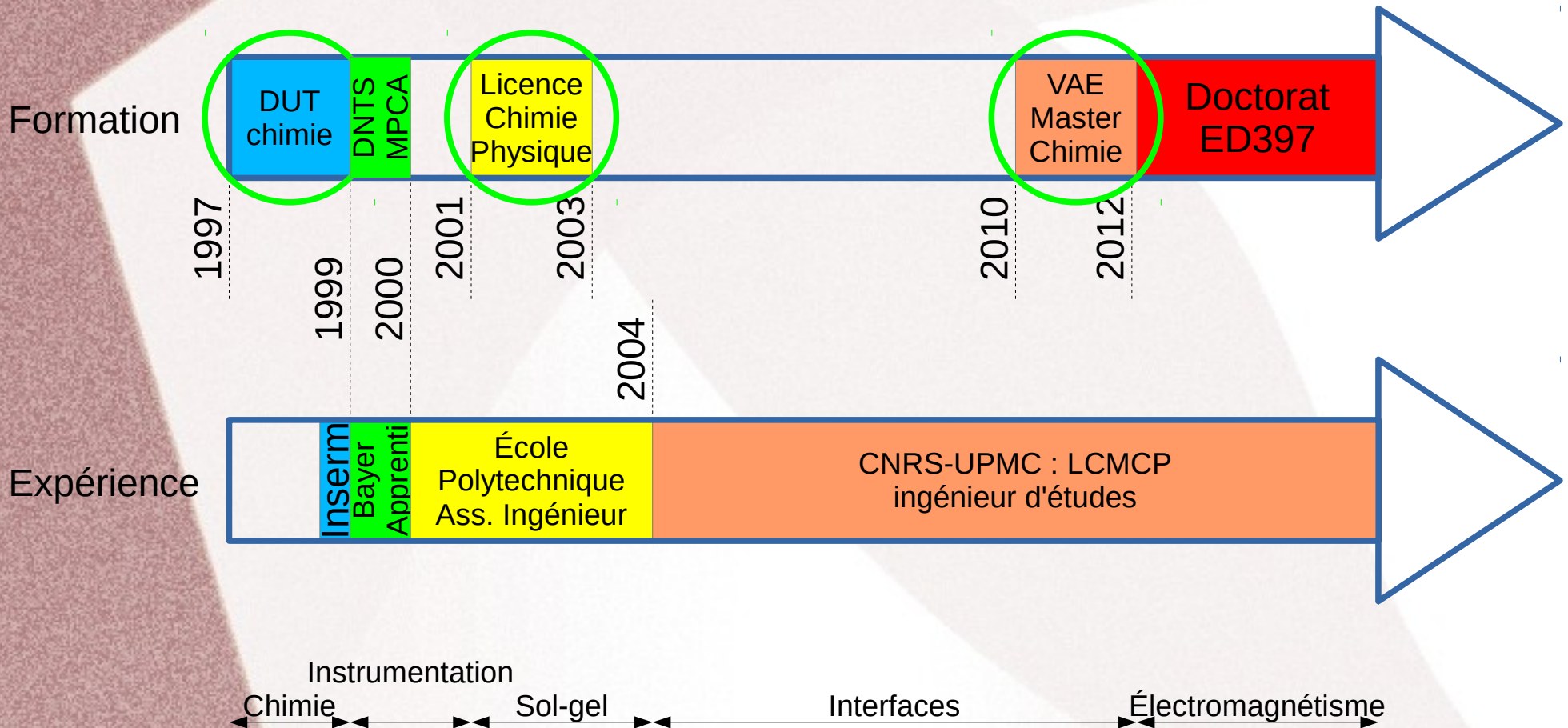
b CEA Saclay/DSM/IRAMIS/SIS2M, CNRS, UMR3299,  
F-91190, Gif-sur-Yvette, France



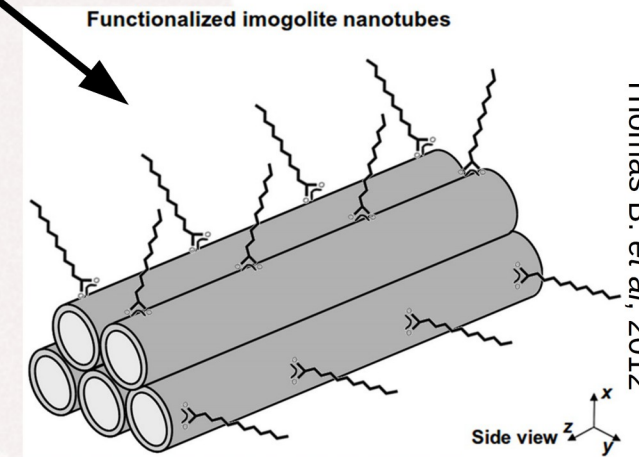
COLLÈGE  
DE FRANCE  
— 1530 —

UPMC  
SORBONNE UNIVERSITÉS

# Parcours

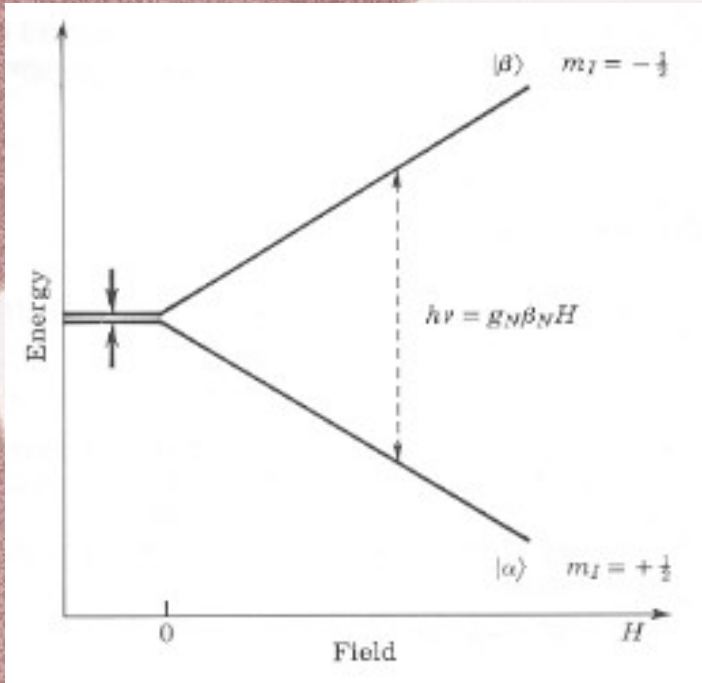


# Qu'est-ce que la RMN ?



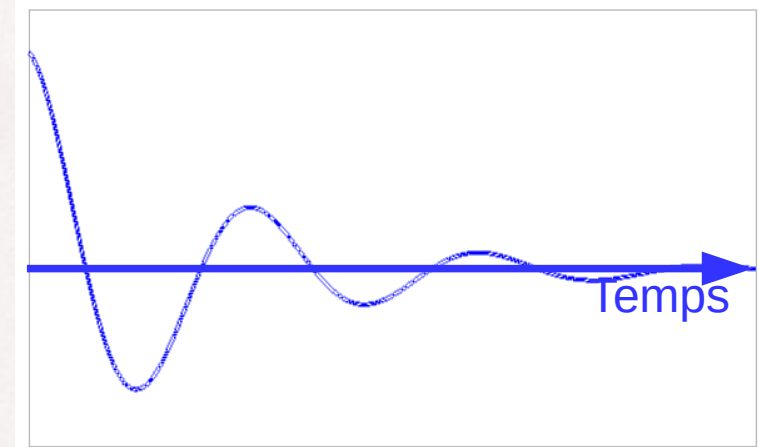
- Spectroscopie, sonde locale
- Contrôle qualité, contrefaçon
- Développement de nouveaux composés
- Outil majeur au laboratoire → proximités, mobilités

Effet Zeeman  
Levée de dégénérescence

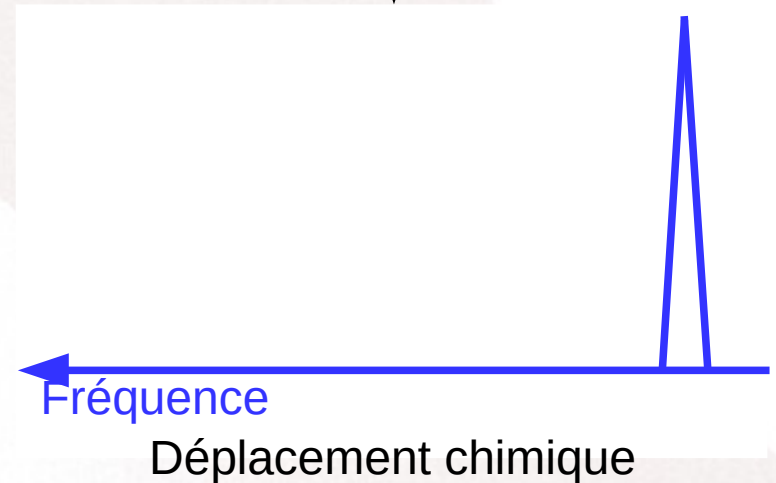


# Principe de la RMN

Impulsion RF



TF



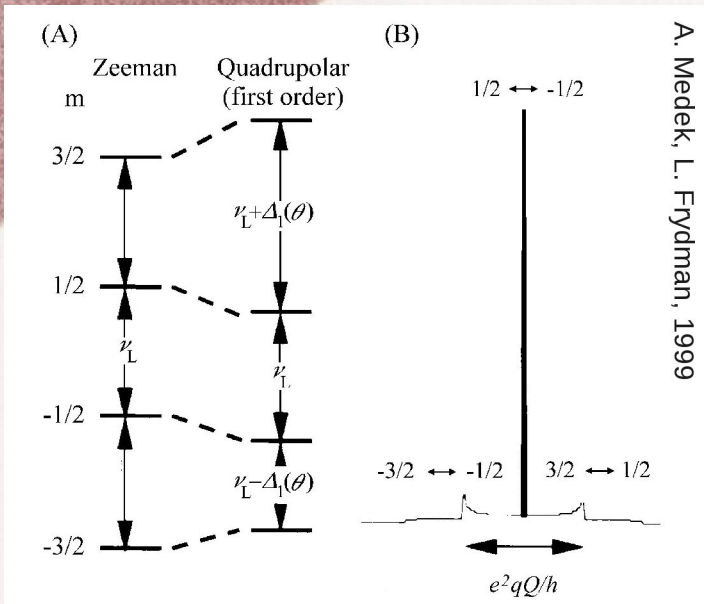
Précis mais peu sensible

# RMN en phase solide

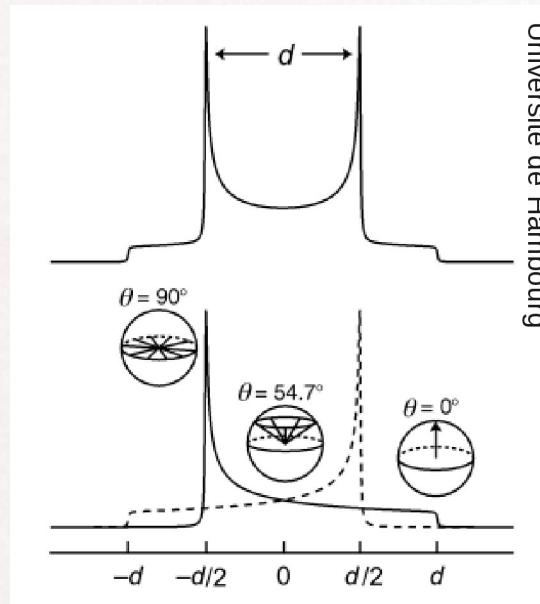
Quadrupolaire ( $I > 1/2$ ),  
ex :  $^{27}\text{Al}$ ,  $^{43}\text{Ca}$

Dipolaire, ex :  $^1\text{H}$

Q  
MHz

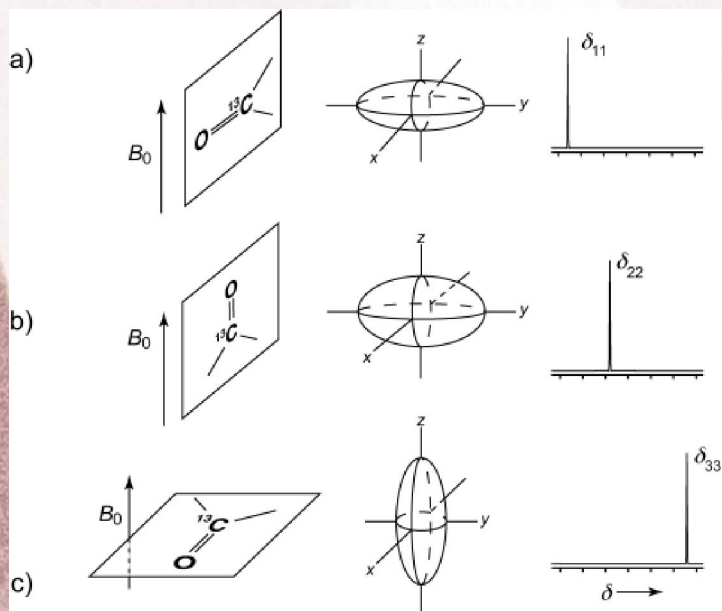


D  
100 kHz

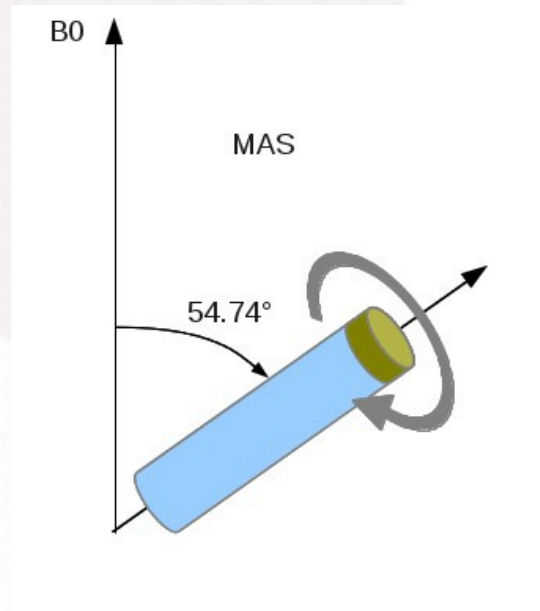


Anisotropie de déplacement chimique, ex :  $^{13}\text{C}$

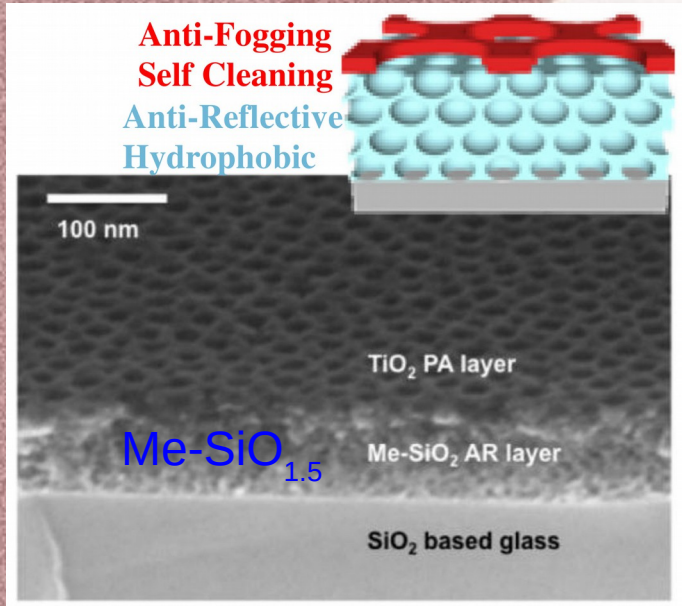
CSA  
100 ppm



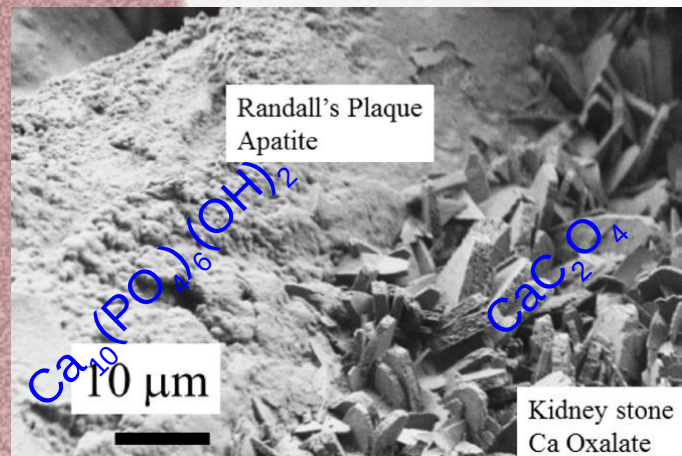
MAS  
10 kHz



# Problématique



M. Faustini et al, 2014

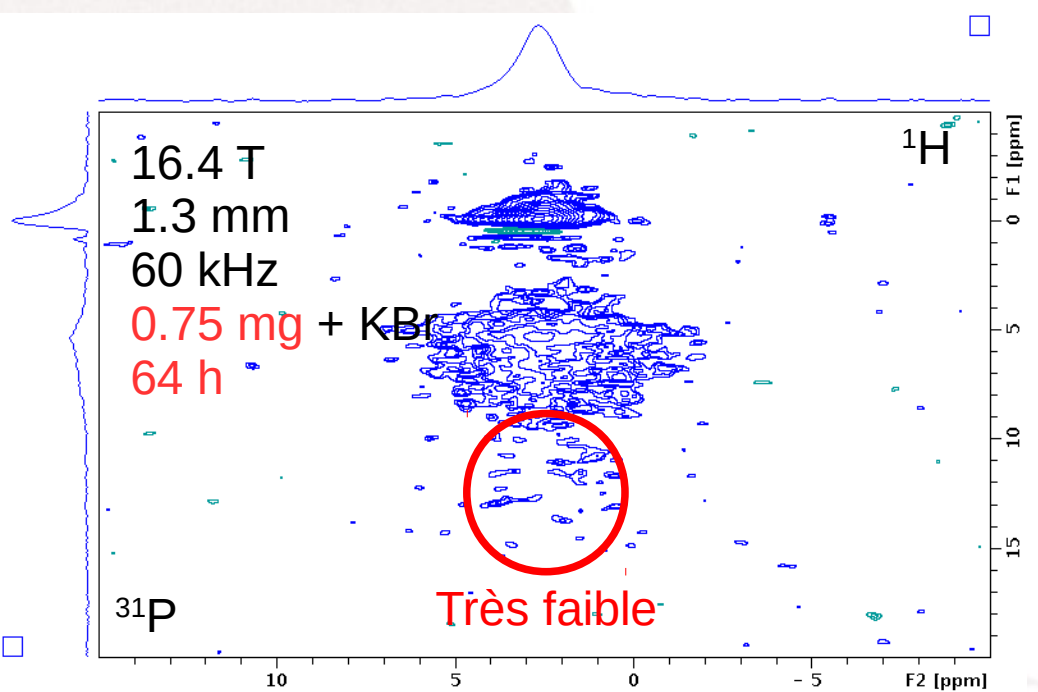
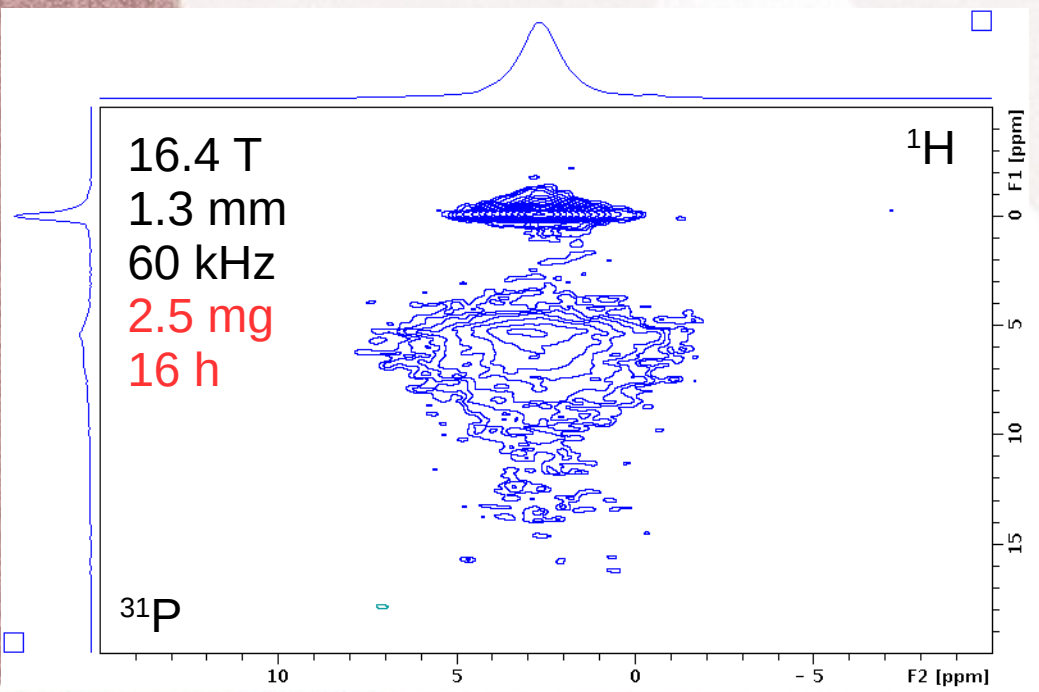
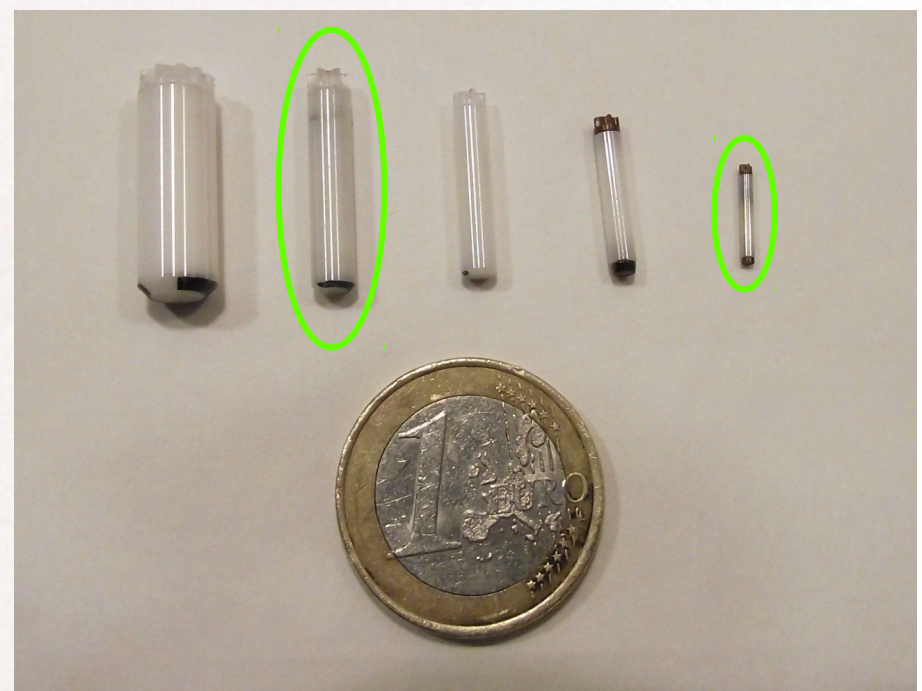
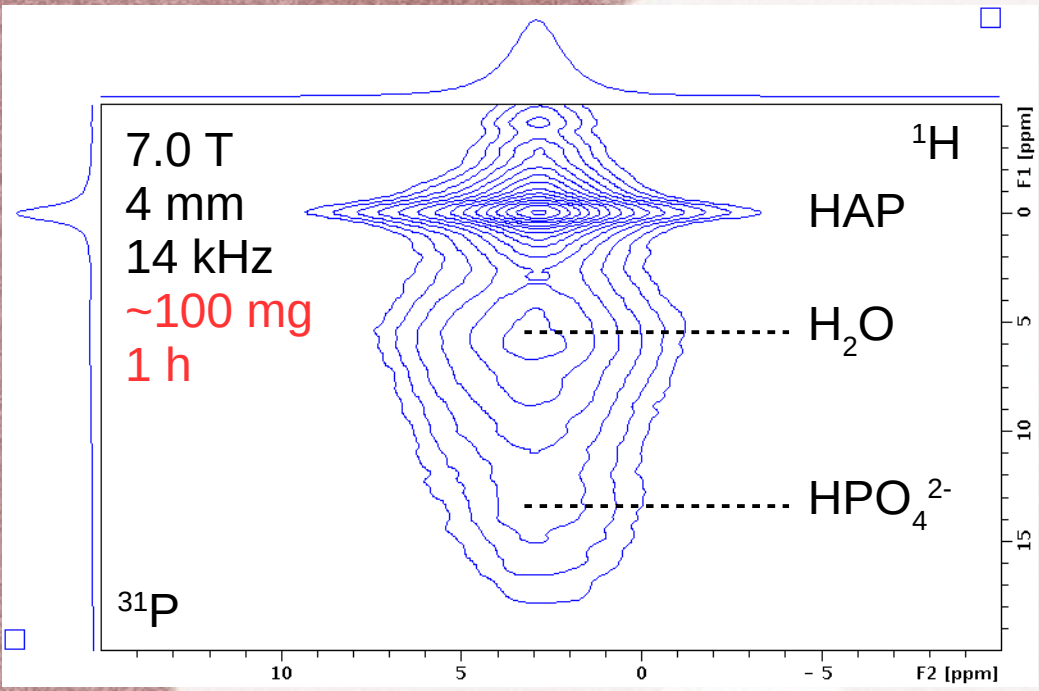


D. Bazin et M. Daudon, 2012

- Faible sensibilité de la RMN  
→ 30-100 mg d'échantillon
- Comment analyser des  $\mu$ -quantités ?
  - film sol-gel gratté
  - plaque de Randall
- → 30-100  $\mu$ g d'échantillon
- Augmenter le coefficient de remplissage → diminuer la taille de la bobine

HETCOR  $\{^1\text{H}\}$ - $^{31}\text{P}$   
 $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \cdot n\text{H}_2\text{O}$

# Sondes commerciales

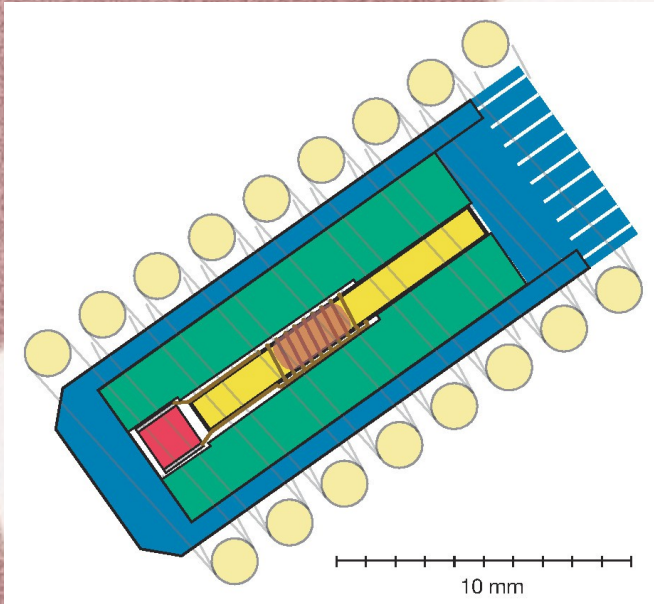


- Instrumentation
  - Microbobines
- Acquisitions rapides
  - Échantillonnage non linéaire
  - Échos
- Traitements du signal
  - Échos
  - Débruitage

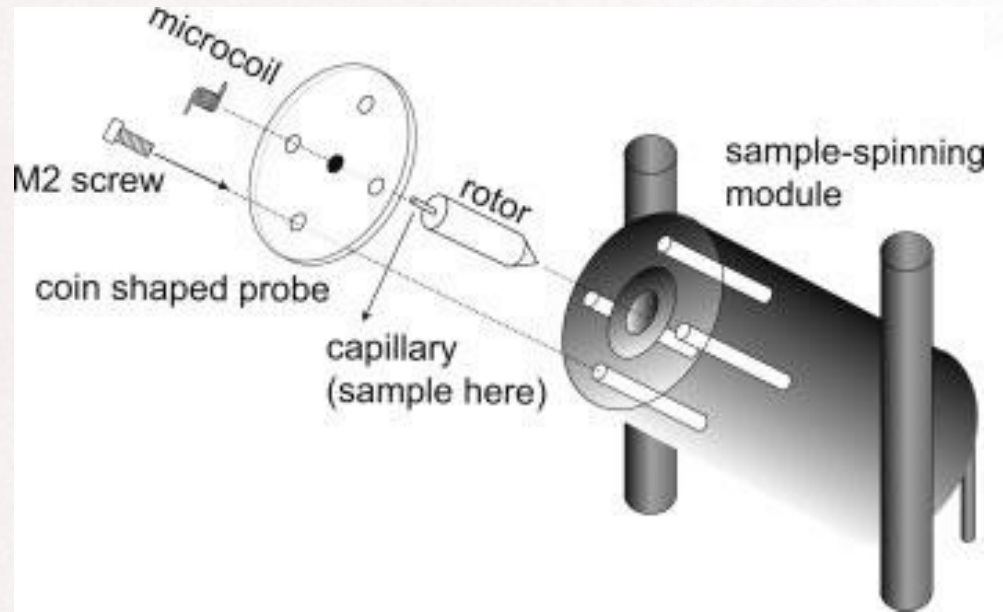


$$\text{SNR}_{\text{puv}} \propto \frac{\omega_0^2 [n/d_{\text{coil}} \sqrt{1 + (h/d_{\text{coil}})^2}]}{\sqrt{(n^2)(n/h)(d_{\text{coil}}/h)}} \propto \frac{\omega_0^2}{\sqrt{nd_{\text{coil}}}}$$

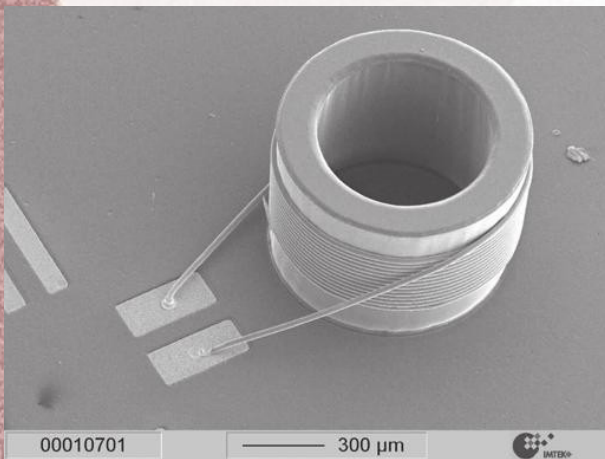
# Solutions existantes



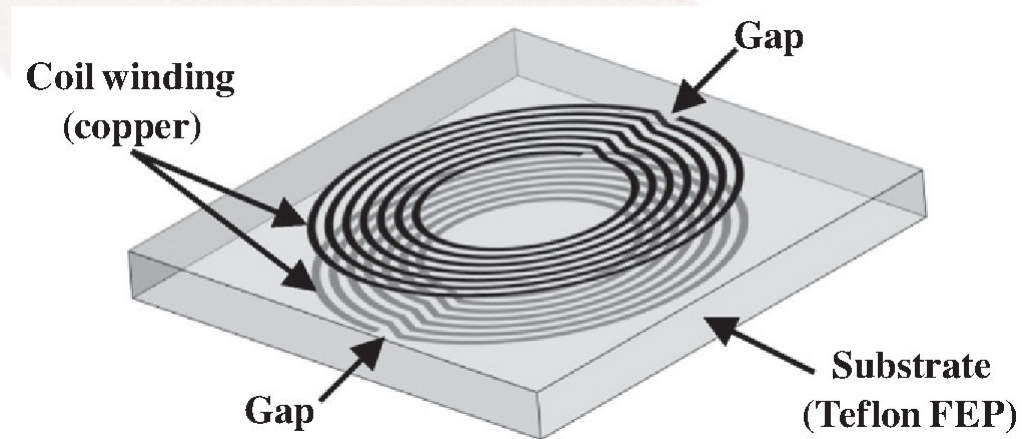
D. Sakellariou *et al*, 2007



M. Inukai, K. Takeda, 2008

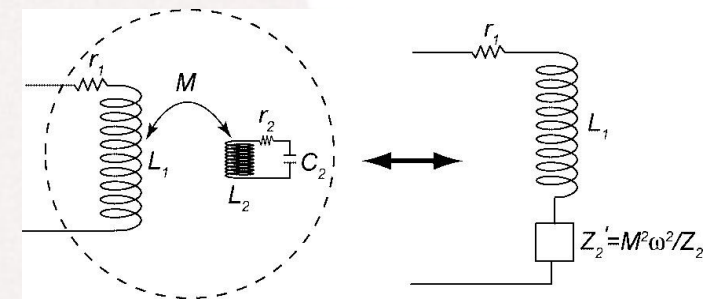
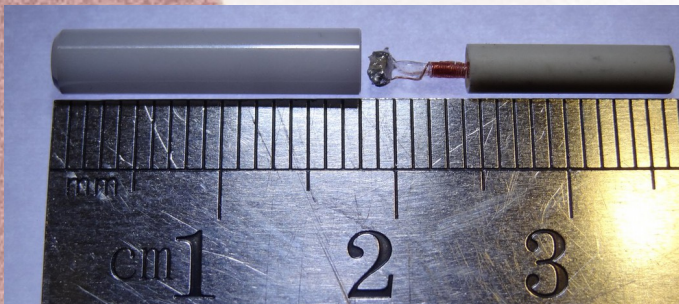
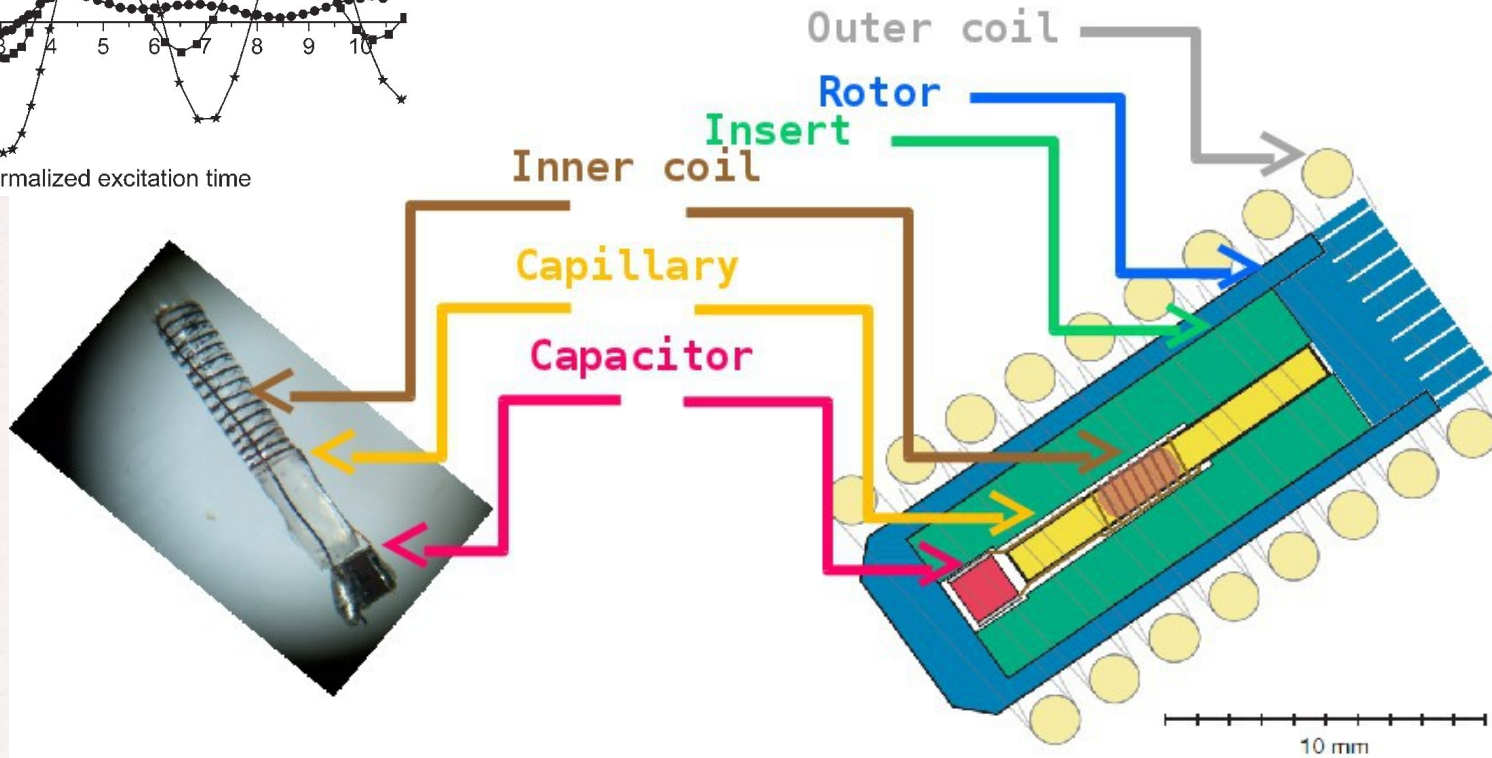
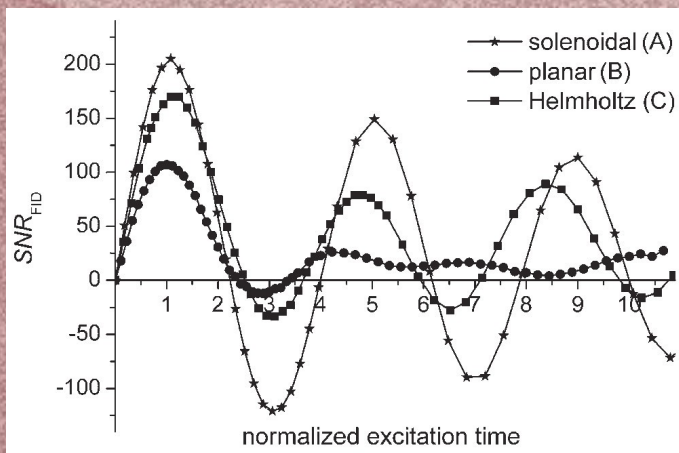


K. Kratt *et al*, 2010



J.-C. Ginefri *et al*, 2012

# Magic Angle Coil Spinning (MACS)



- [1] K. Ehrmann *et al*, *Lab Chip*, vol. 7, no. 3, pp. 373–380, Mar. 2007.
- [2] D. Sakellariou and J.-F. Jacquinet, *WO 2007/020537*, A3, 23-Feb-2007.
- [3] D. Sakellariou *et al*, *Nature*, vol. 447, no. 7145, pp. 694–697, Jul. 2007.
- [4] J.-F. Jacquinet and D. Sakellariou, *Concept. Magn. Reson. A*, vol. 38A, pp. 33–51, 2011.

# Choix des composants

Circuit RLC série

$$v = \frac{1}{2\pi\sqrt{LC}}$$

↓  
 Fréquence (Hz)

→ Capacité (F)  
 → Inductance (H)

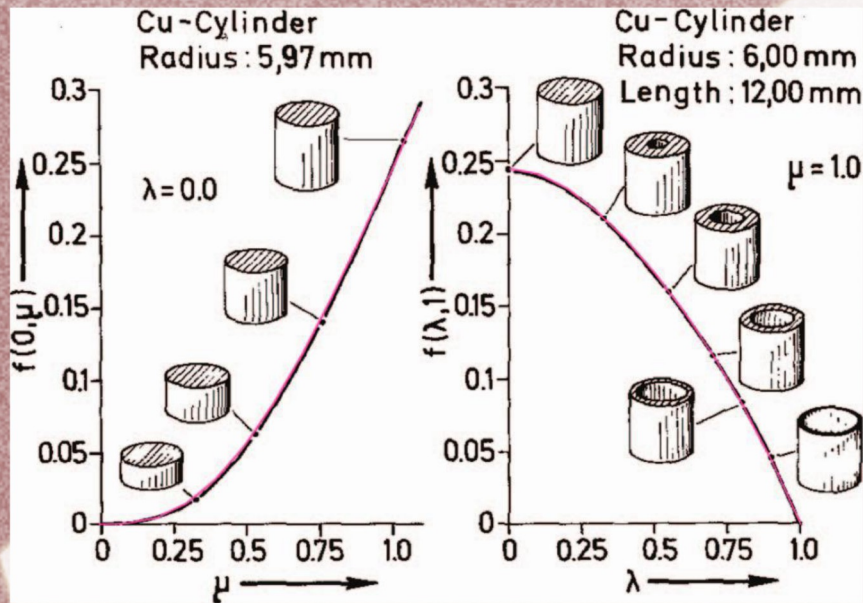
$$L = \frac{4\pi^2 N_{turns}^2 r_{coil}^2}{l_{coil}} k_L - 0.004\pi r_{coil} N_{turns} (k_S + k_M)$$

Nombre de spires  
 Rayon de la bobine (m)  
 Longueur de la bobine (m)  
 Coefficient de Nagaoka =  $f(2*r_{coil}/l_{coil})$   
 Auto-inductance =  $f(p_{inter-fil} r_{fil})$   
 Inductance mutuelle =  $f(N_{turns})$

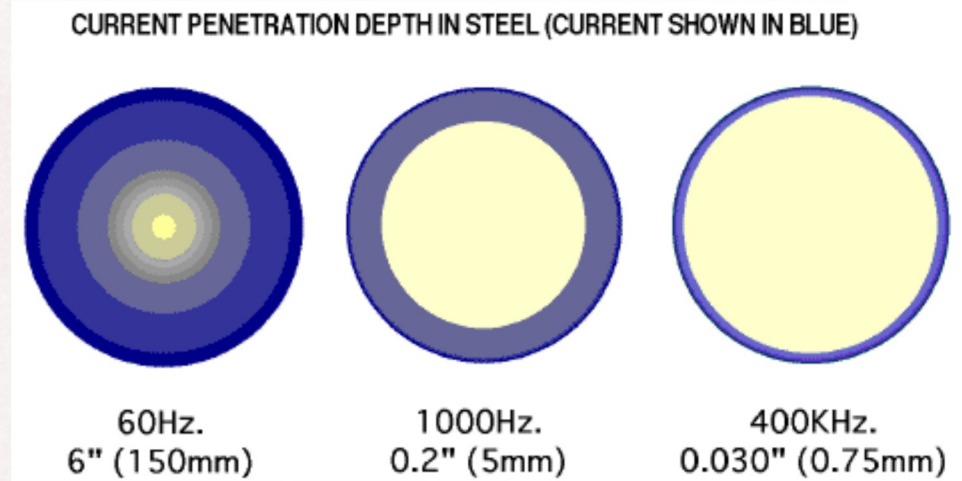
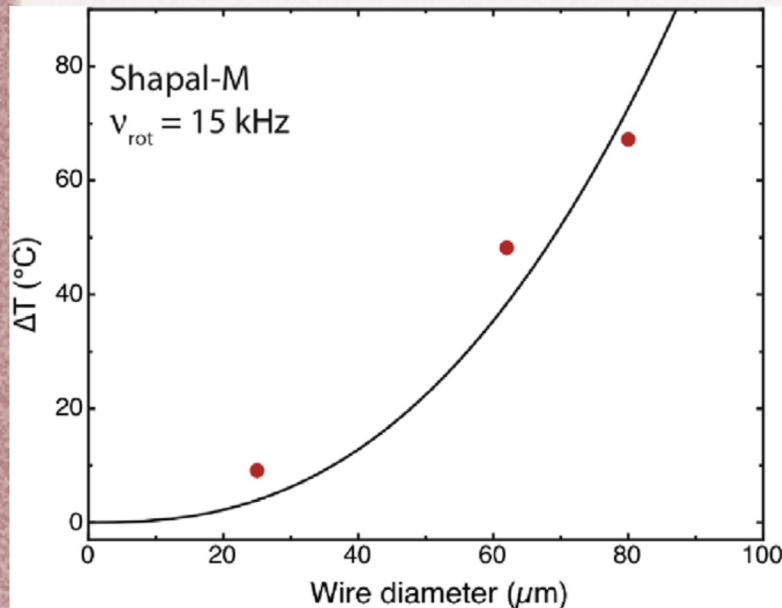
[1] H. Nagaoka, *The Journal of the College of Science, Imperial University of Tokyo, Japan*, vol. 27, no. 6, 1909.

[2] E. B. Rosa and F. W. Grover, *Bulletin of the Bureau of Standards*, vol. 8, no. 1, pp. 1–237, Dec. 1916.

# Choix du fil



**Courants de Foucault :**  
échauffement, gradients



<http://tymkrs.tumblr.com>

Diamètre du fil > 3x effet de peau

$$\delta = \sqrt{\frac{\rho}{\pi \mu_0 \nu}}$$

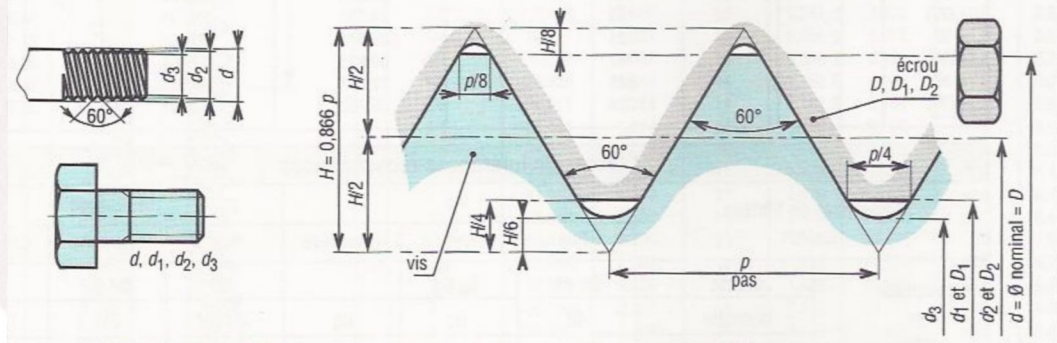
$\rho$  → Résistivité ( $\Omega \cdot \text{m}$ )  
 $\nu$  → Fréquence (Hz)  
 $\mu_0$  → Perméabilité magnétique ( $\text{H} \cdot \text{m}^{-1}$ )

- [1] R. Schäfer and C. Heiden, *Appl. Phys.*, vol. 9, no. 2, pp. 121–125, Feb. 1976.
- [2] M. D. Harpen, *Phys. Med. Biol.*, vol. 33, no. 3, p. 329, Mar. 1988.
- [3] P. M. Aguiar, J.-F. Jacquinet, and D. Sakellariou, *J. Magn. Reson.*, vol. 200, no. 1, pp. 6–14, Sep. 2009.
- [4] G. Aubert, J.-F. Jacquinet, and D. Sakellariou, *J. Chem. Phys.*, vol. 137, no. 15, pp. 154201–154201–14, Oct. 2012.

# Fabrication des microbobines



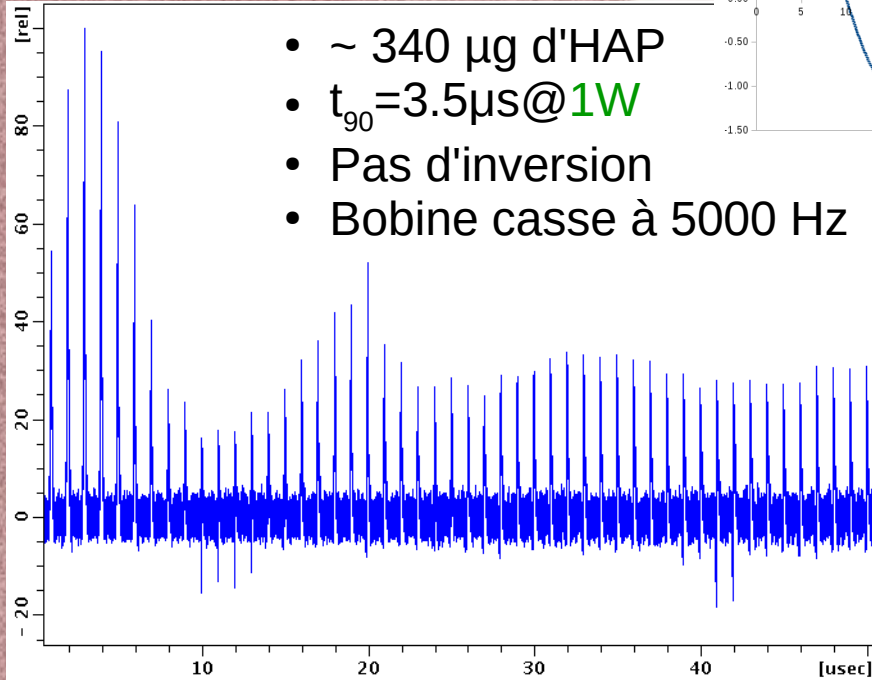
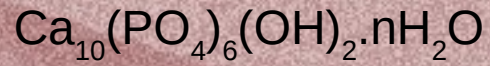
$p$  = pas  
 $H$  = hauteur du filetage =  $0,866p$   
 $D = d$  = diamètre nominal (vis et écrou)  
 $D_2 = d_2$  = diamètre sur flanc (vis et écrou) =  $d - 0,6495p$   
 $D_1 = d_1$  = diamètre intérieur du taraudage (écrou) =  $d - 1,0825p$   
 $d_3$  = diamètre intérieur du filetage (vis) =  $d - 1,2268p$   
 $d_3$  = diamètre du noyau



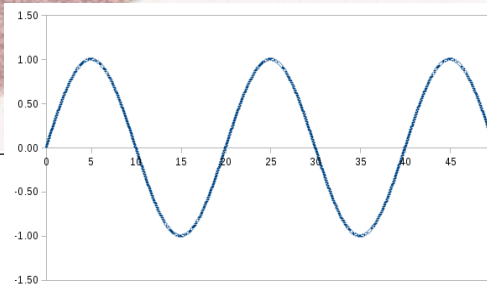
[1] J.-L. Fanchon, *Guide des sciences et technologies industrielles*. Paris, Nathan, 1994.

Meilleur résultat à la main, sous binoculaire

# Résultats

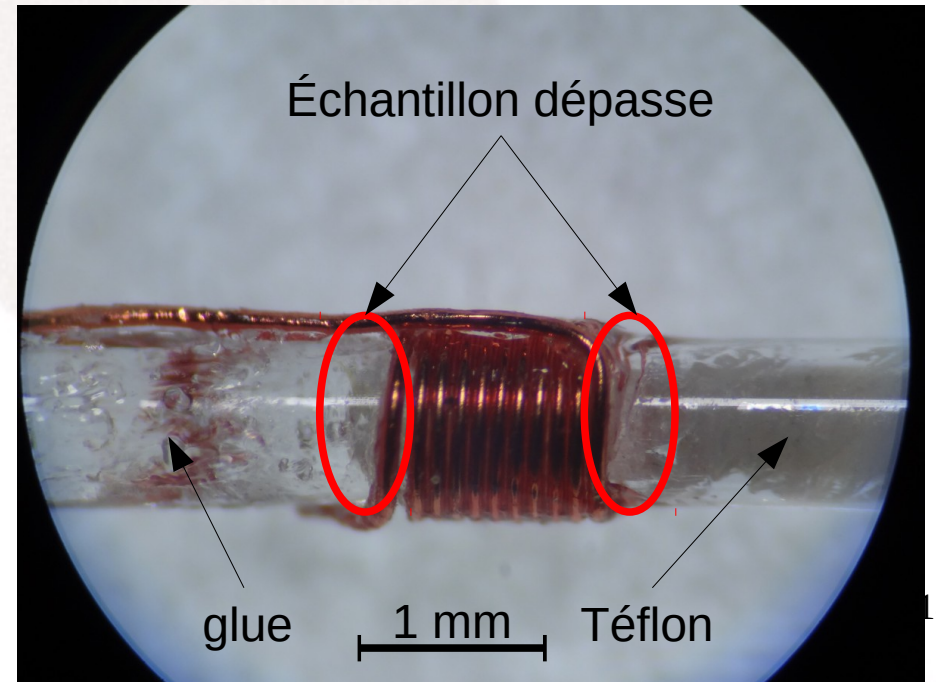
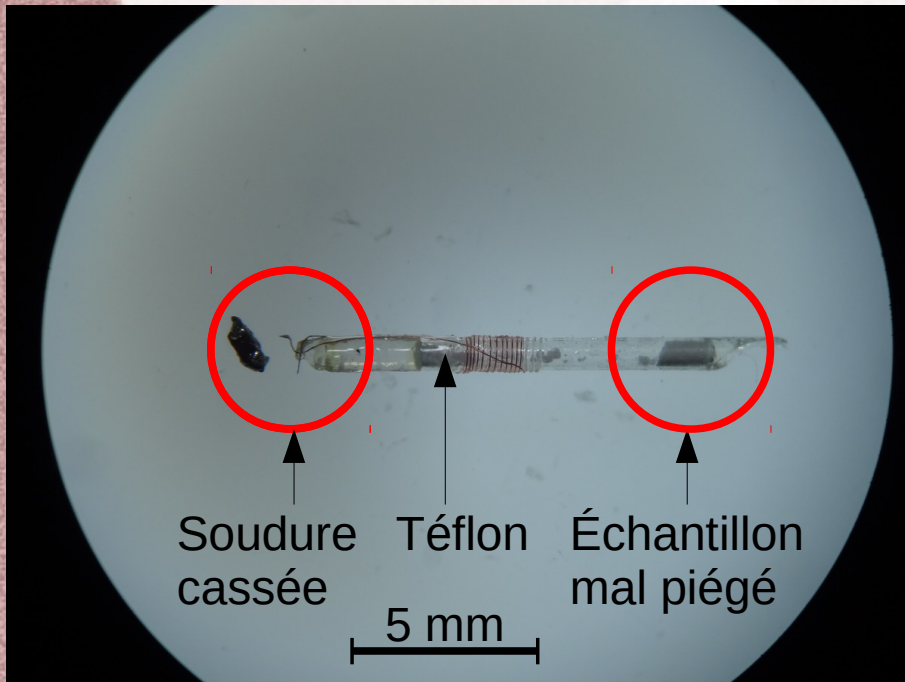
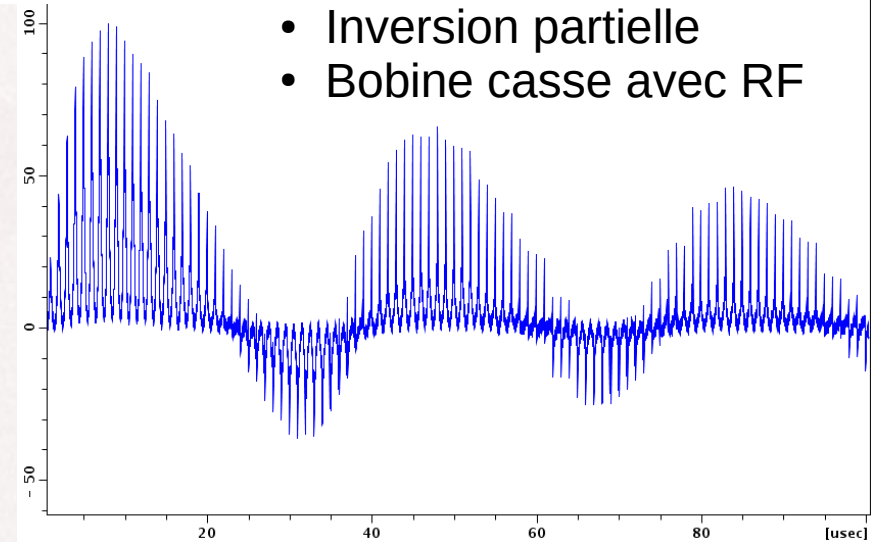


- ~ 340  $\mu\text{g}$  d'HAP
- $t_{90} = 3.5 \mu\text{s}$  @ 1W
- Pas d'inversion
- Bobine casse à 5000 Hz

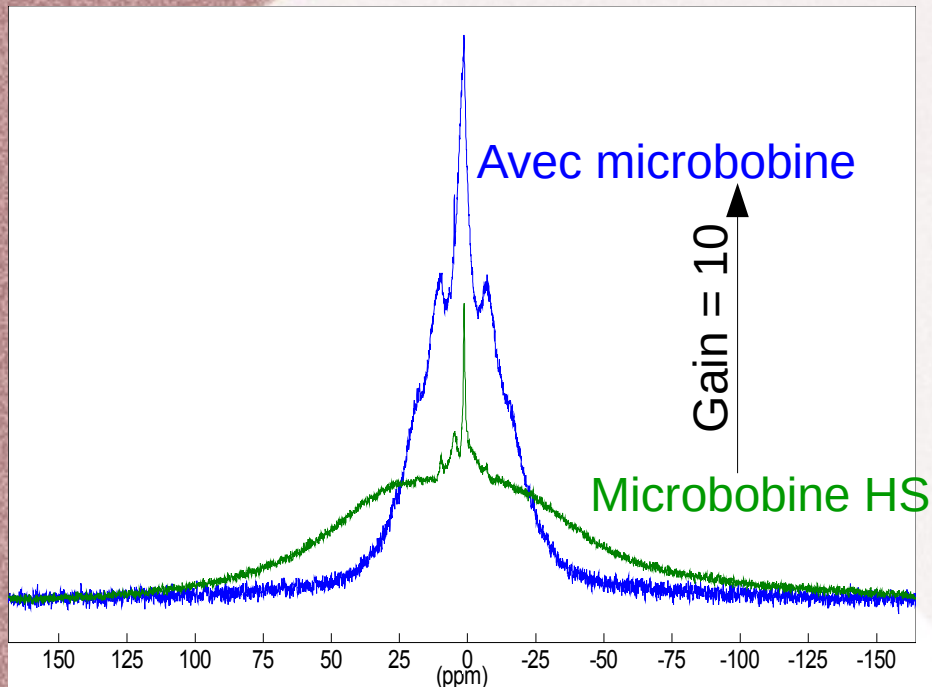


finished. plw1=0.1W  
Experiment 8: P1 = 8.000000 P2 = 1.00

- ~ 270  $\mu\text{g}$  d'adamantane
- $t_{90} = 10 \mu\text{s}$  @ 0.1W
- Inversion partielle
- Bobine casse avec RF



$^1\text{H}$   
7T, MAS 2.5 kHz  
~ 250-270  $\mu\text{g}$  d'adamantane



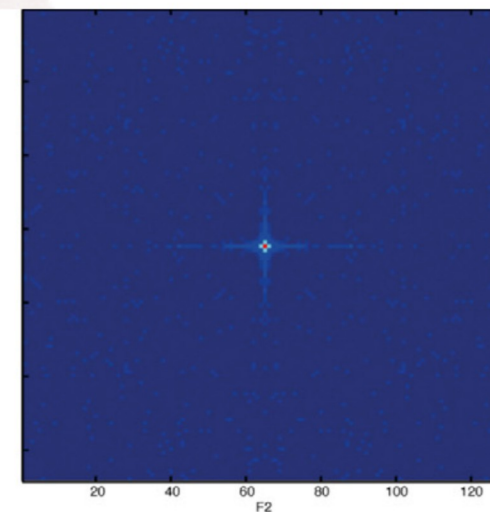
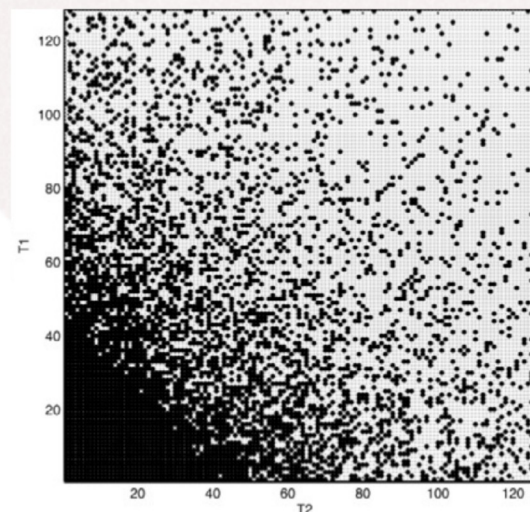
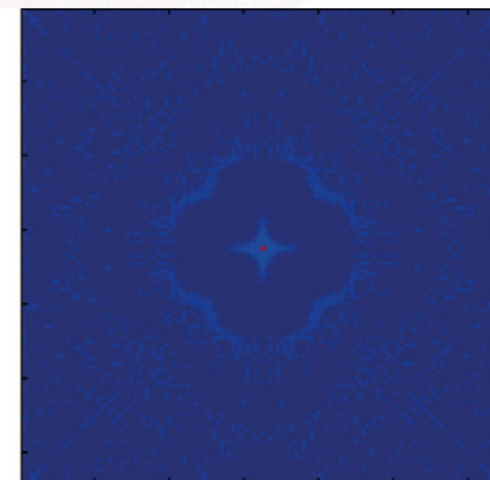
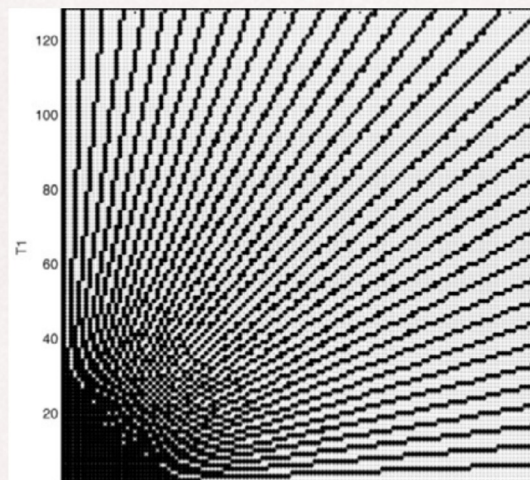
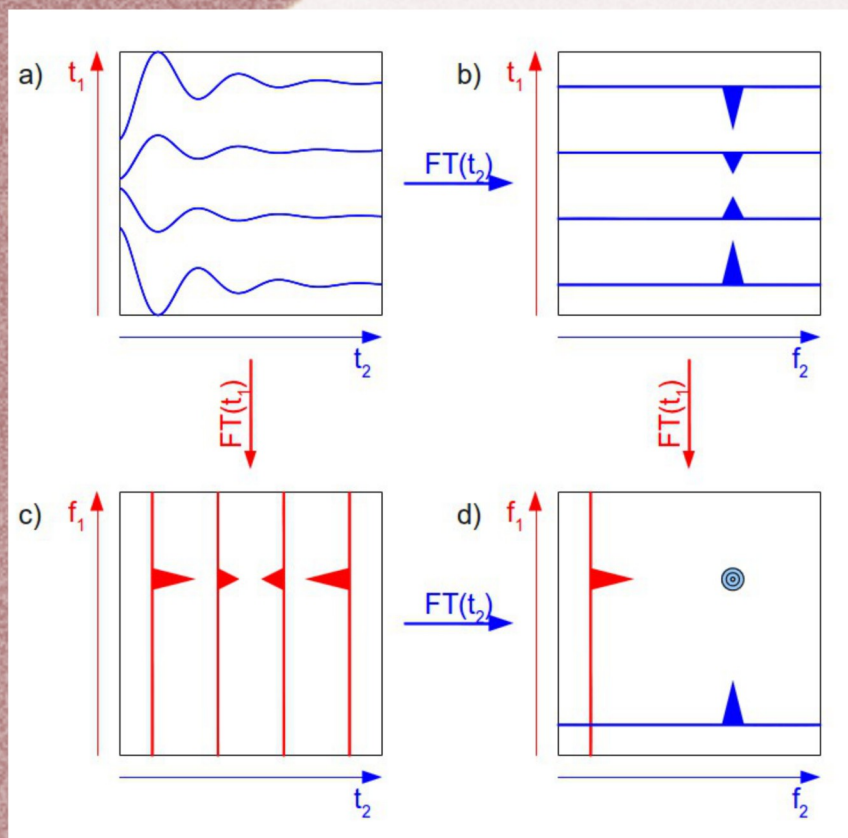
- 100 fois plus rapide
- 100 fois moins de puissance
- Diminution du signal de sonde
- Homogénéité RF insuffisante pour CP  $^1\text{H} \rightarrow ^{13}\text{C}$
- 2D à venir

- Instrumentation
  - Microbobines
- **Acquisitions rapides**
  - Échantillonnage non linéaire
  - Échos
- Traitements du signal
  - Échos
  - Débruitage



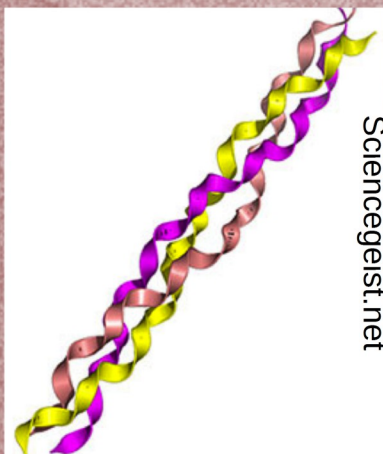
# Échantillonnage non linéaire NUS

30 %

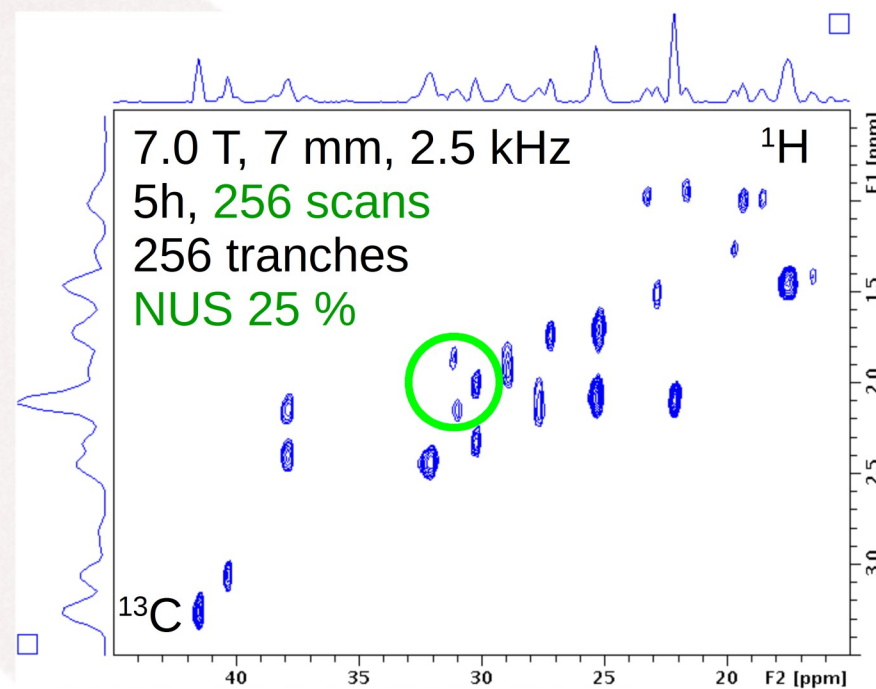
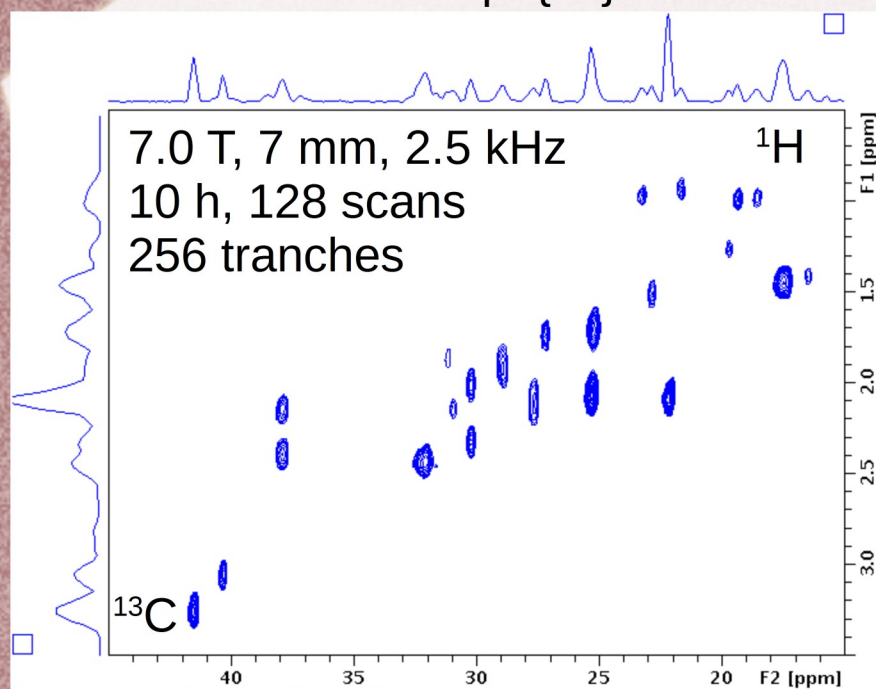


- [1] V. Y. Orekhov, I. V. Ibraghimov, and M. Billeter, *J Biomol NMR*, vol. 20, no. 1, pp. 49–60, May 2001.
- [2] M.-A. Delsuc and D. Tramesel, *CR Chim*, vol. 9, no. 3–4, pp. 364–373, Mar. 2006.
- [3] M. Mobli and J. C. Hoch, *Prog. Nucl. Magn. Res. Sp.*, vol. 83, pp. 21–41, Nov. 2014.

# Échantillonnage non linéaire NUS



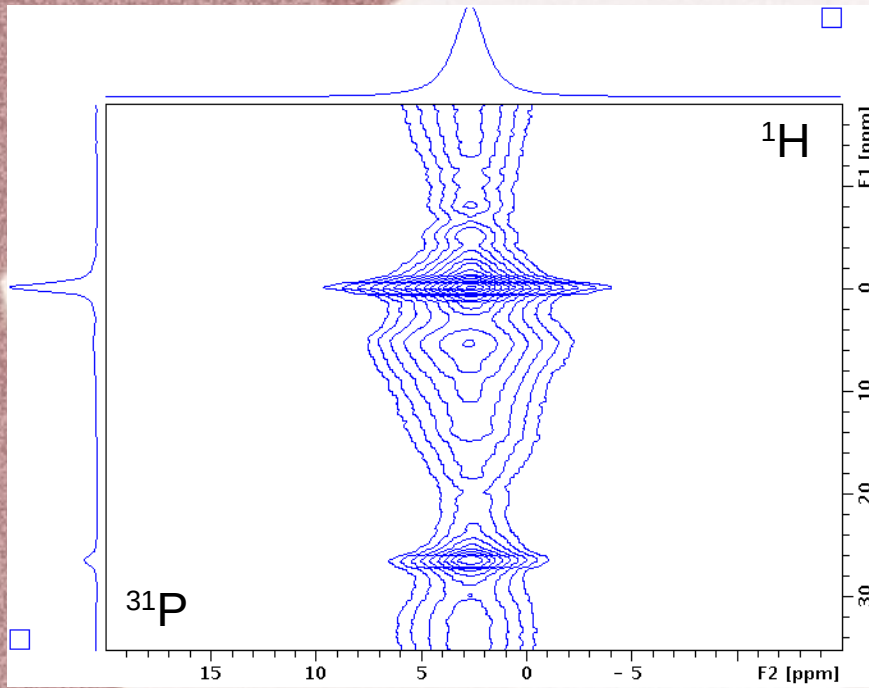
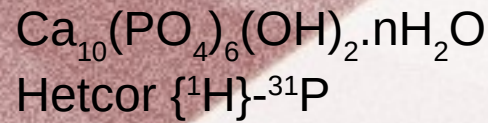
Collagène  
Inept  $\{^1\text{H}\}$ - $^{13}\text{C}$



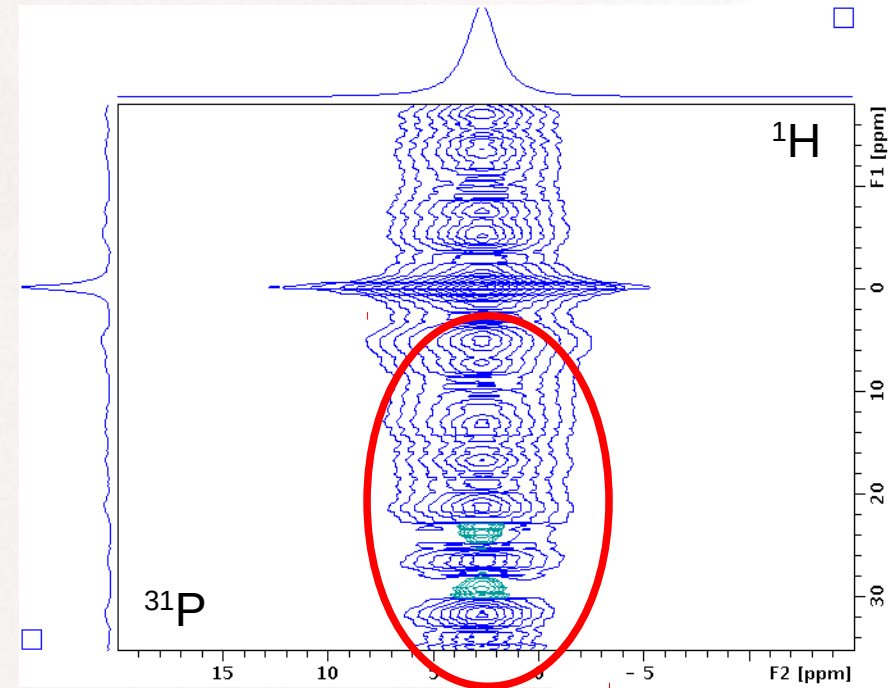
Licence spécifique  
2 fois plus rapide et gain en signal / bruit

# Échantillonnage non linéaire

# NUS



7.0 T, 8kHz  
4 mm 2/3 plein + Teflon  
12h30, 280 tranches



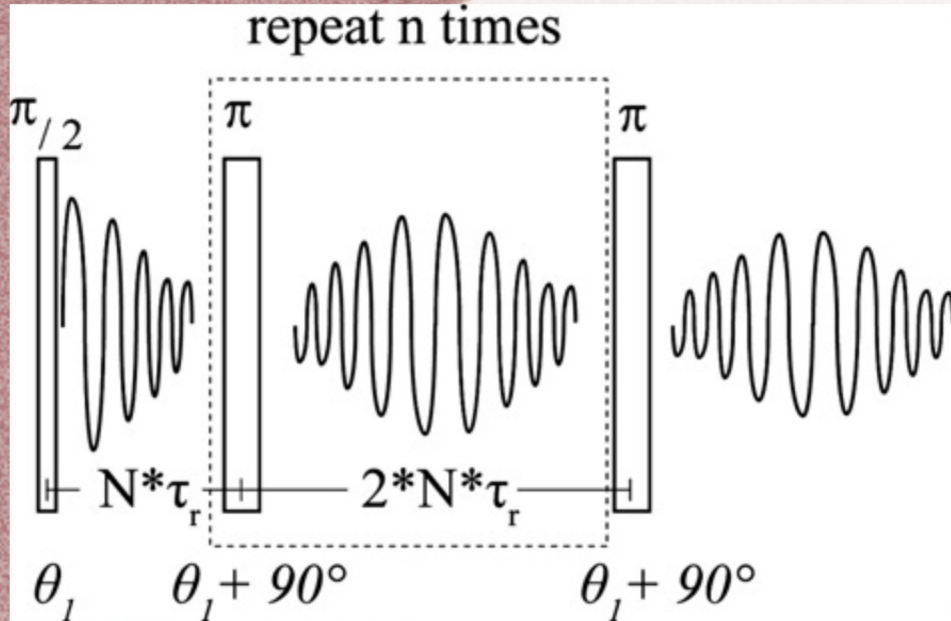
7.0 T, 8kHz  
4 mm 2/3 plein + Teflon  
3h, 280 tranches, NUS 25 %

4 fois plus rapide

Nécessité d'un signal discret

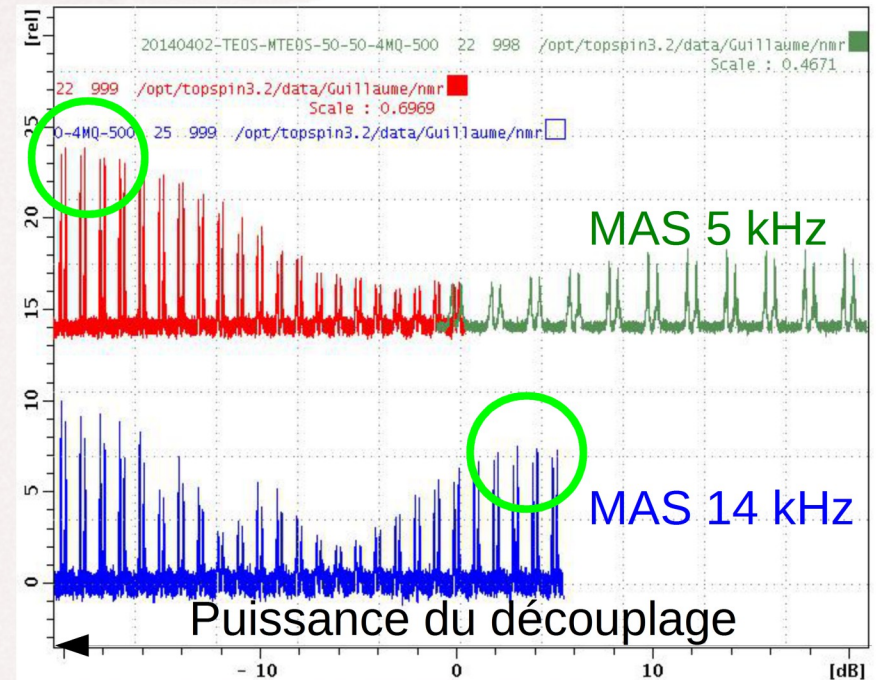
# Échos CPMG

## Refocalisation



Paramètres clés :

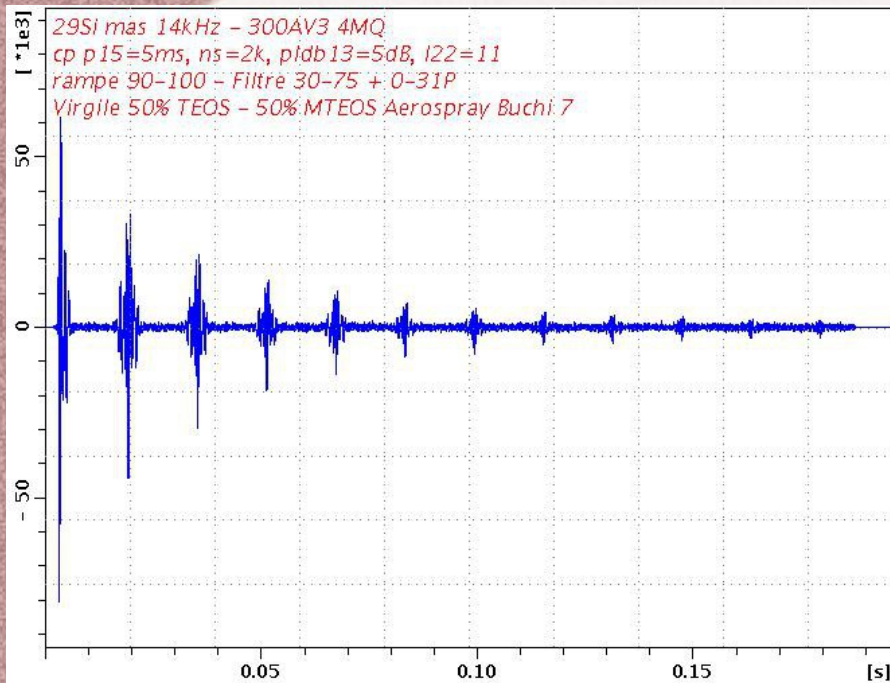
- Durée de l'écho
- Nombre d'échos
- Vitesse de rotation MAS
- Puissance du découplage pour ne pas endommager la sonde



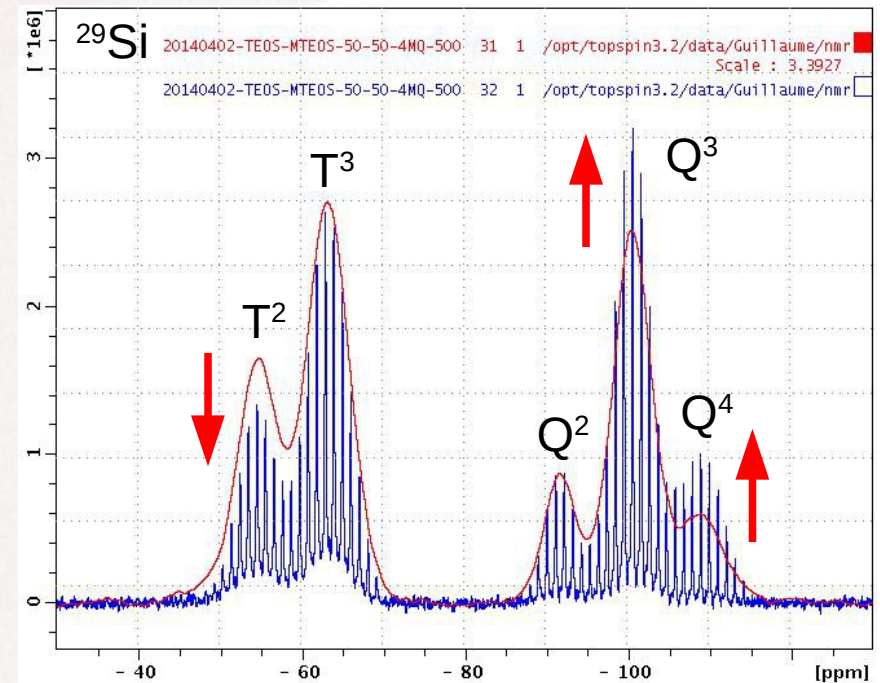
- [1] H. Y. Carr and E. M. Purcell, *Phys. Rev.*, vol. 94, no. 3, pp. 630–638, May 1954.
- [2] S. Meiboom and D. Gill, *Rev. Sci. Instrum.*, vol. 29, no. 8, pp. 688–691, Jun. 1958.
- [3] W. J. Malfait and W. E. Halter, *J. of Non-Cryst. Solids*, vol. 354, no. 34, pp. 4107–4114, Sep. 2008.

# Échos CPMG

TEOS / MTEOS : 50 / 50



MAS 14 kHz : 11 échos



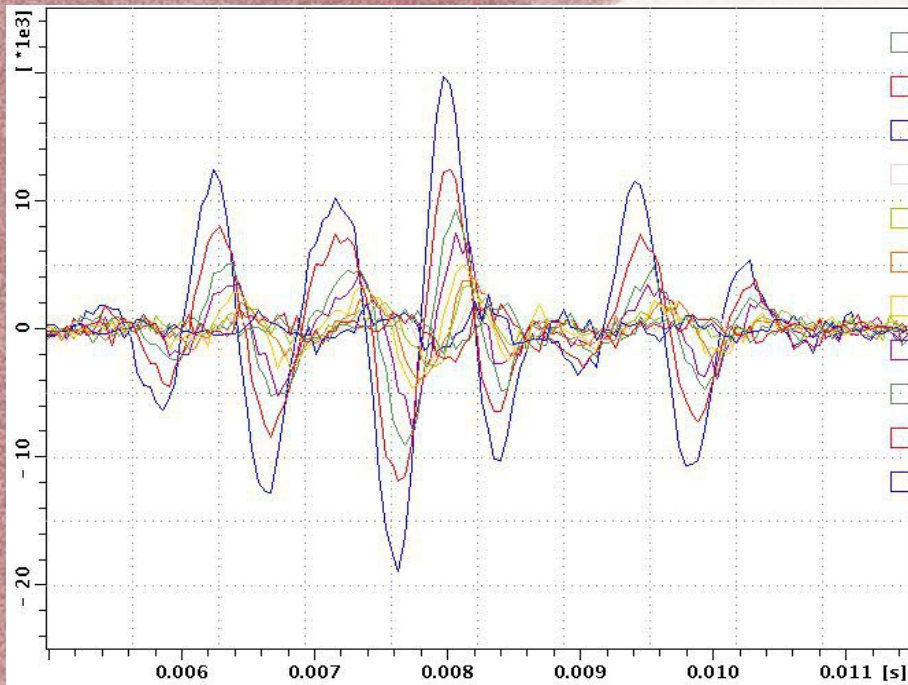
Intensités relatives des pics à corriger

4 fois plus rapide

Comment reconstruire le spectre ?

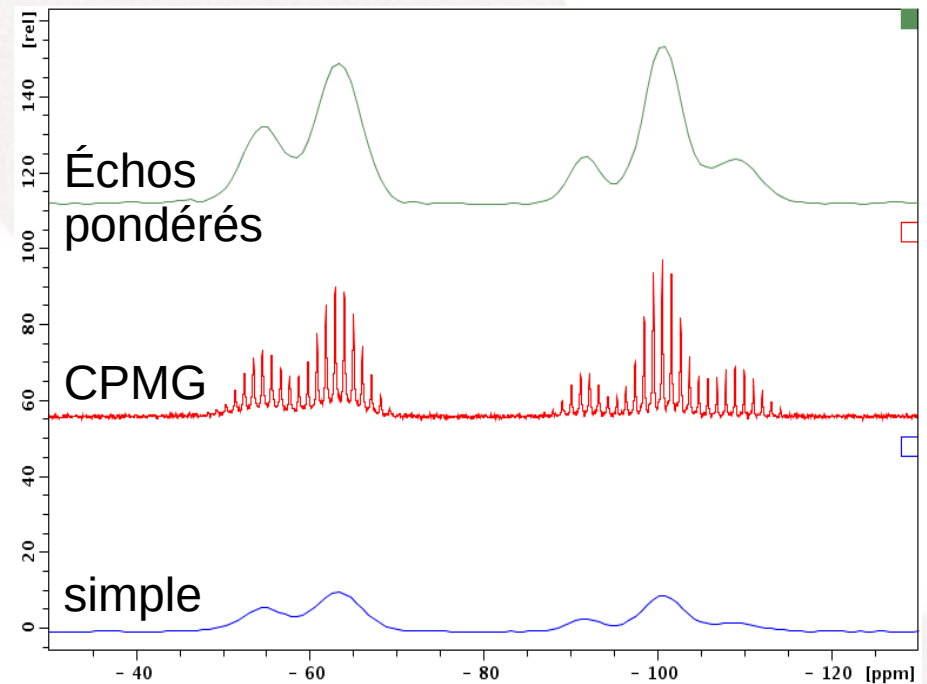
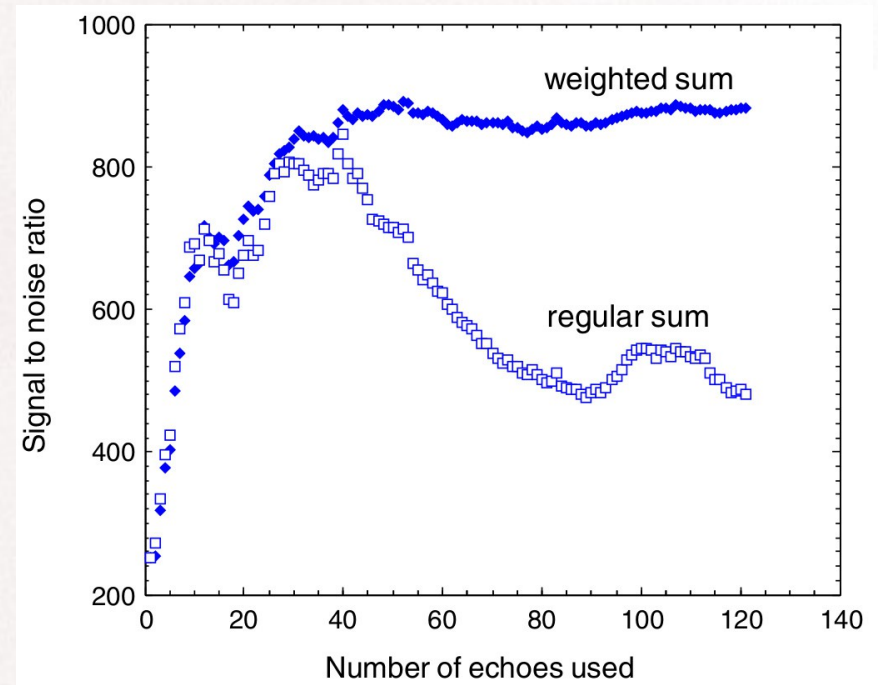
- Instrumentation
  - Microbobines
- Acquisitions rapides
  - Échantillonnage non linéaire
  - Échos
- **Traitements du signal**
  - Échos
  - Débruitage

# Échos CPMG



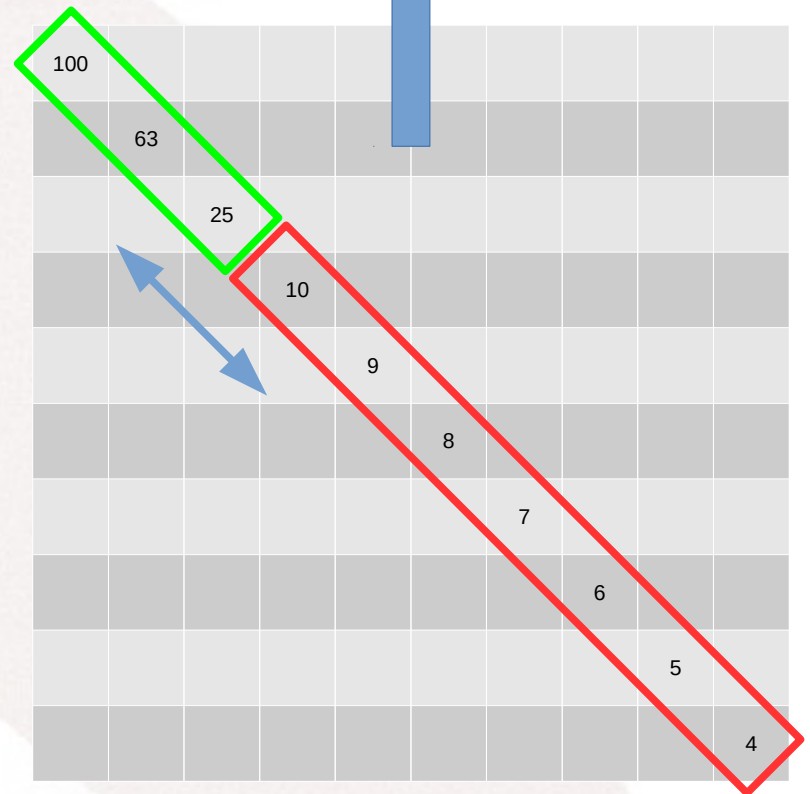
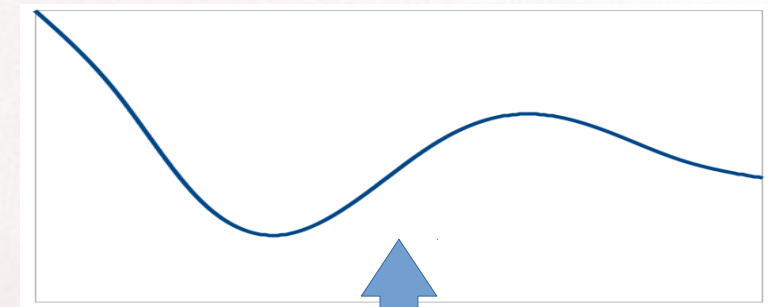
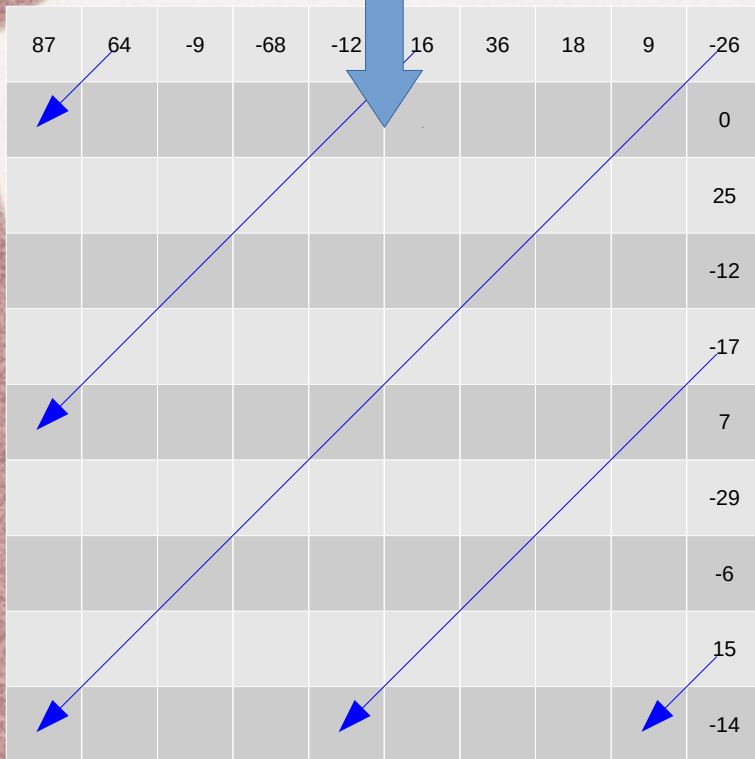
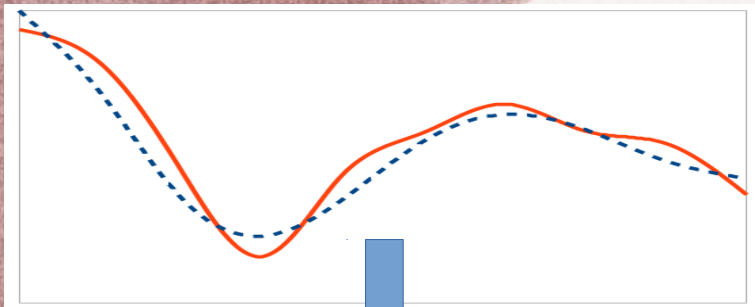
14 kHz : 11 échos

- Synchronisation des échos
- Pondération des échos en fonction de leur signal / bruit
- Pondération des pics selon leur relaxation
- 4 fois plus rapide



# Débruitage SVD

Signal temporel

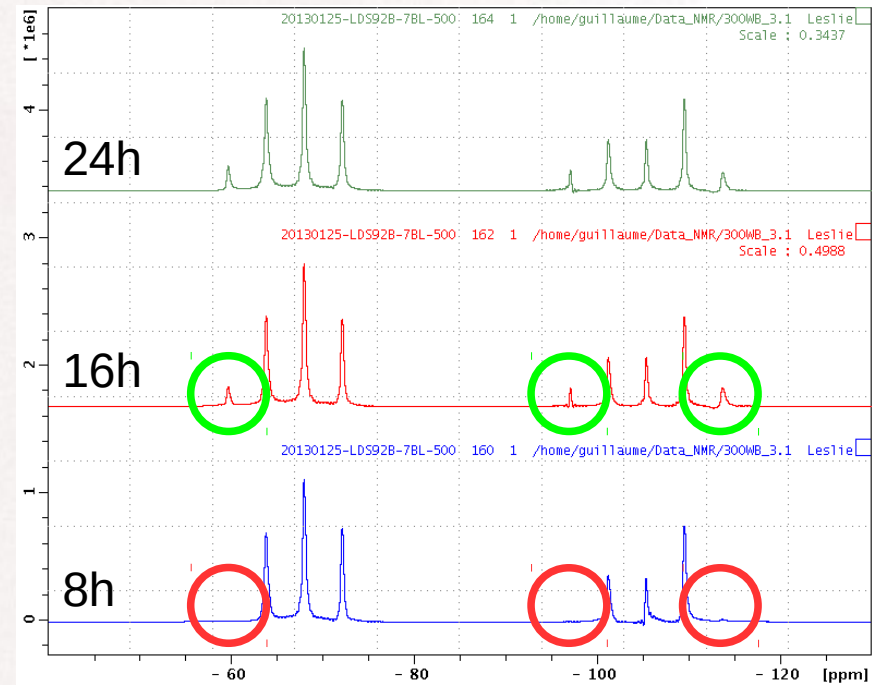
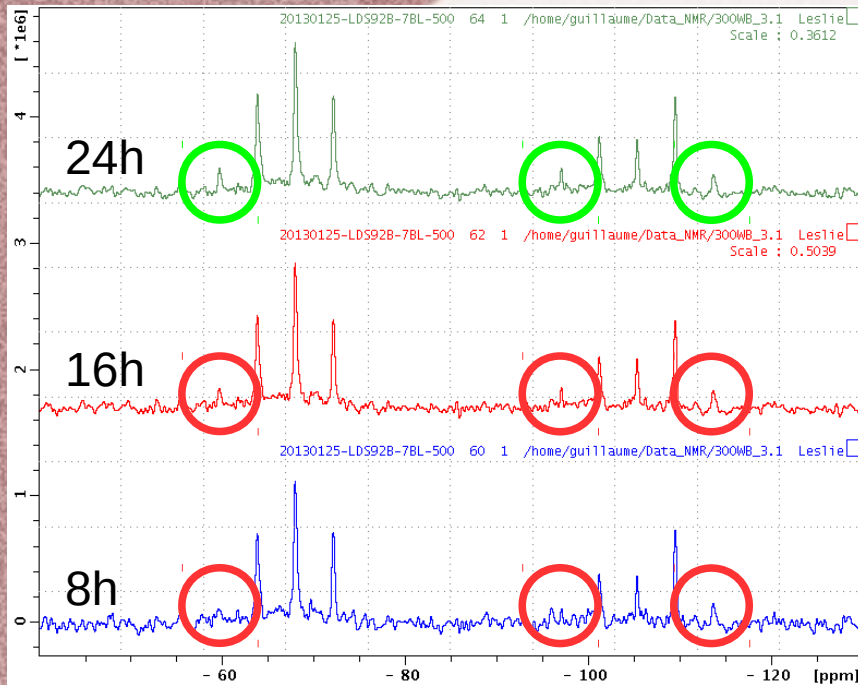


Quelques secondes pour 1024 points

- [1] J.A. Cadzow, *IEEE Trans. Acoust. Speech Signal Process*, vol. 36, pp 49–62, 1988.
- [2] P. Man, C. Bonhomme, F. Babonneau, *Solid State Nucl. Mag.*, vol. 61-62, pp. 28-34, 2014.



# Débruitage SVD



- Choix du nombre de valeurs propres
- Signal / bruit minimum de 2
- Possibilité d'artefacts
- 2 à 4 fois plus rapide

Spectres débruités

# ***Conclusions***

- Gain en sensibilité → gain en temps  
MACS (100), NUS (4), CPMG (4), SVD (4)
- Électromagnétisme
- Micromécanique
- Fragilité

# ***Perspectives***

- ANR Microgram NMR
- Améliorer la robustesse
- Analyseur de fréquences
- Combiner les techniques

# Remerciements



Collège de France



CEA de Saclay

