



**IFSC** UNIVERSIDADE  
DE SÃO PAULO  
Instituto de Física de São Carlos



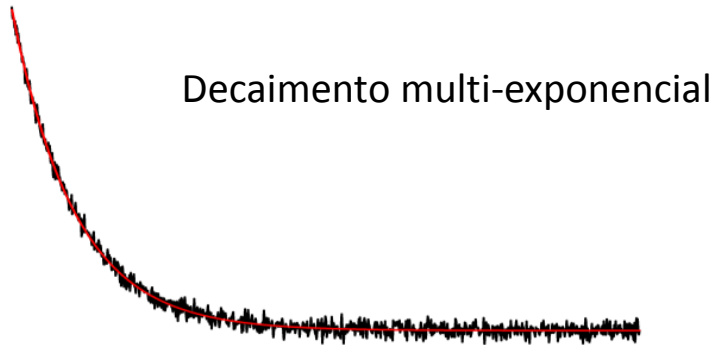
# Análise exponencial através do Método da Diagonalização Filtrada

Moraes, T.B., Montrazi, E.T., Colnago, L.A.,  
Bonagamba, T.J., Magon, C.J.

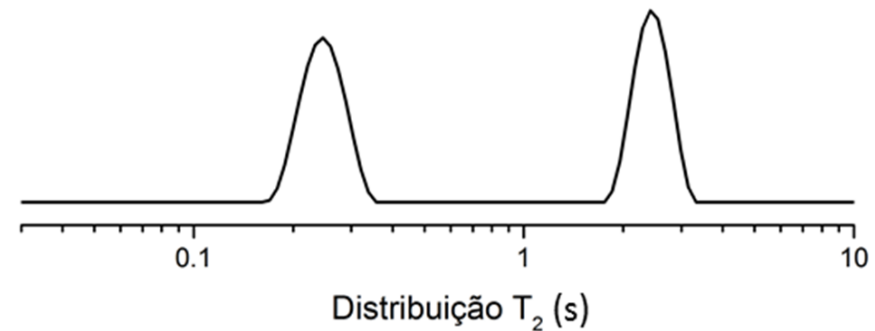
# Introdução

## RMN: Baixa resolução & Alta resolução

- Relaxometria
- Difusão (DOSY, PGSE, ...)
- Meios porosos / alimentos



Transformada Inversa de Laplace

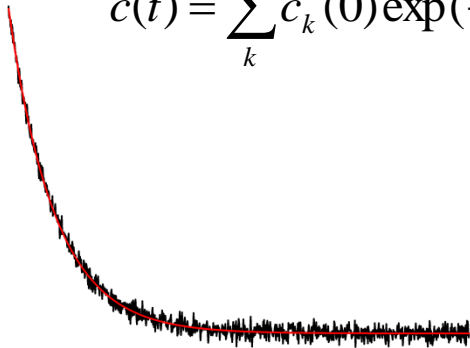


# Transforma Inversa de Laplace

# Transformada Inversa de Laplace

Soma decaimentos exponenciais

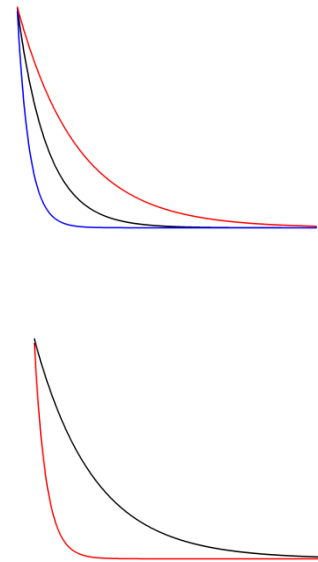
$$c(t) = \sum_k c_k(0) \exp(-t/T_{2k})$$



Fitting ótimo



➤ Problema inverso 'mal-posto'



?

✓ Sensível ao ruído

➤ Regularização ( $\alpha$ )

Lanczos, Applied Analysis, Prentice-Hall, 1959 p. 272

Y.Q. Song, L. Venkataramanan, L. Burcaw; *Determining the resolution of Laplace inversion spectrum*, **J. Chem. Phys.**, 2005, 122, 104104.

# Transformada Inversa de Laplace

- Provencher, S.W.; CONTIN: A general purpose constrained regularization program for inverting noisy linear algebraic and integral equations, **Comput. Phys. Commun.**, 27, 229, 1982. **CONTIN**  
Reg. Tikhonov
- J.P. Butler, J.A. Reeds and S.V. Dawson, Estimating solutions of the first kind integral equations with nonnegative constraints and optimal smoothing, **SIAM J. Numer. Anal.**, 18, 381, 1981.  
Butler, Reeds e Dawson (BRD)
- G.C. Borgia, R.J.S. Brown, P. Fantazzini; *Uniform-Penalty Inversion of Multiexponential Decay Data*, **Journal Mag. Res.**, 65, 132, 1998.  
non-negative least-squares (NNLS)  
WinDXP ILT software, Maran, Oxford Instruments
- Venkataramanan, L. ; Yi-Qiao Song ; Hurlimann, Martin D.; Solving Fredholm integrals of the first kind with tensor product structure in 2 and 2.5 dimensions, **IEEE**, 50, 5, 2002.  
Schlumberger-Doll Research center
- Maojin T., Peng W., Keyu M., Comparative study of inversion methods of three-dimensional NMR and sensitivity to fluids, **Journal of Applied Geophysics**, 103, 12, 2014
- Mathias Nilsson, The DOSY Toolbox: A new tool for processing PFG NMR diffusion data **Journal Mag. Res.**, 200, 296, 2009.  
High resolution

# Transformada Inversa de Laplace

Assume-se uma distribuição contínua de  $T_2$

$$c(t) = \int g(T_2) \exp(-t/T_2) dT_2$$

G.C. Borgia, R.J.S. Brown, P. Fantazzini; **Uniform-Penalty Inversion of Multiexponential Decay Data**, JMR, 65, 132, 1998.

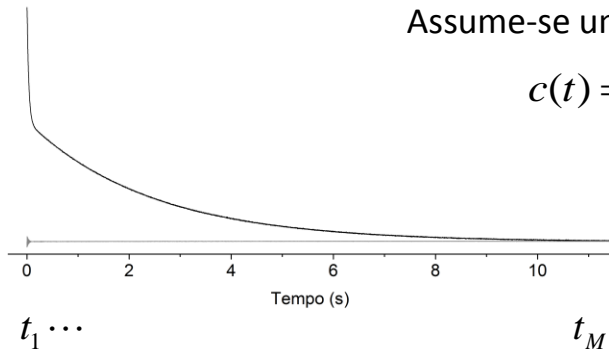
(NNLS – ILT)

Somatória com Kernel  $K$

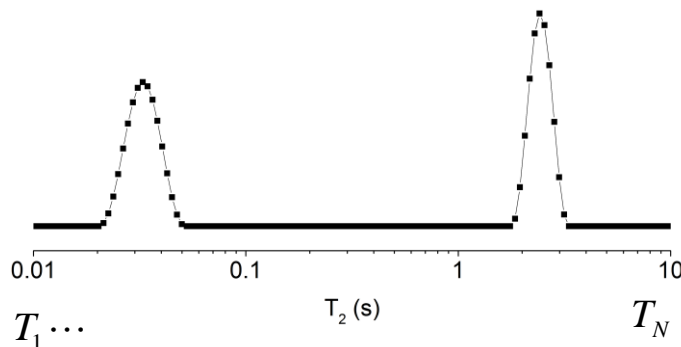
$$c(t_n) = \sum_{j=1}^N g(T_{2j}) K(t_n, T_{2j}) + \varepsilon_n$$

Minimização dos erros quadráticos

$$\chi^2 = \|c(t) - F(t)\|^2$$



$M$  pontos



Definir Grade:  $N$  pontos

$$K = \begin{pmatrix} e^{-t_1/T_1} & e^{-t_1/T_2} & \dots & e^{-t_1/T_N} \\ e^{-t_2/T_1} & e^{-t_2/T_2} & & e^{-t_2/T_N} \\ \vdots & & \ddots & \vdots \\ e^{-t_M/T_1} & e^{-t_M/T_2} & \dots & e^{-t_M/T_N} \end{pmatrix}$$

Regularização Tikhonov ( $\alpha$ ) suaviza solução

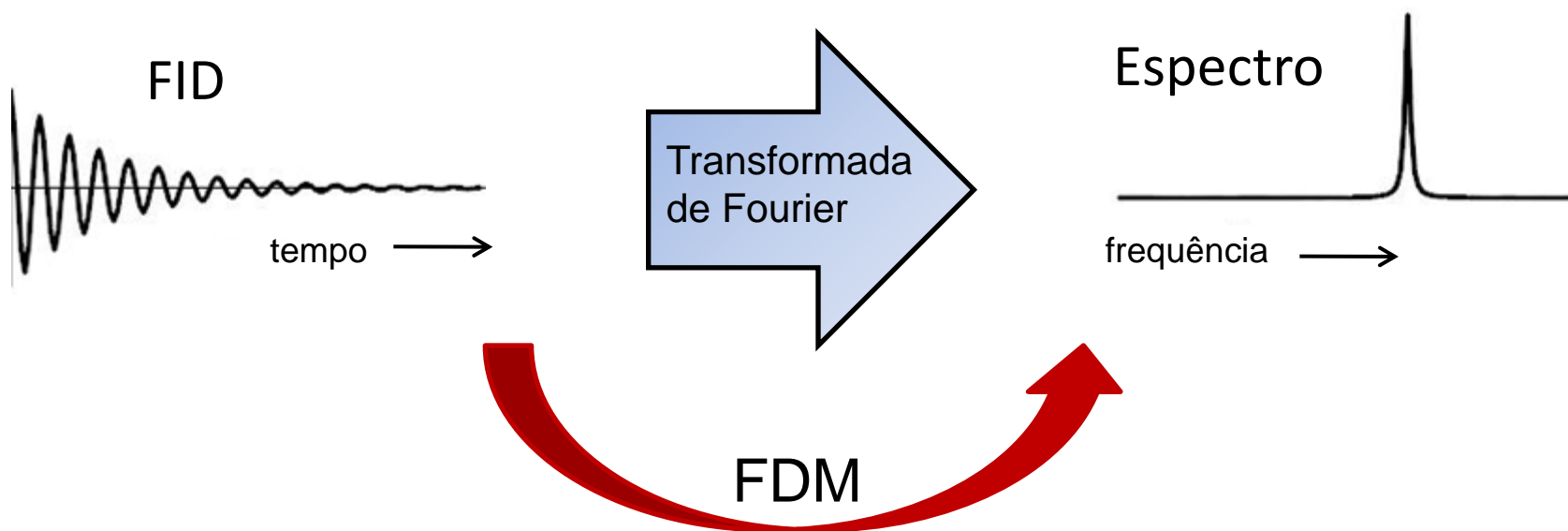
# interações para obter distribuição contínua e não negativa

➤ Pacote Matlab

# FDM

Moraes, T.B.; **O Método da Diagonalização Filtrada e suas aplicações para a Ressonância Magnética**, dissertação mestrado IFSC - USP, 2011.

Prof. Dr. Cláudio José Magon



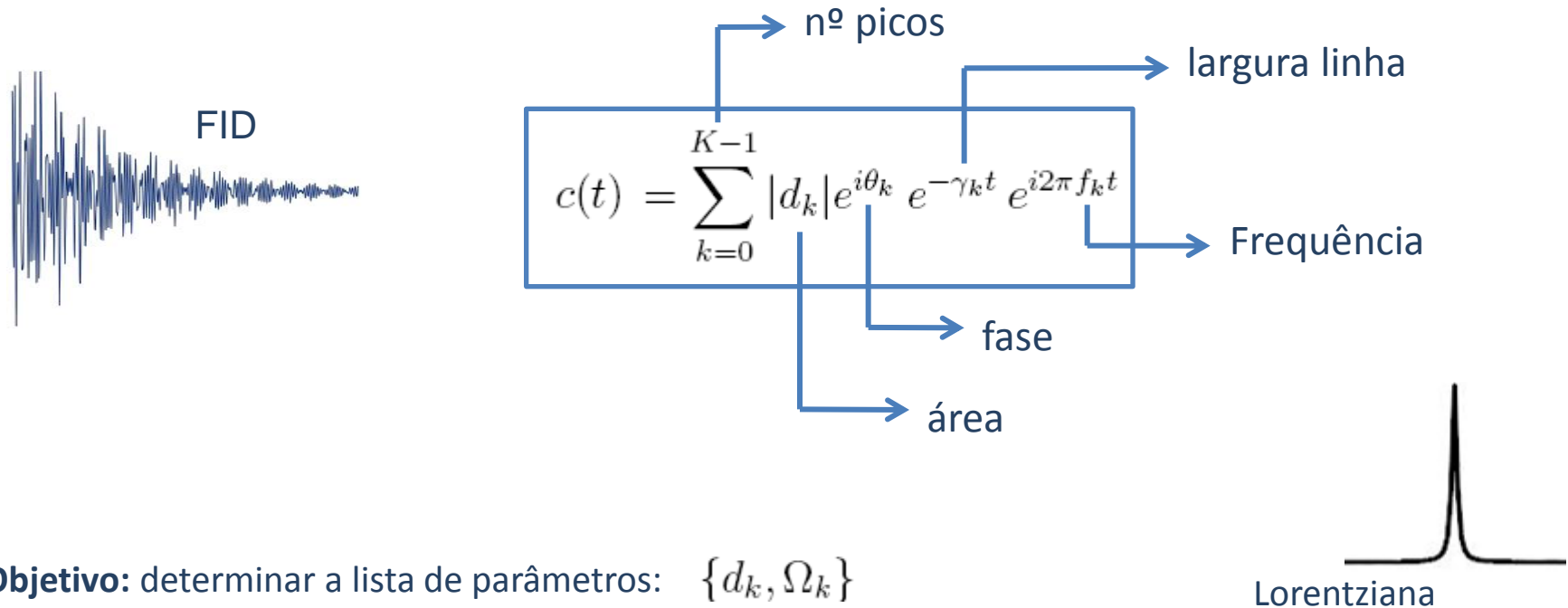
- Truncado, tempo morto, deconvolução, componente eco, experimentos 2D



# Método da Diagonalização Filtrada (FDM)

Moraes, T.B.; **O Método da Diagonalização Filtrada e suas aplicações para a Ressonância Magnética**, dissertação mestrado IFSC - USP, 2011.

Prof. Dr. Cláudio José Magon

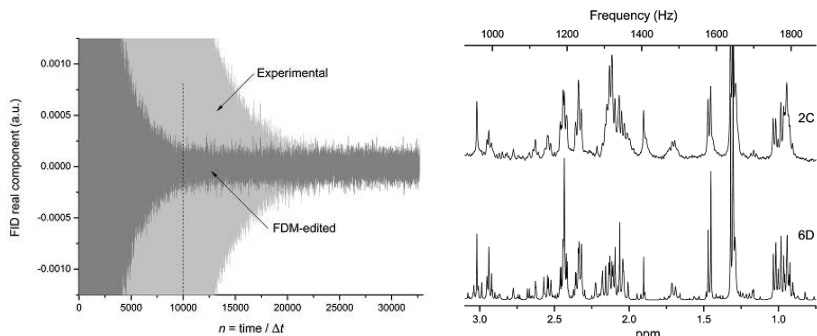


**Objetivo:** determinar a lista de parâmetros:  $\{d_k, \Omega_k\}$

Álgebra linear: Equação de autovalores generalizada

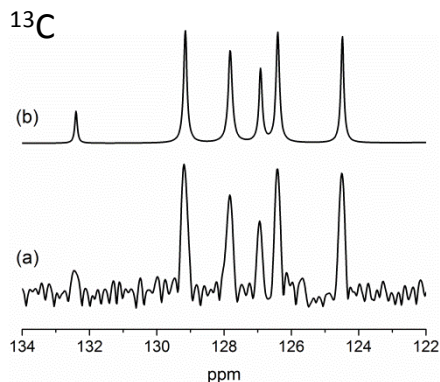
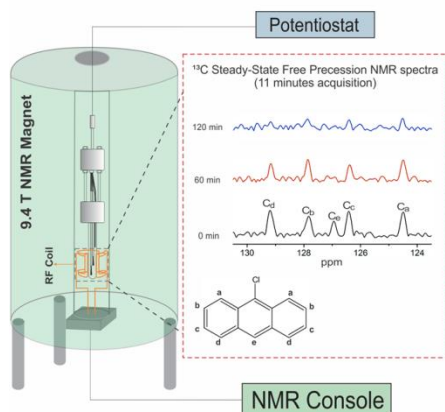
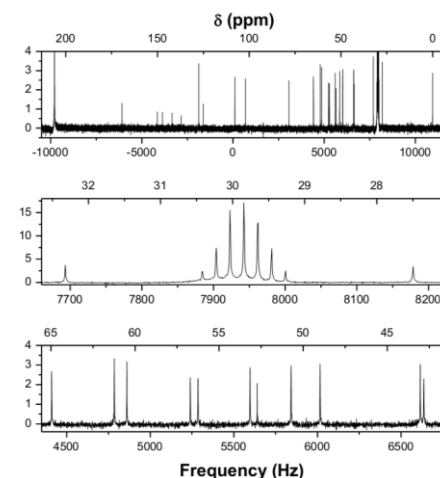
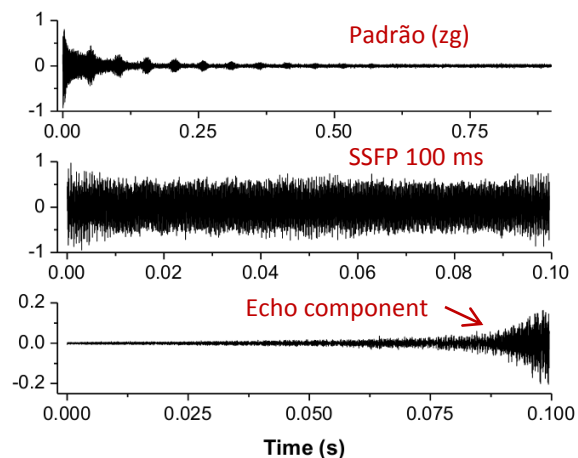
$$U^{(1)} B_k = \mu_k U^{(0)} B_k$$

# FDM



Maria, R.M., Moraes, T.B., et. al. *Processing of high resolution magic angle spinning spectra of breast cancer cells by the filter diagonalization method*, **Analyst**, 137, 4546, 2012.

Moraes, T.B., Santos, P.M., Magon, C.J., Colnago, L.A., *Suppression of Spectral Anomalies in SSFP-NMR signal by the Krylov Basis Diagonalization Method*, **Journal Magnetic Resonance**, 243c, 74-80, (2014).



Nunes, L., Moraes, T.B., Barbosa, L., Mazo, L., Colnago, L.A., *Monitoring electrochemical reactions in situ using steady-state free precession  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy*, **Analytica Chimica Acta**, 840c, 2014.

# Objetivos

# Objetivos

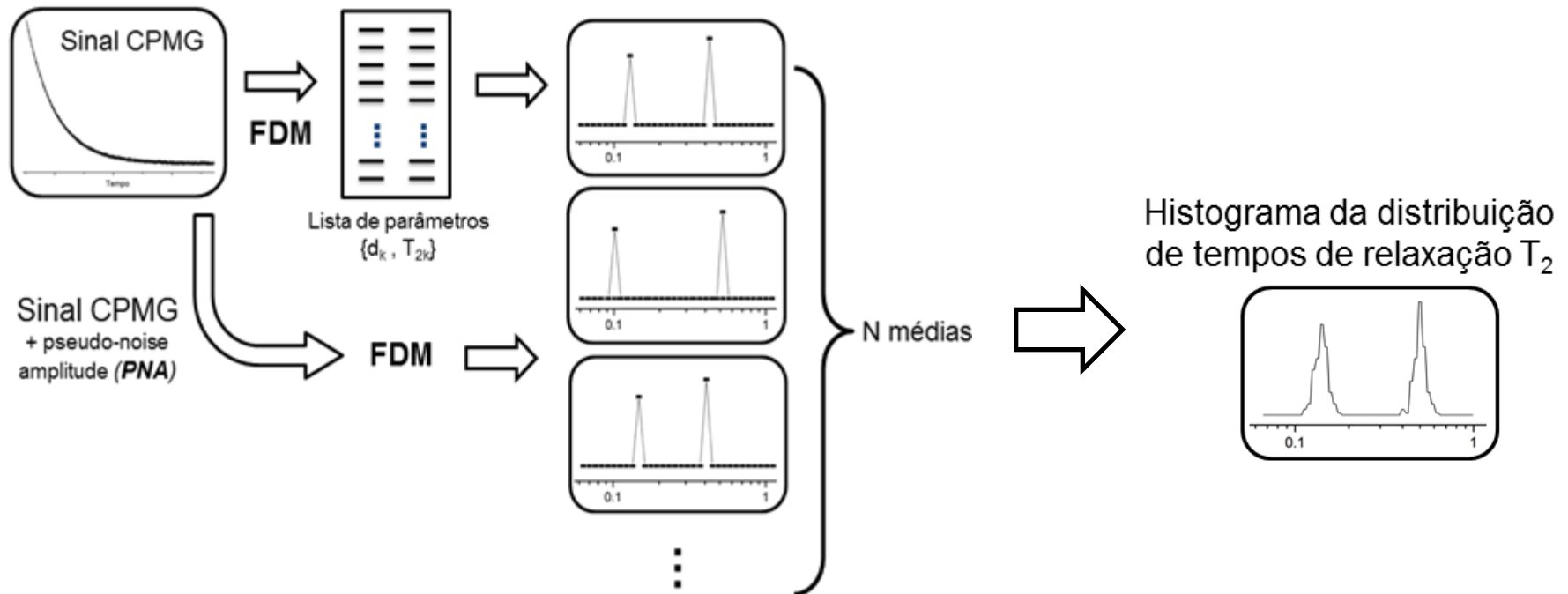
- ❑ Desenvolver uma versão do FDM para análise da distribuição de tempos de relaxação (CPMG);
- ❑ Avaliar o algoritmo através de sinais experimentais;
- ❑ Comparar com métodos estabelecidos de Transformada Inversa de Laplace.

# FDM Distribuição $T_2$

□ FDM / KBDM

Moraes, T.B., Montrazi, E.T., Colnago, L.A., Bonagamba, T.J., Magon, C.J.  
Exponential analysis by Filter Diagonalization Method

➤ FDM regularização *pseudo-noise averaging*



➤ Implementação Matlab / Origin

# Resultados

# Resultados

Medidas realizadas em:

0,047 T                      2 MHz

0,47 T                        20 MHz

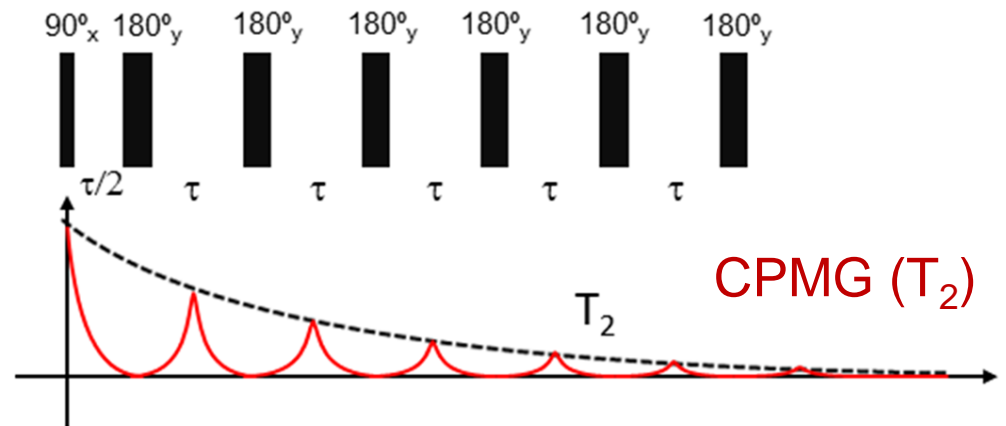
0,26 T                        11 MHz

TecMag LapNMR  
Spin Lock SLK-200

Soluções aquosas de  $\text{CuSO}_4$   
 $\tau = 500 \mu\text{s} / \text{Cyclops}$

Cerâmicas / Rock cores  
 $\tau = 200 \text{ ms} / 2, 8, 32 \text{ e } 128 \text{ scans}$

Óleo Lubrificante / Sementes  
 $\tau = 200 \mu\text{s} / \text{Cyclops}$



NNLS - ILT

FDM

# Resultados

Cerâmica alumina caracterizada por porosimetria de intrusão de mercúrio (MIP) e microtomografia de raio-X ( $\mu$ CT). (E.T. Montrazi)

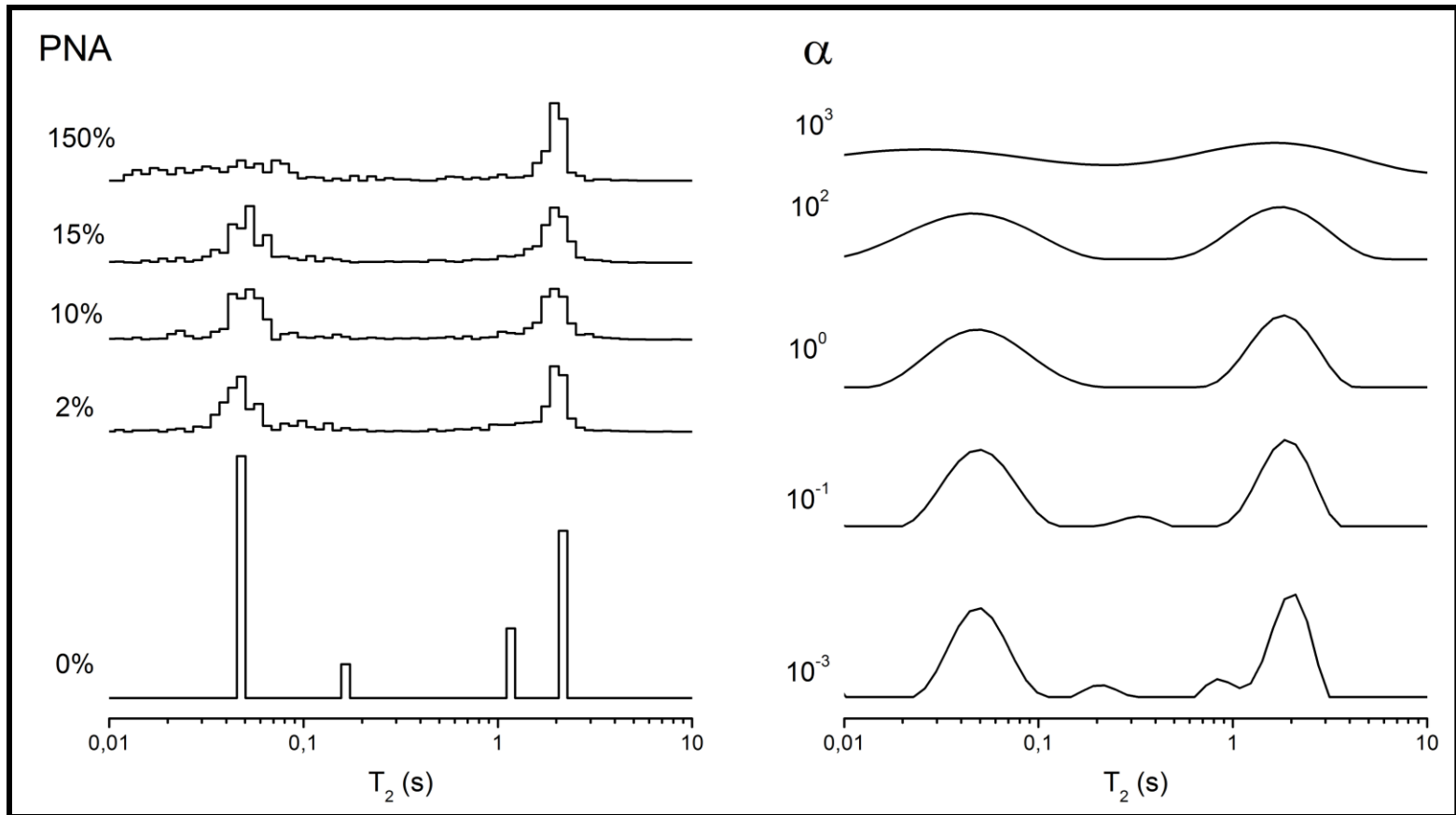
TecMag LapNMR 20 MHz

$\tau = 200 \mu\text{s} / 2, 8, 32 \text{ e } 128 \text{ scans.}$

## Parâmetro regularização

FDM

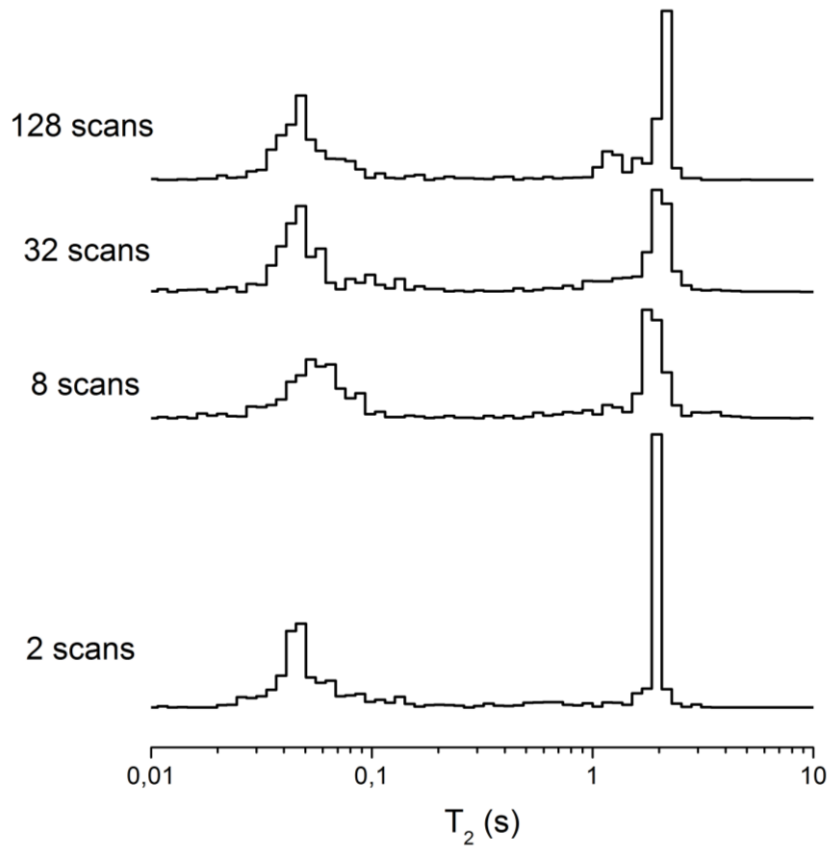
ILT



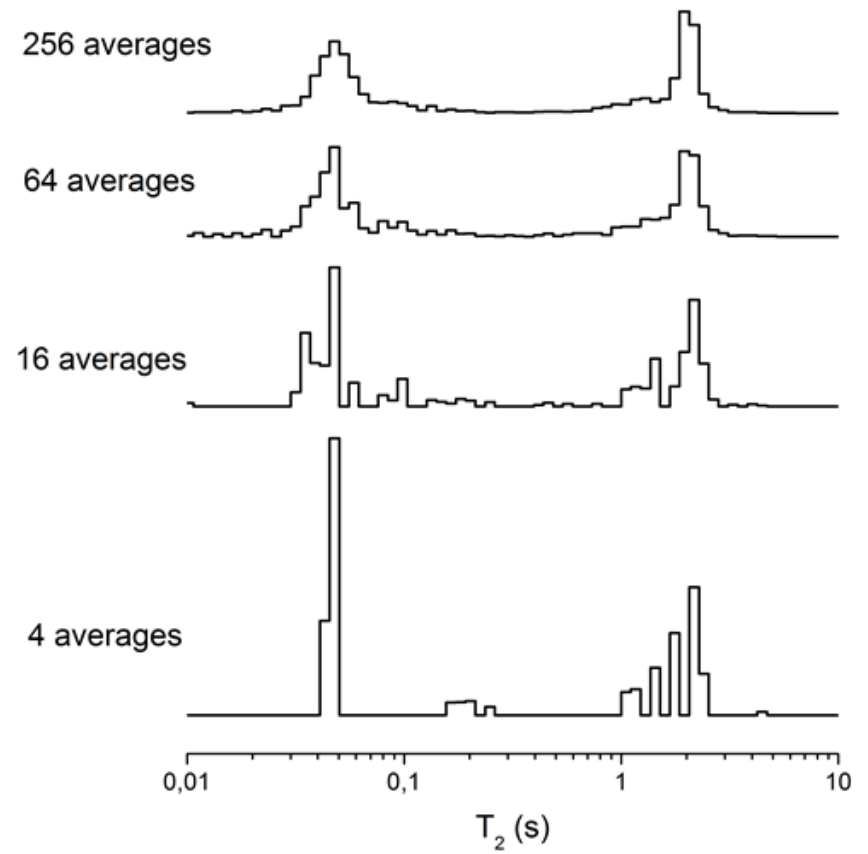


# Resultados

## CPMG scans

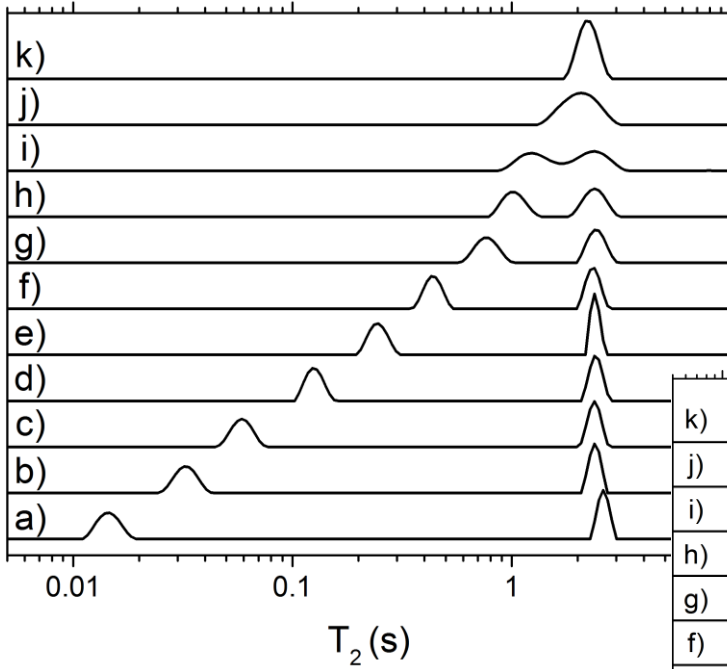


## FDM interações



# Resultados

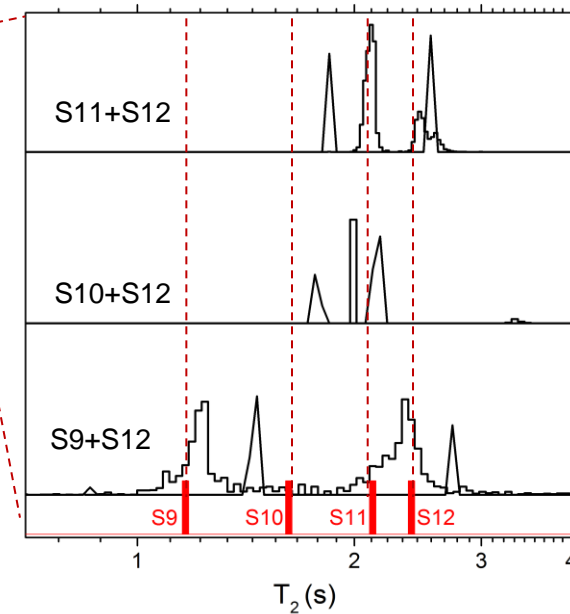
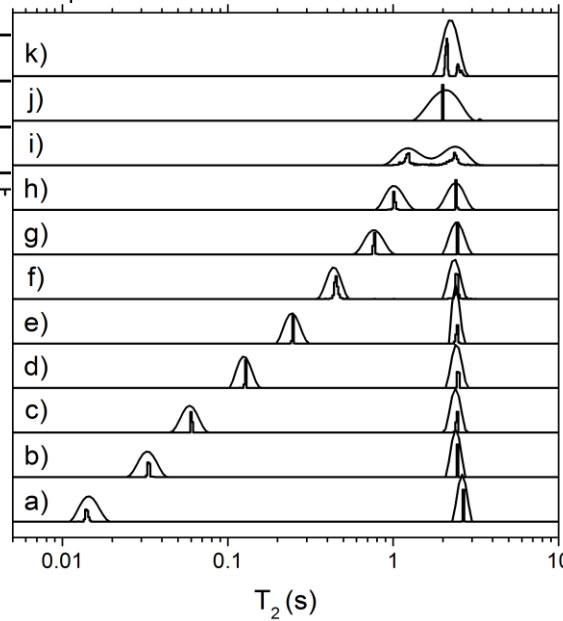
Soluções aquosas com diferentes concentrações de  $\text{CuSO}_4$



SpinLock SLK-200  
11 MHz  
 $\tau = 500 \mu\text{s} / \text{Cyclops}$



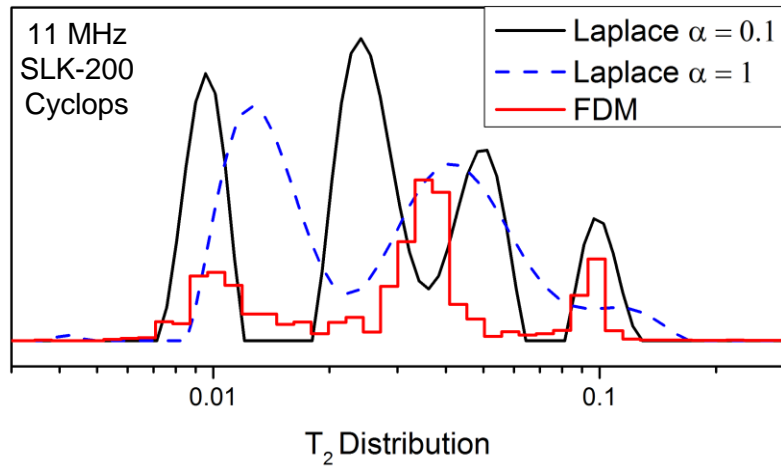
- S1 + S12
- S2 + S12
- S3 + S12
- S4 + S12
- S5 + S12
- S6 + S12
- S7 + S12
- S8 + S12
- S9 + S12
- S10 + S12
- S11 + S12



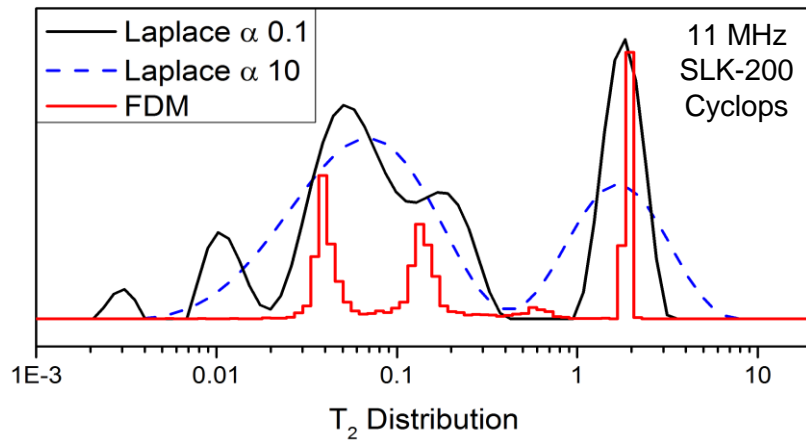
*Fitting mono-exponencial*

# Resultados

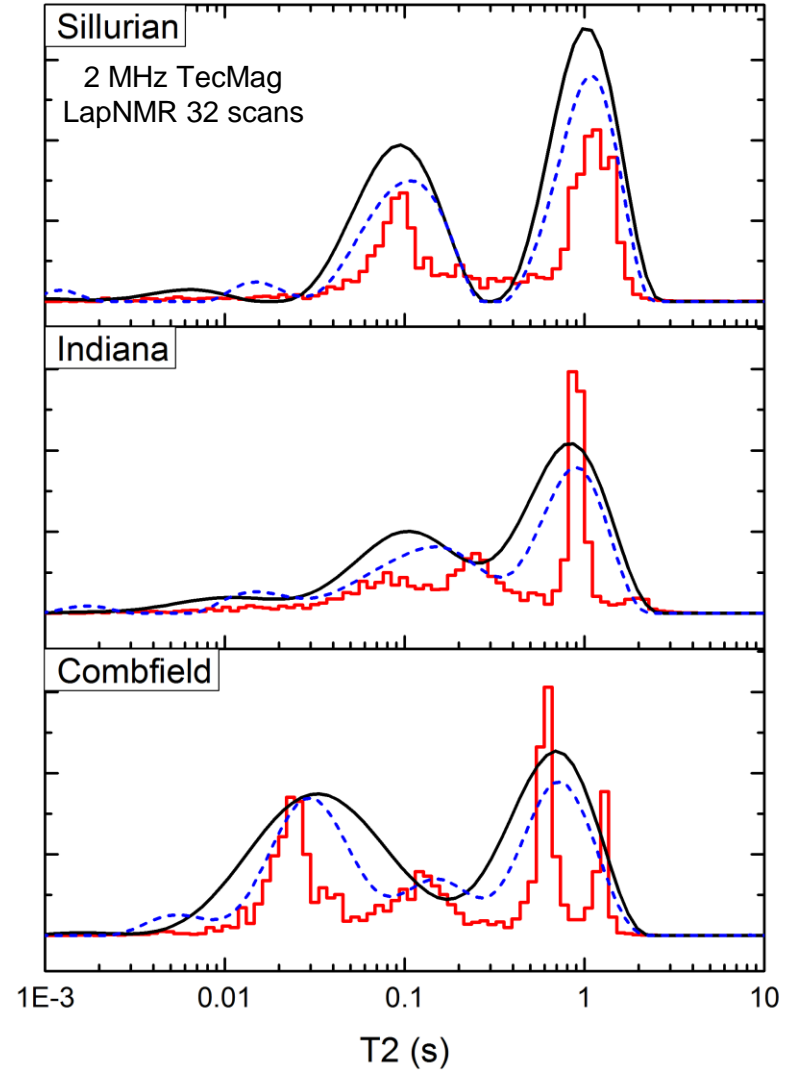
Óleo lubrificante



Amendoim + água



Rock cores



## FDM vs ILT

- ❑ Método robusto e confiável;
- ❑ Distribuições  $T_2$  compatível com NNLS-ILT;
  - ✓ Soluções aquosa com  $\text{CuSO}_4$ ;
  - ✓ Sementes, óleos;
  - ✓ Cerâmicas e rochas porosas *Sillurian, Indiana e Combfield*.
- ❑ Uma nova ferramenta para análise de decaimentos multi-exponenciais;

# Próximas atividades

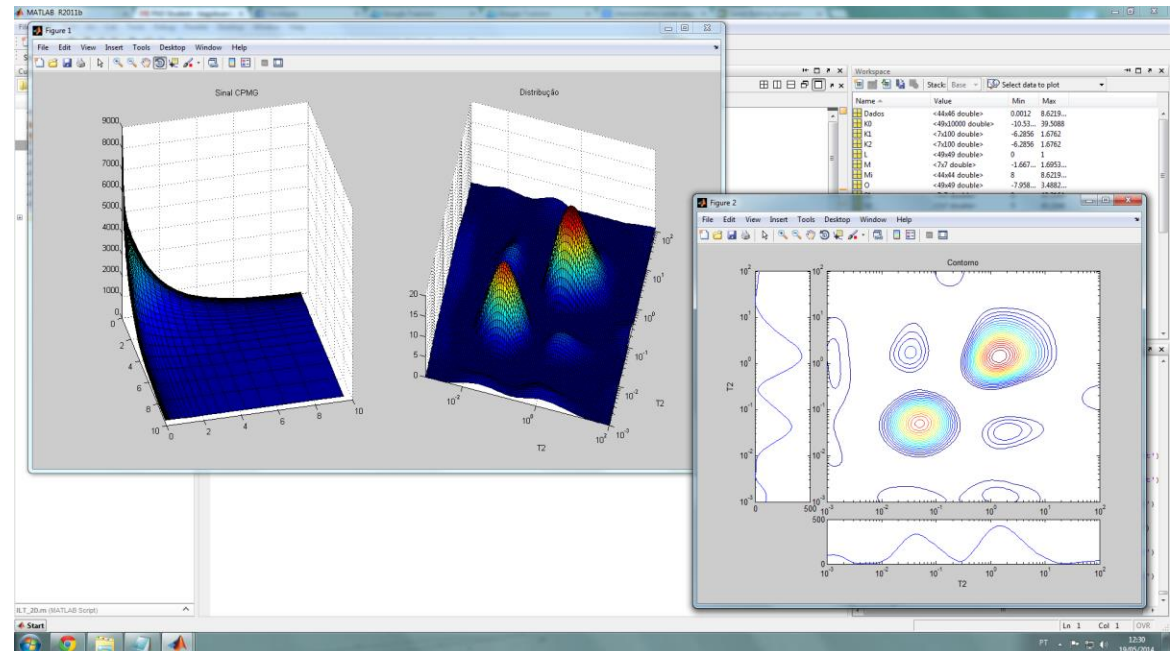
## FDM

- ❑ Artigo em fase final de escrita;

## FDM - 2D Laplace

- ❑ FDM-2D para Inversão de Laplace experimentos bi-dimensionais;

- Relaxometria D-T1, T1-T2, T2-T2
- Alta Resolução (DOSY)



# Agradecimentos

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Exponential analysis by Filter Diagonalization Method

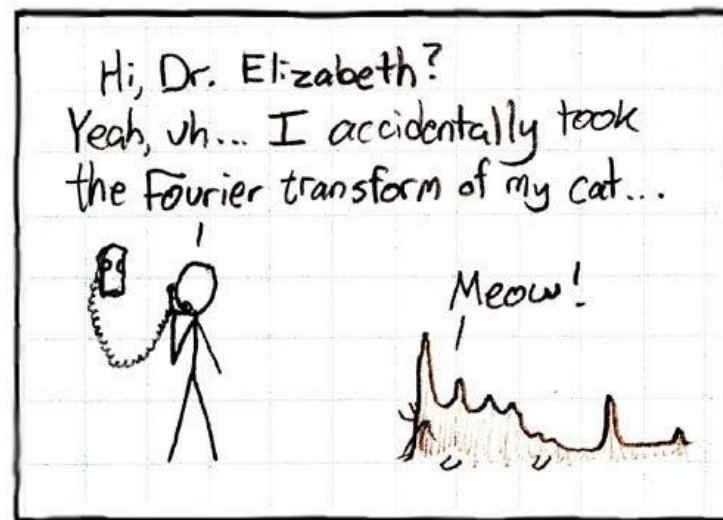
Prof. Dr. Luiz Alberto Colnago  
Prof. Dr. Tito José Bonagamba  
Prof. Dr. Cláudio José Magon

Proc. 2011/111-60



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XIII JORNADA BRASILEIRA DE  
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MINI CURSOS EM RMN 

04 a 08 de Agosto de 2014 • Pirenópolis, Goiás - Brasil