Fundamentos e aplicações de RMN no estado sólido

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Sumário

- Fundamentos de RMN:
  - Relaxometria por RMN.
  - Aplicações:
    - Meios porosos.
    - Petrofísica.
    - Imagens.
    - Alimentos.

Distribuição de tempos de relaxação

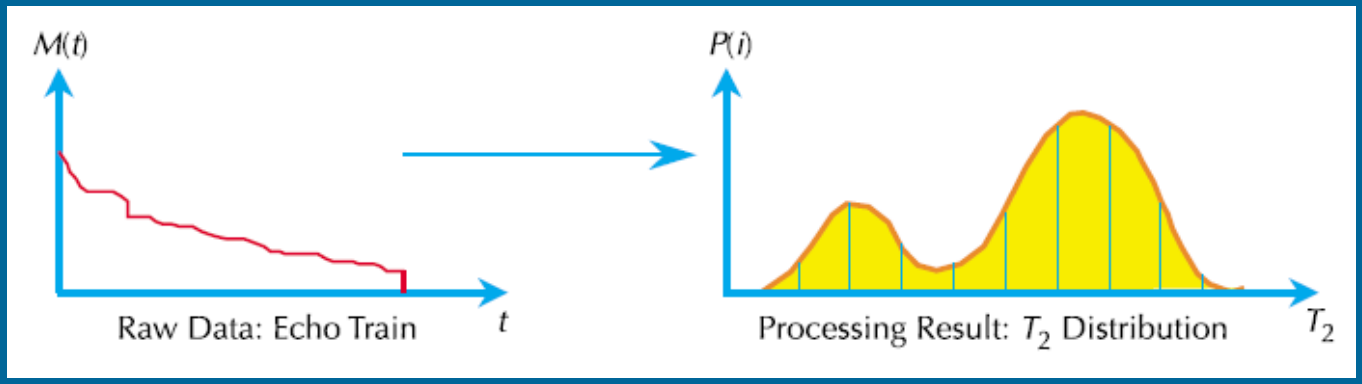
Transformada de Laplace Inversa (ILT):

$$M(t) = \sum_{k=1}^{N} A(T_{2k}) e^{-t/T_{2k}}$$

$$M(t) \xrightarrow{\text{ILT}} A(T_2)$$

Algoritmo de regularização: CONTIN

Aplicações: fluidos complexos (petróleo), meios porosos, alimentos, etc.



Relaxometria por RMN de ^1H

NMR Logging
Principles and Applications

Halliburton Energy Services

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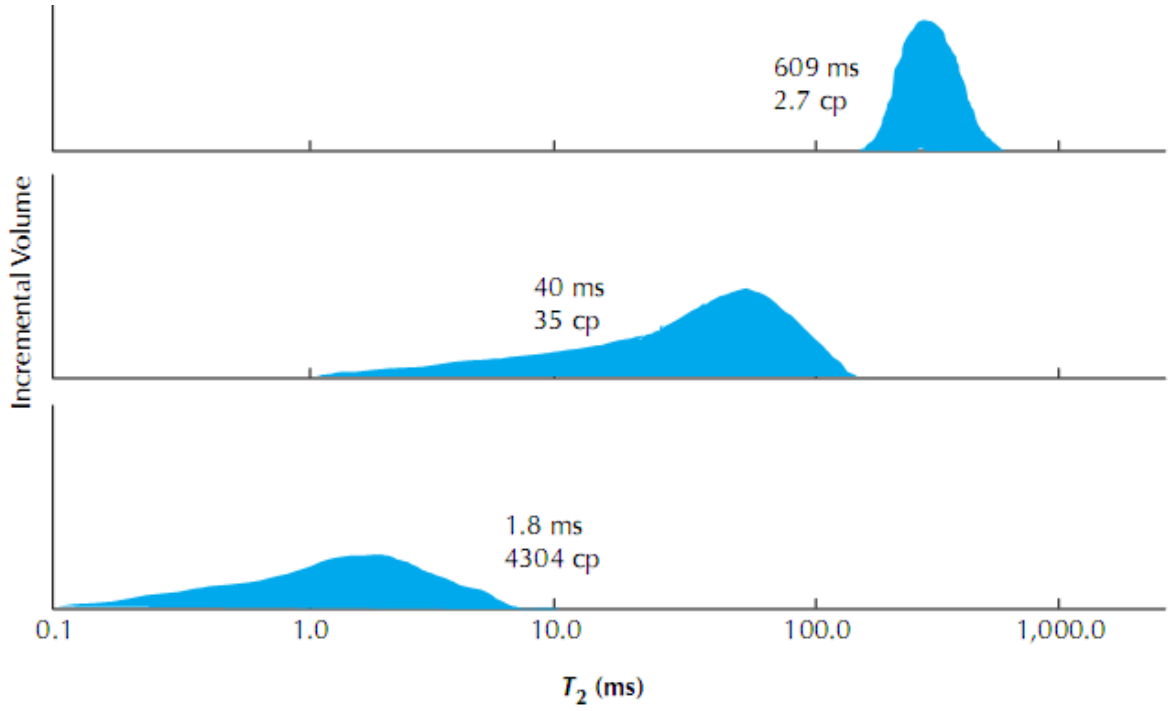

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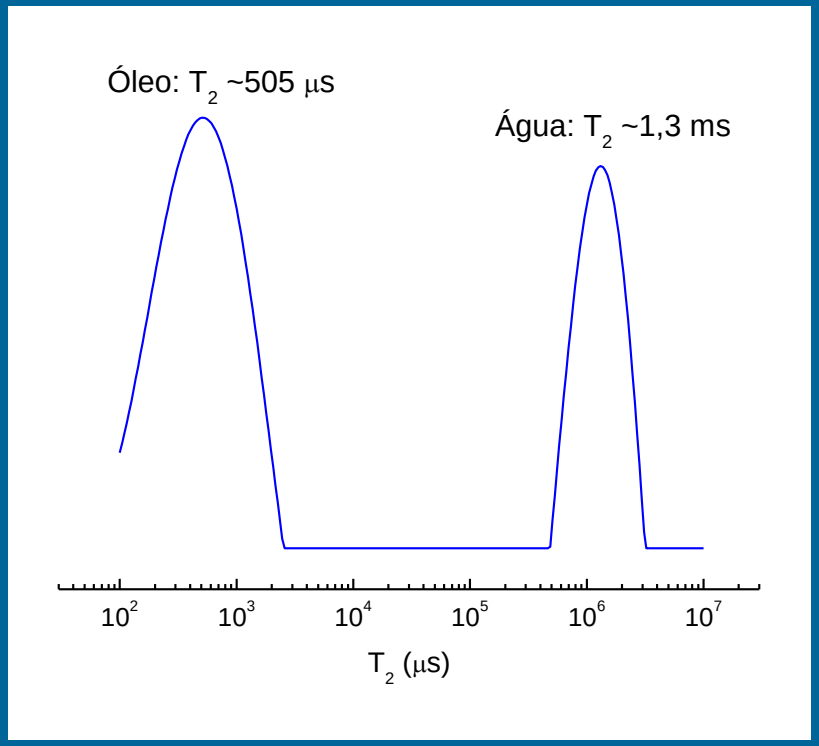
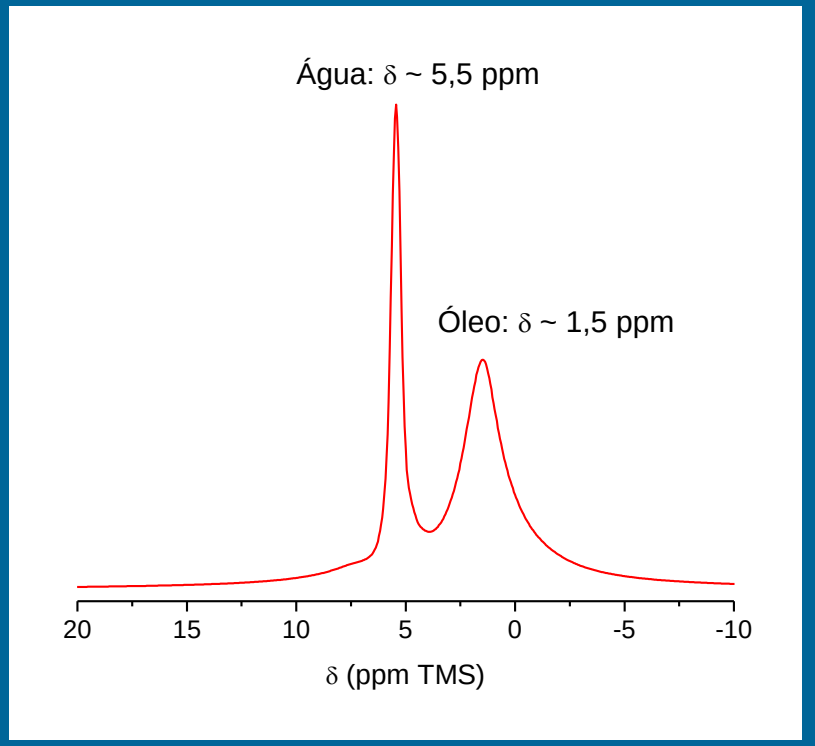
Figure 4.1—The T_2 of crude oil varies with viscosity, as shown in these T_2 distributions for three oil samples. For the light oil (top), which has a viscosity of 2.7 cp, the measured T_2 values are clustered tightly about a single value, namely, 609 ms. For the medium-viscosity oil (middle), which has a viscosity of 35 cp, the measured T_2 values form a broad distribution with a lower-end tail and a geometric mean of 40 ms. For a much heavier crude oil (bottom), which has a viscosity of 4304 cp, the measured T_2 values also form a broad distribution with a lower-end tail but with a geometric mean of only 1.8 ms.

RMN de ^{1}H em petróleo pesado

Relaxometria: 2,0 MHz

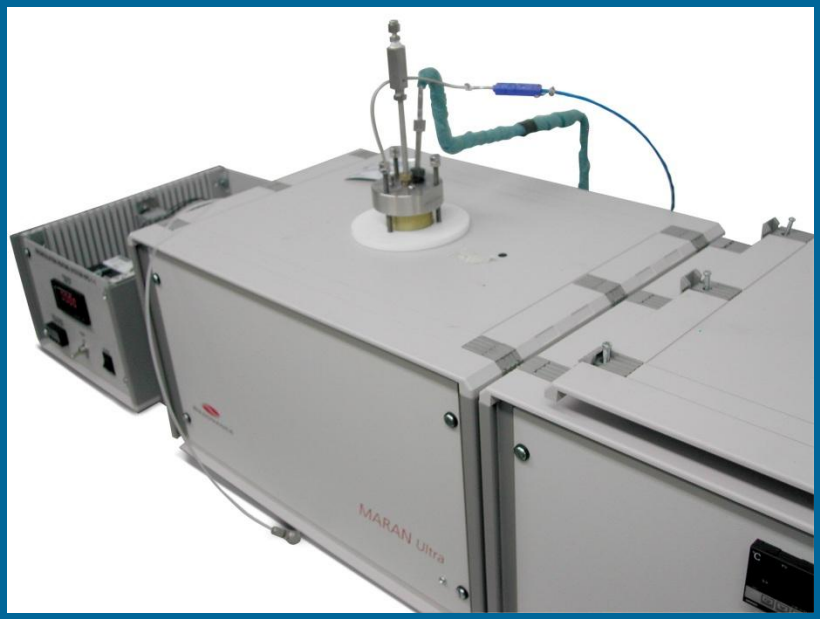


Espectroscopia: 400 MHz

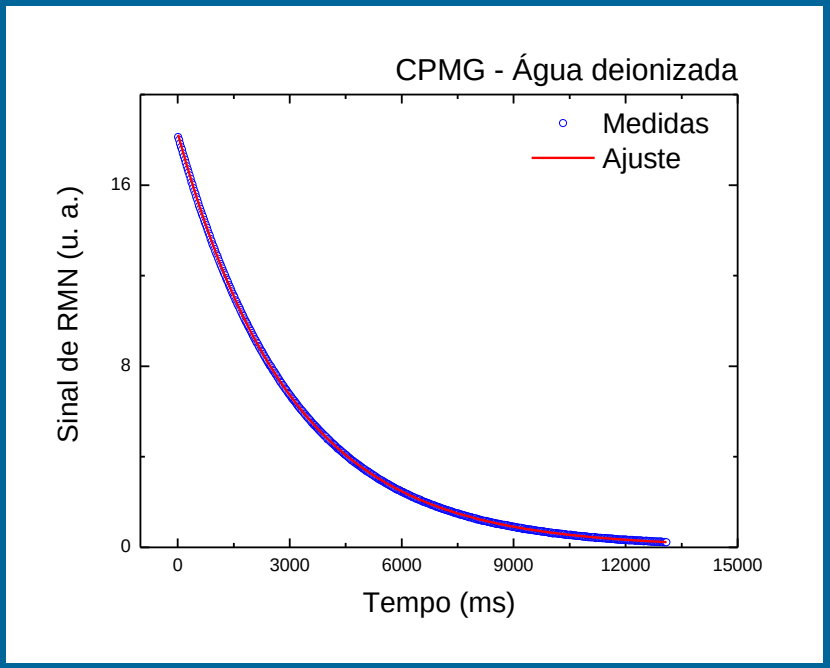


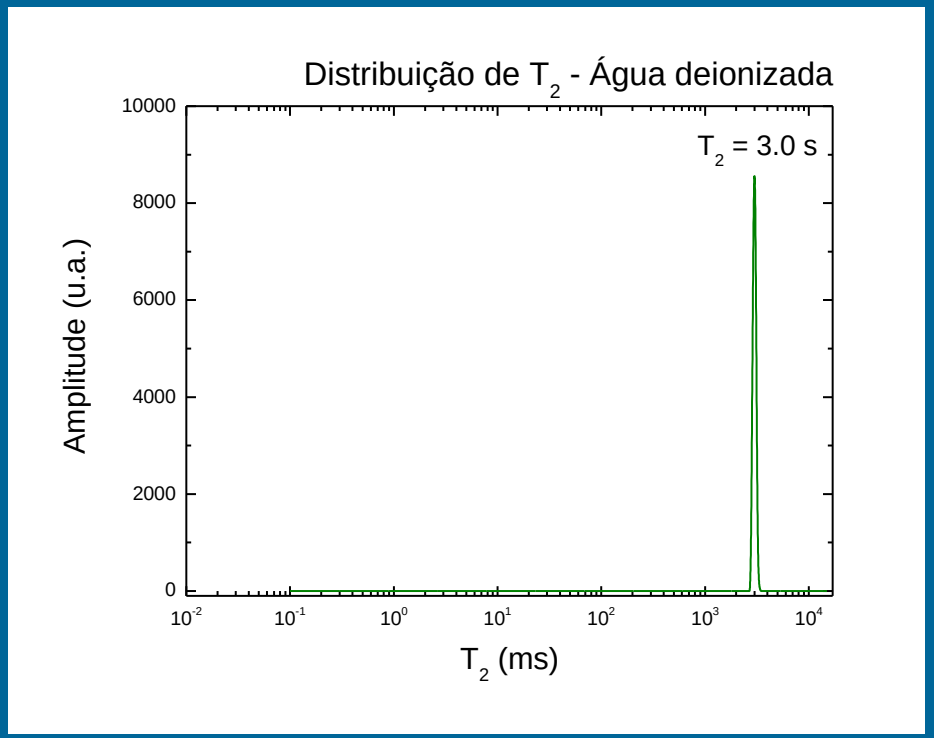
Relaxometria por RMN de ^{1}H

Aplicações em petrofísica:



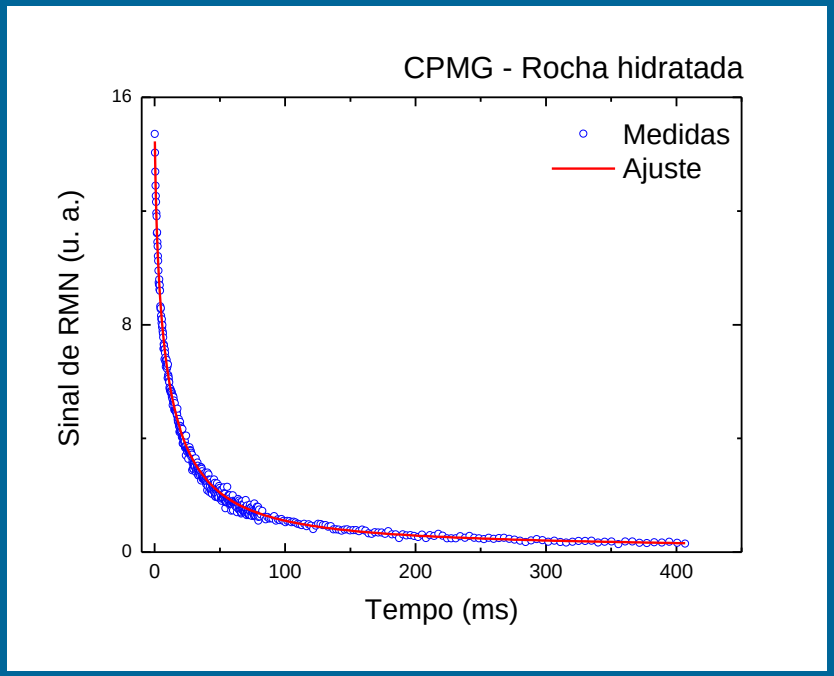
Relaxometria por RMN de ^1H

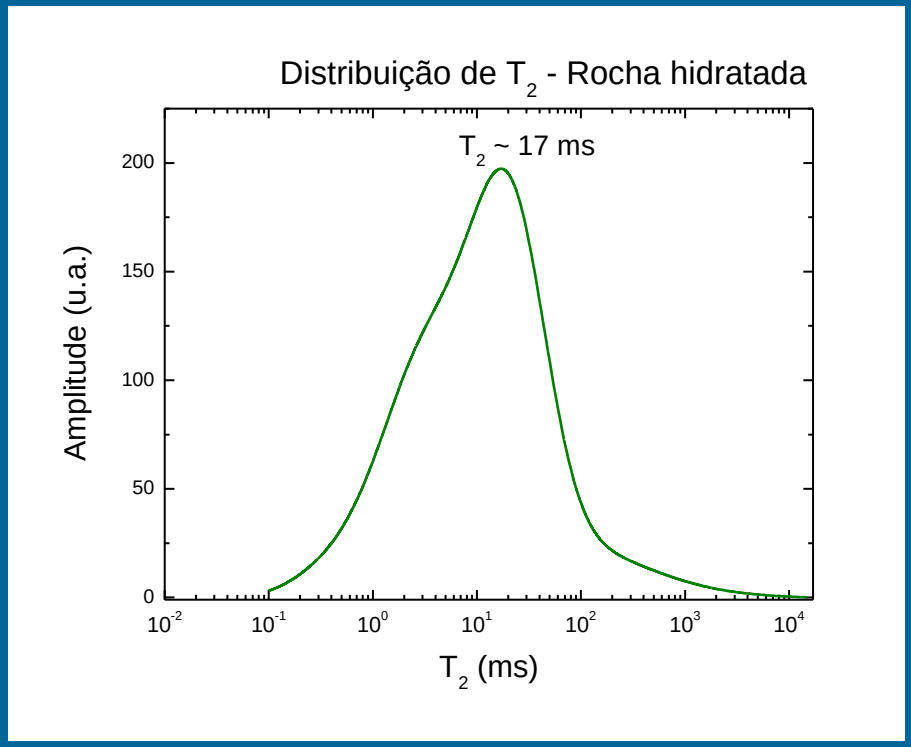




f_L = 2,0 MHz; B_0 = 47mT

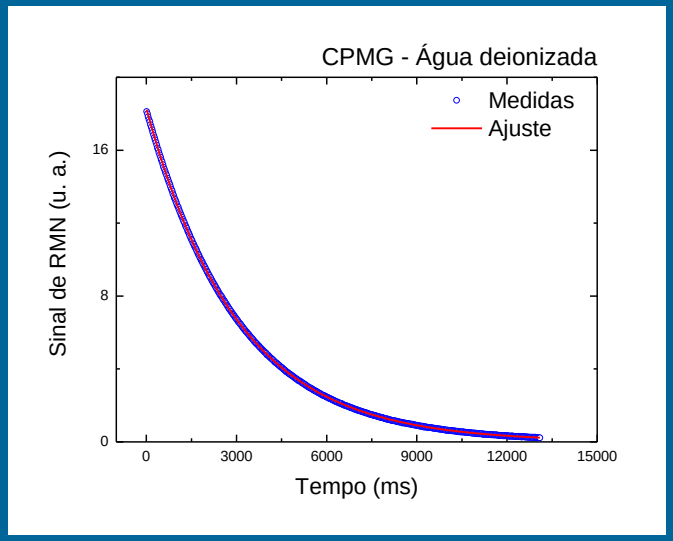
Relaxometria por RMN de ^1H

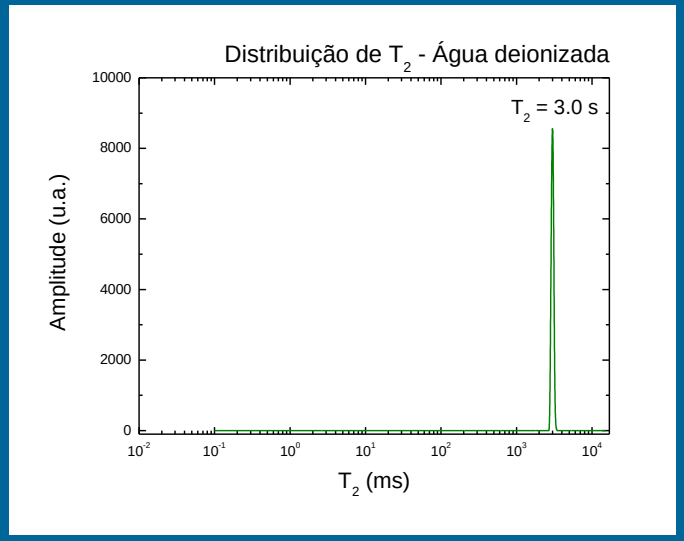


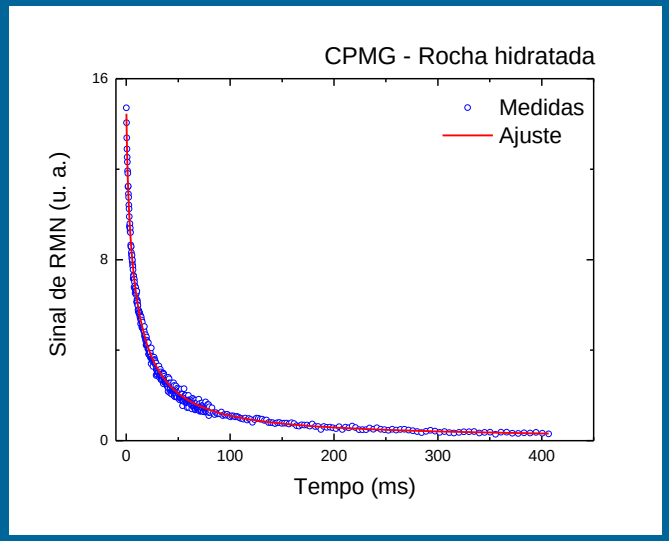


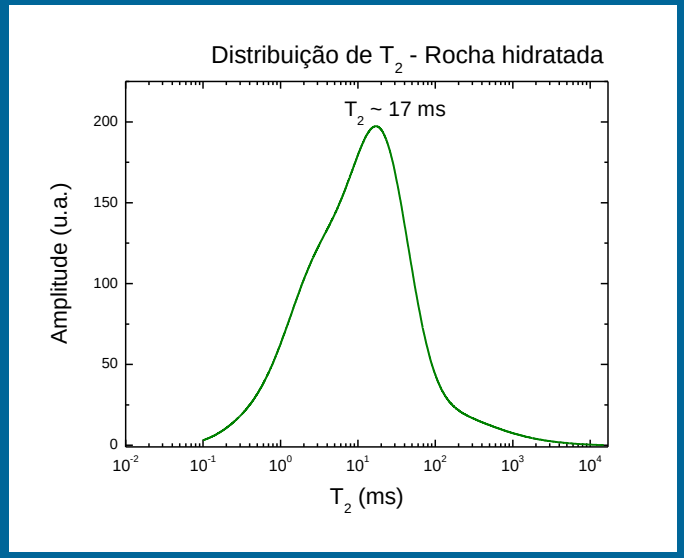
f_L = 2,0 MHz; B_0 = 47mT

Relaxometria por RMN de ^1H



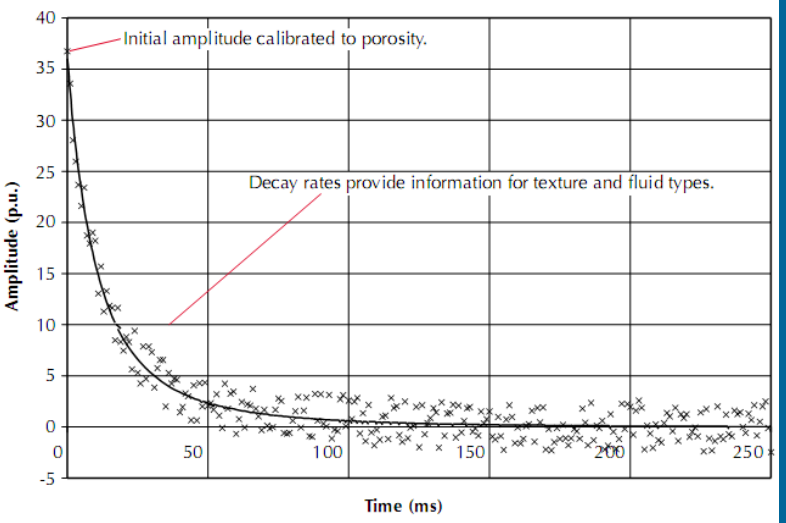






Aplicações em petrofísica

Figure 1.4—The decay of a spin-echo train, which is a function of the amount and distribution of hydrogen present in fluids, is measured by recording the decrease in amplitude of the spin echoes over time. Petrophysicists can use decay-rate information to establish pore-fluid types and pore-size distributions. In this example, the spin echoes are recorded at 1-ms inter-echo spacing. The discrete points in this figure represent the raw data, and the solid curve is a fit to that data.



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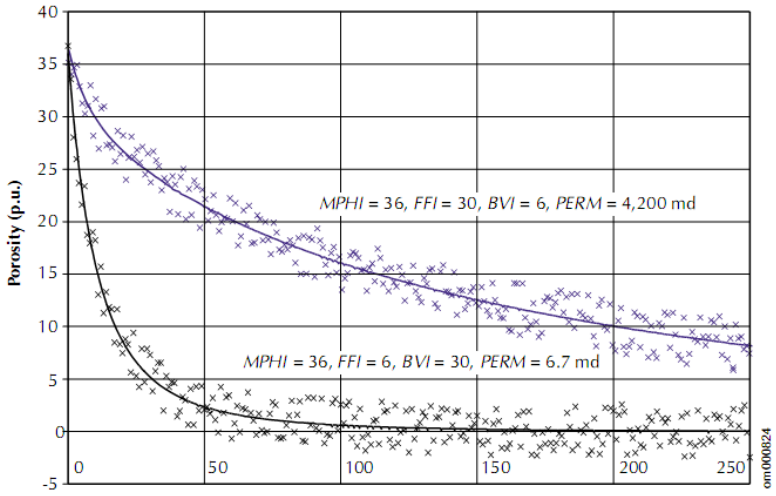
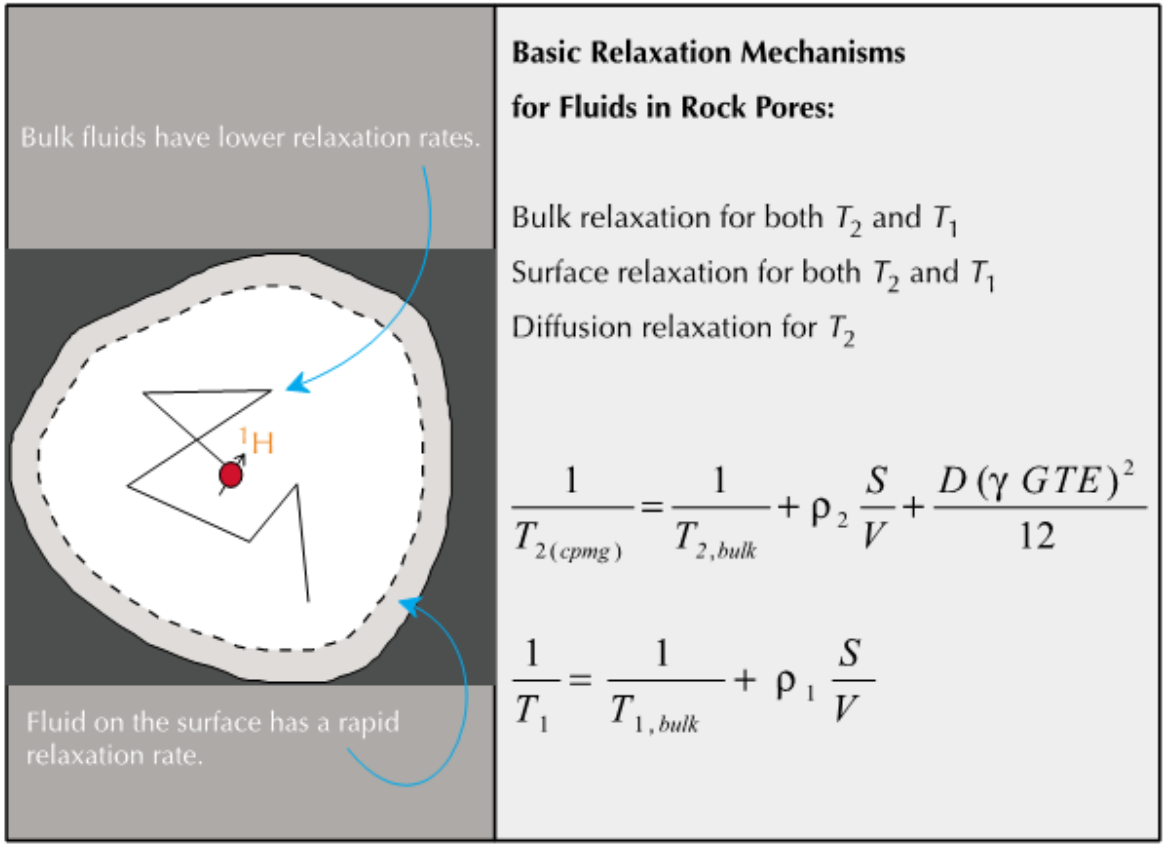


Figure 1.10—Two echo trains were obtained from formations with different permeability. Both formations have the same porosity but different pore sizes. This difference leads to shifted T_2 distributions, and therefore to different values of the ratio of *MFFI* to *BVI*. The permeabilities computed from the Coates model $\{k = [(MPHI/C)^2(MFFI/BVI)]^2$, where k is formation permeability and C is a constant that depends on the formation} also are indicated in the figure.

Aplicações em petrofísica

Figure 3.1—The relaxation of pore fluids is due to bulk, surface, and diffusion mechanisms.



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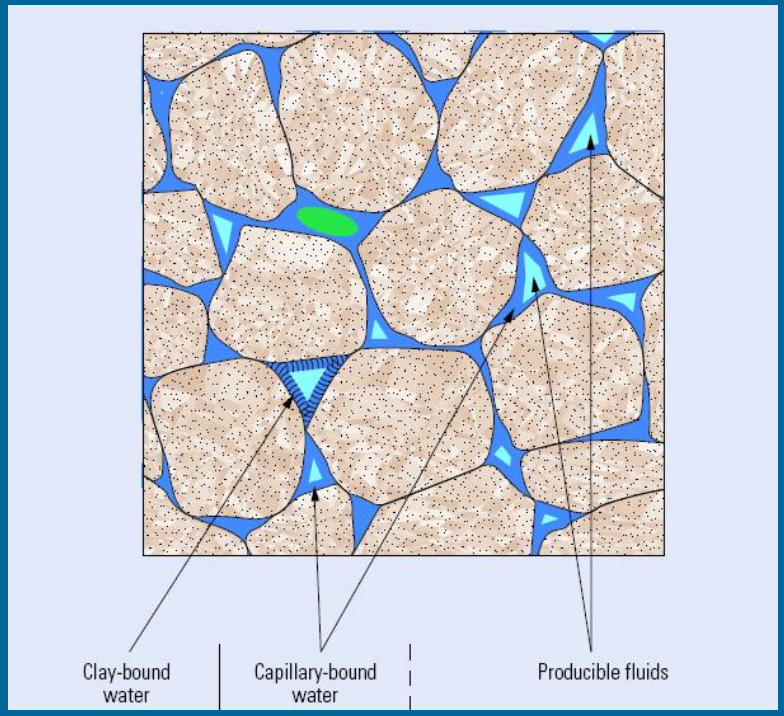
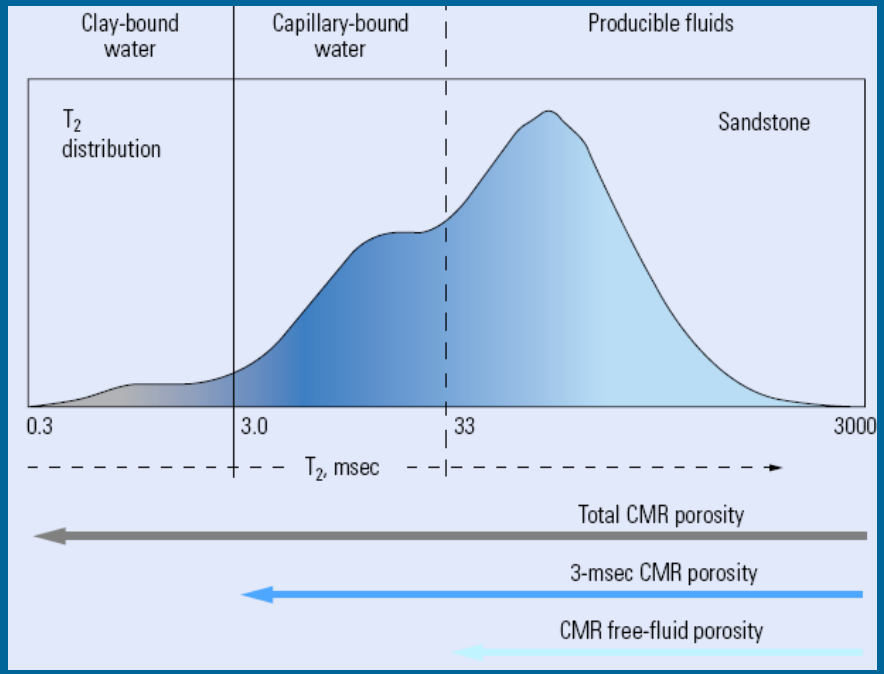
Aplicações em petrofísica





Aplicações em petrofísica

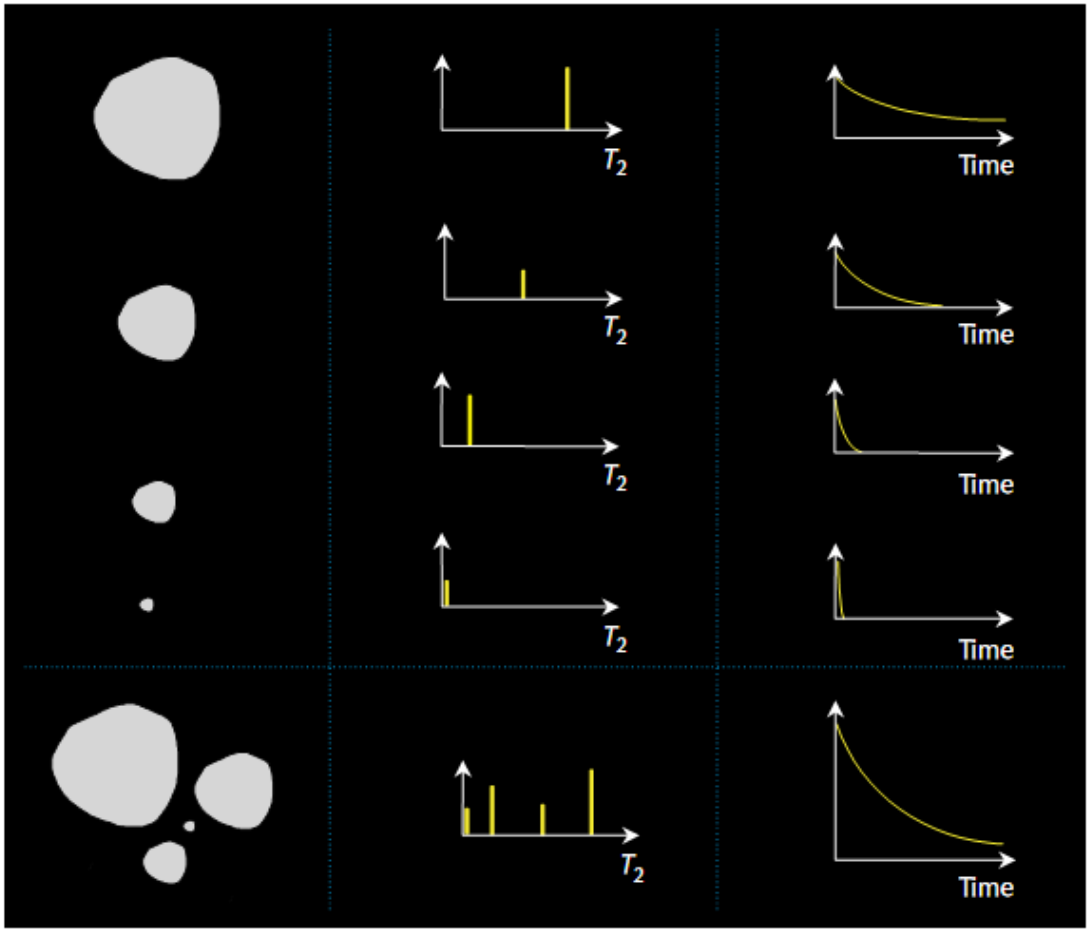


Figure 3.2—A 100% water-saturated pore (upper left) has a single T_2 value (upper center) that depends on pore size, and thus its spin-echo train exhibits a single-exponential decay (upper right) that also depends on pore size. Multiple pores at 100% water saturation (bottom left) have multiple T_2 values (bottom center) that depend on the pore sizes, and thus their composite spin-echo train exhibits multi-exponential decay (bottom right) that also depends on the pore sizes.

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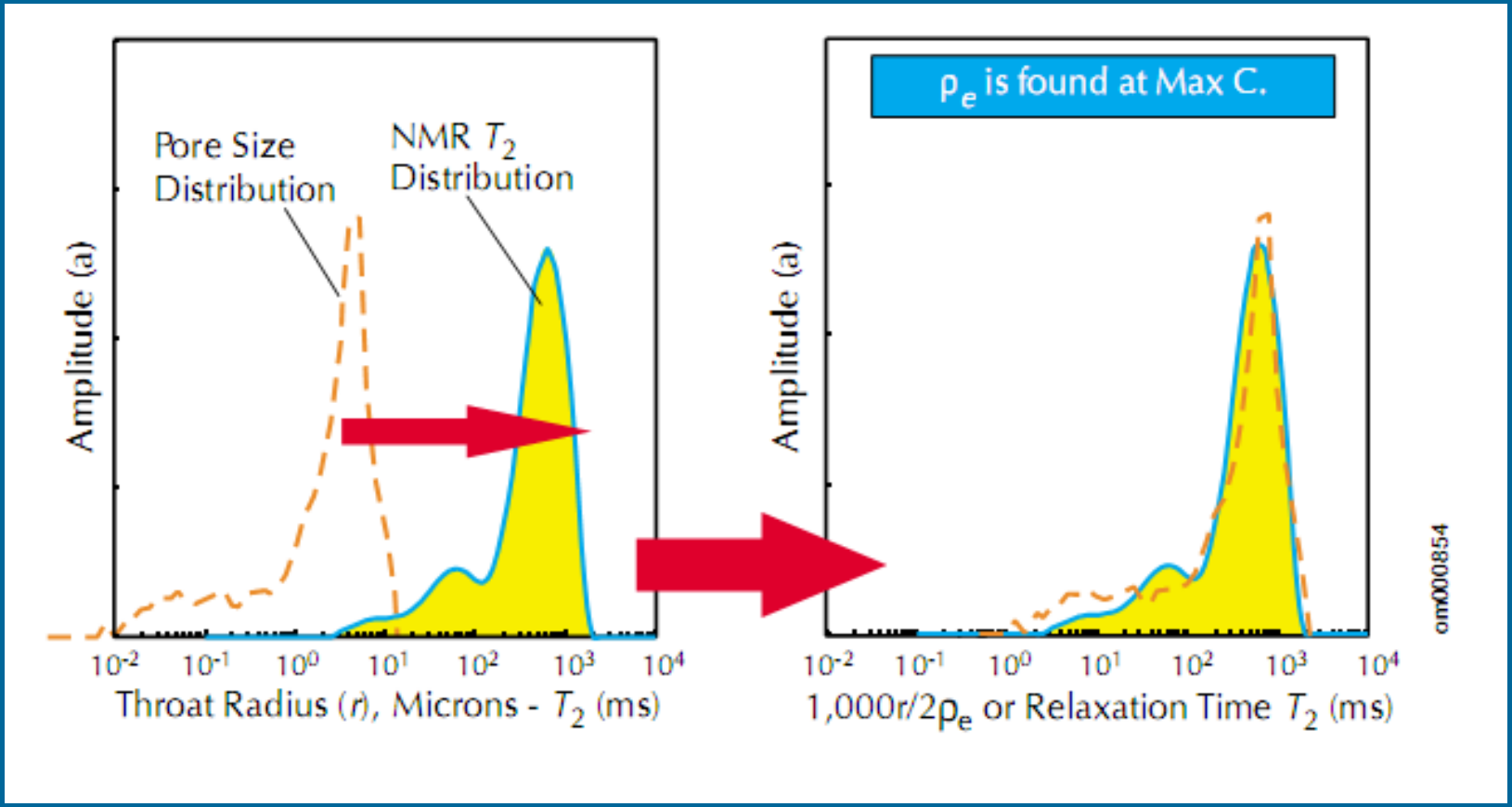
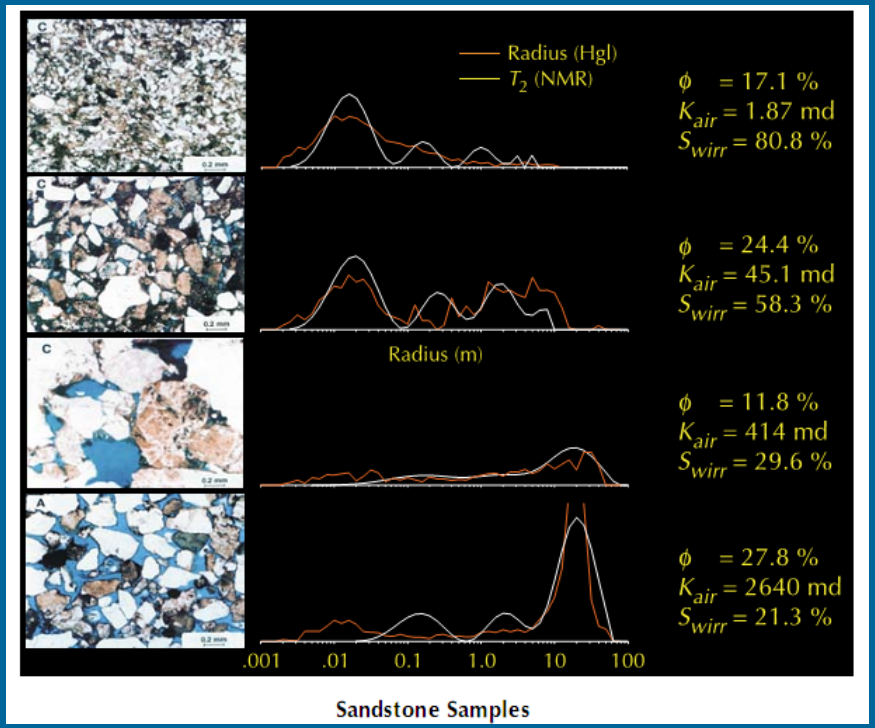
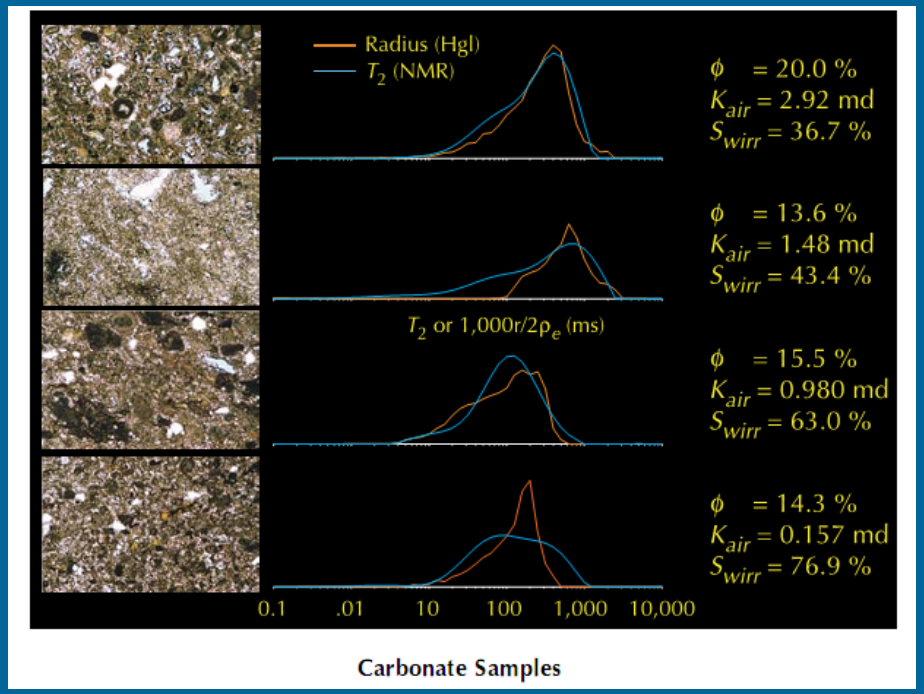
Distribuição de T_2 e de tamanhos de poros



Distribuição de T_2 e de tamanhos de poros



Sandstone Samples



Carbonate Samples

Aplicações em perfilagem de poços de petróleo

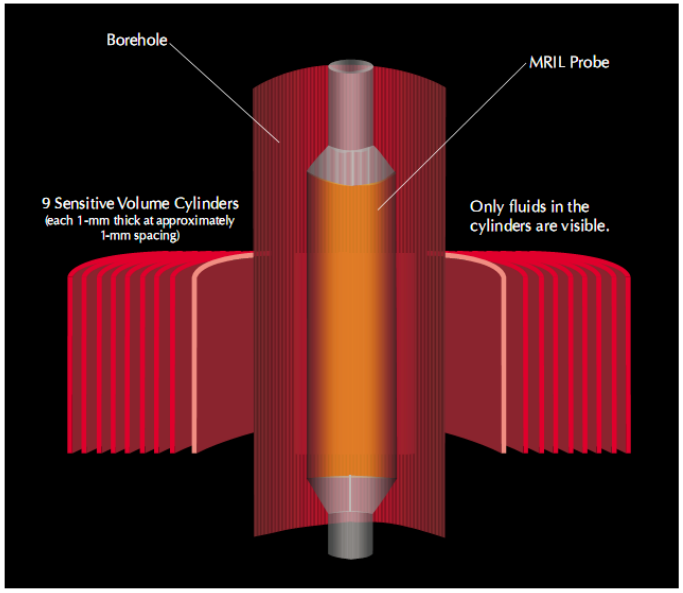


Figure 1.2—The MRIL-Prime tool can be operated at nine separate frequencies. The use of multiple frequencies allows independent information to be obtained from multiple concentric cylinders, thereby improving the signal-to-noise ratio, enabling faster logging speeds, and permitting different pulse-timing sequences for complex data acquisition.

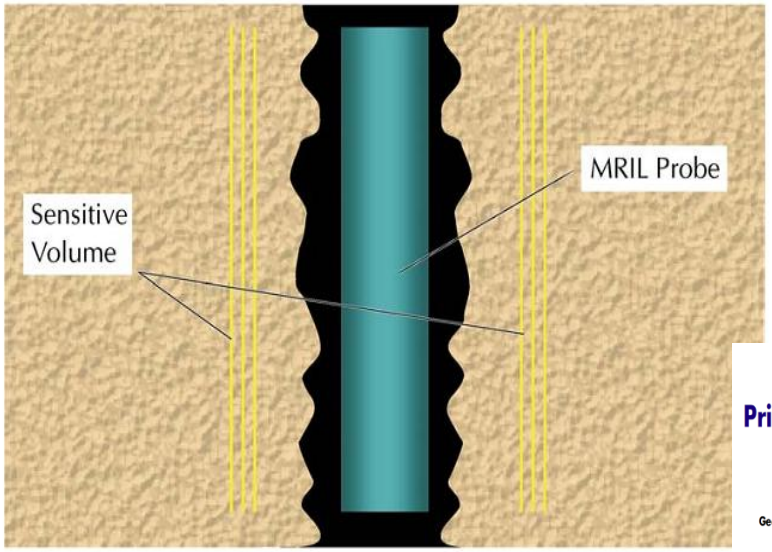


Figure 1.22—The depth of investigation of an MRIL tool is about 18 in. when operating at low frequency and about 16 in. at high frequency. Thus, in a 12-in. borehole, rugosity with an amplitude smaller than 2 in. will not affect the MRIL signal.

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Aplicações em perfilagem de poços de petróleo

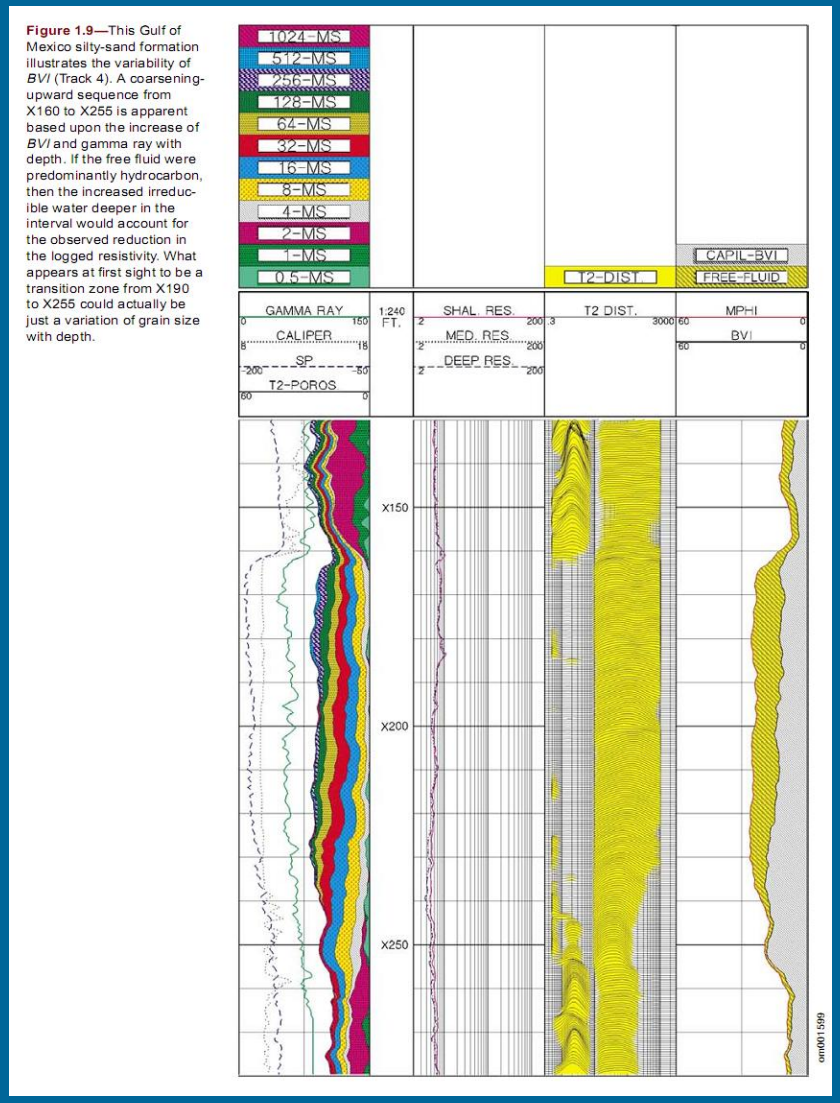
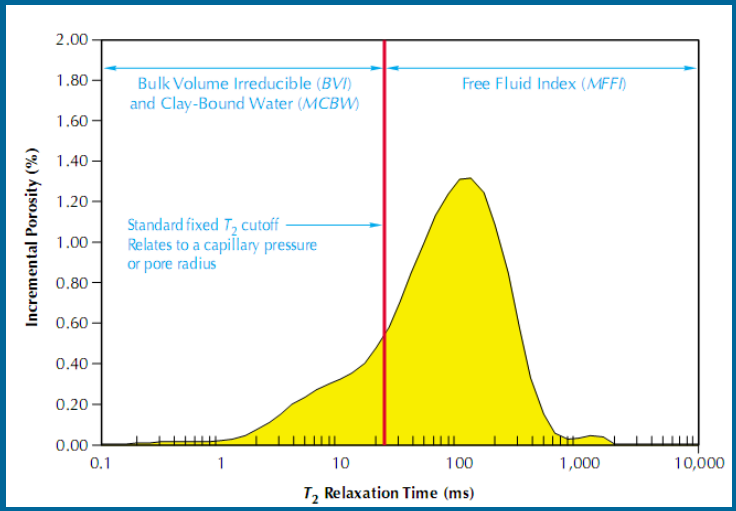
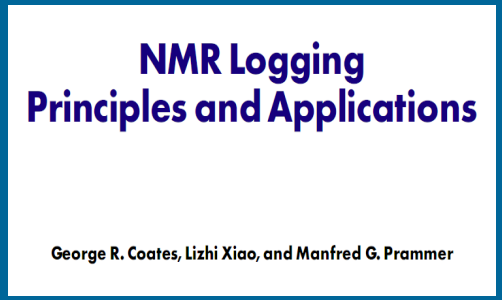


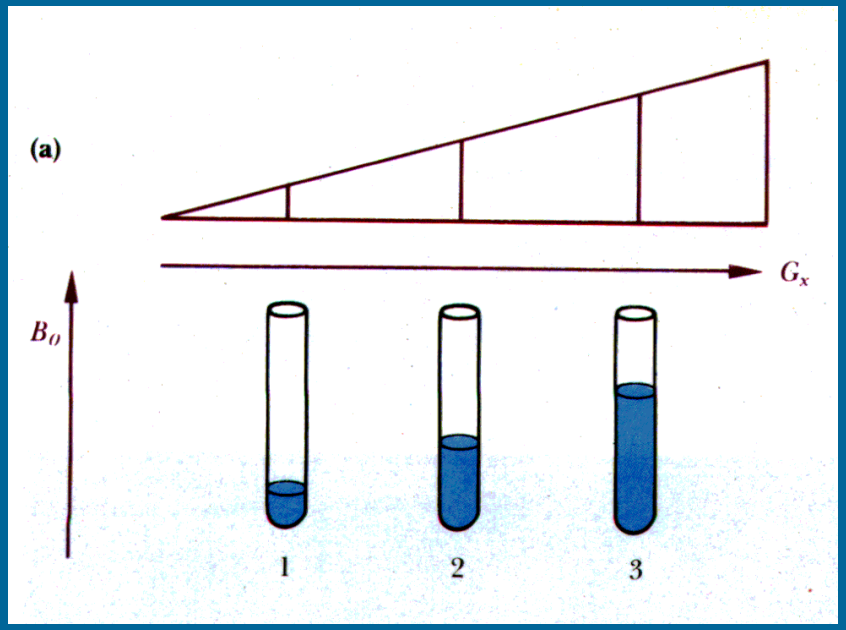
Figure 1.9—This Gulf of Mexico silty-sand formation illustrates the variability of *BVI* (Track 4). A coarsening-upward sequence from X160 to X255 is apparent based upon the increase of *BVI* and gamma ray with depth. If the free fluid were predominantly hydrocarbon, then the increased irreducible water deeper in the interval would account for the observed reduction in the logged resistivity. What appears at first sight to be a transition zone from X190 to X255 could actually be just a variation of grain size with depth.

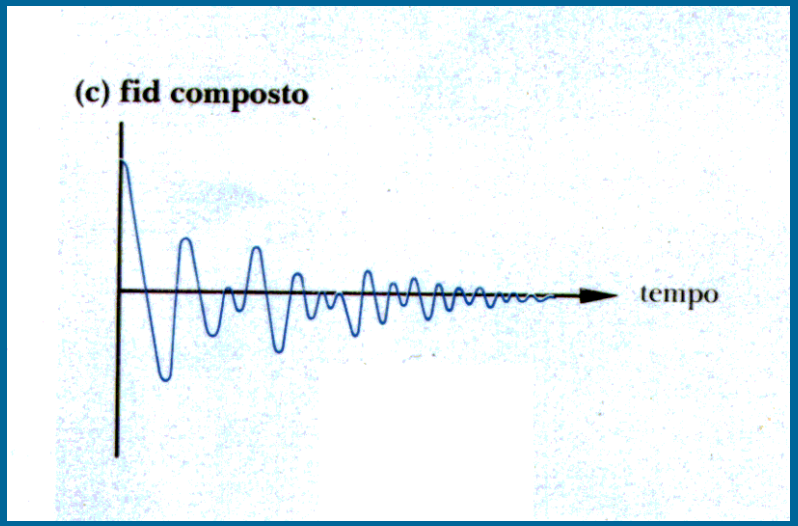


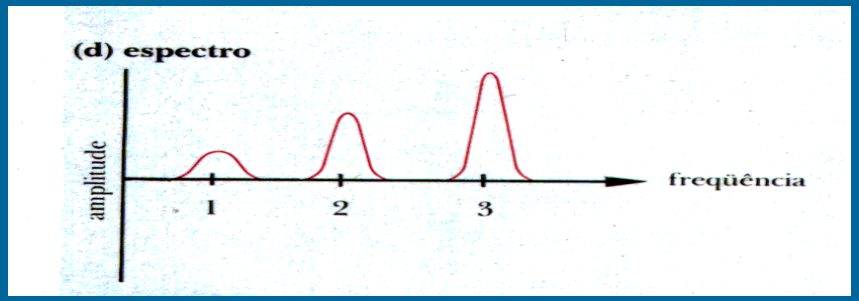


Formação de imagens por RMN (MRI)

- Utilização de gradientes de campo magnético:

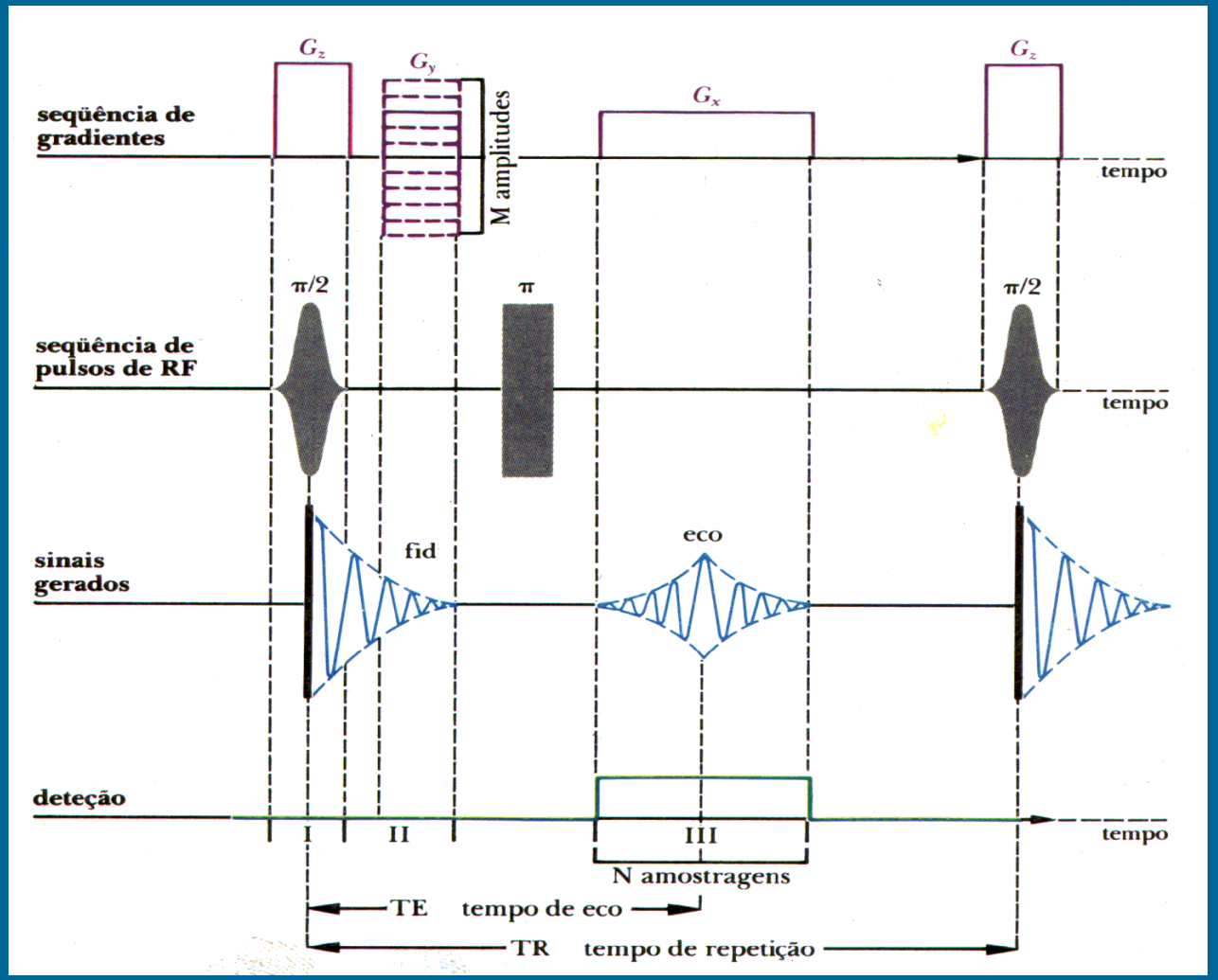






- Discriminação espacial de freqüências.
- Distribuição de densidade de prótons.

Seqüência de pulsos – TF 2D

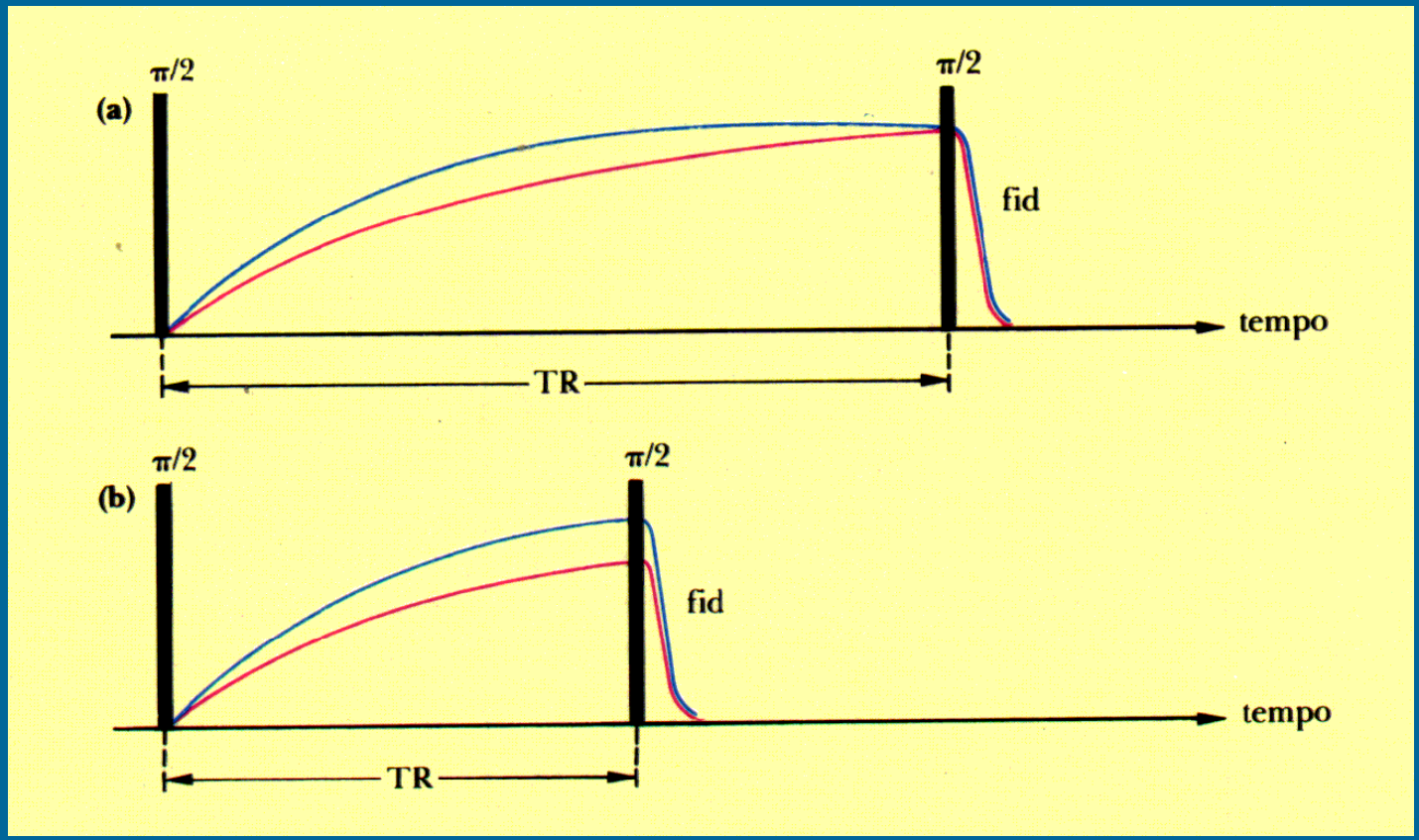


Técnicas de contraste

- Contraste pela densidade de prótons.
- Contraste por T_1 (relaxação longitudinal).
- Contraste por T_2 (relaxação transversal).

	T_1 (s) Tumoral	T_1 (s) Normal
Tórax	1,08	0,37
Pele	1,05	0,62
Fígado	0,83	0,57
Pulmão	1,11	0,79
Próstata	1,11	0,80
Ossos	1,03	0,55

Contraste por T_1

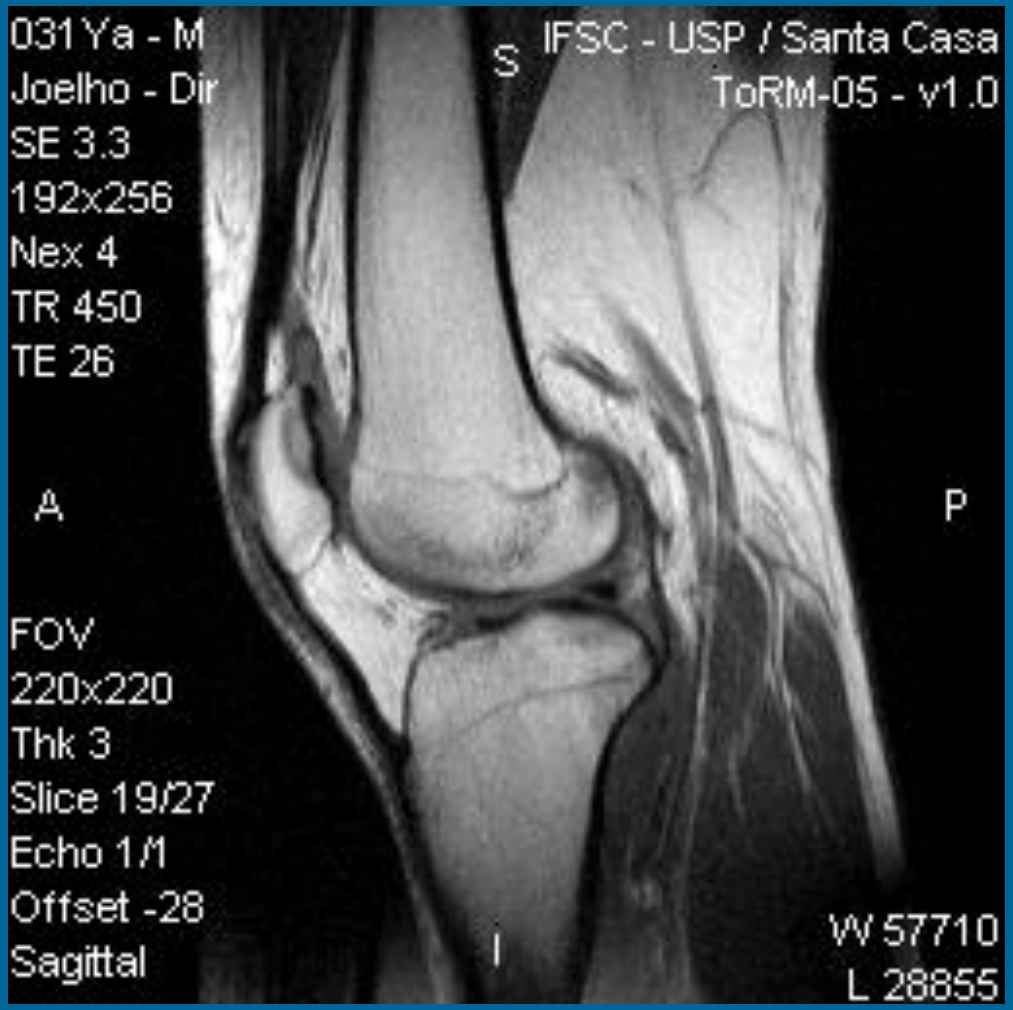


Métodos: saturação/recuperação; inversão/recuperação; spin-eco

Exemplo de contraste por T_1

http://mri.if.sc.usp.br

Exemplo de contraste por T_1



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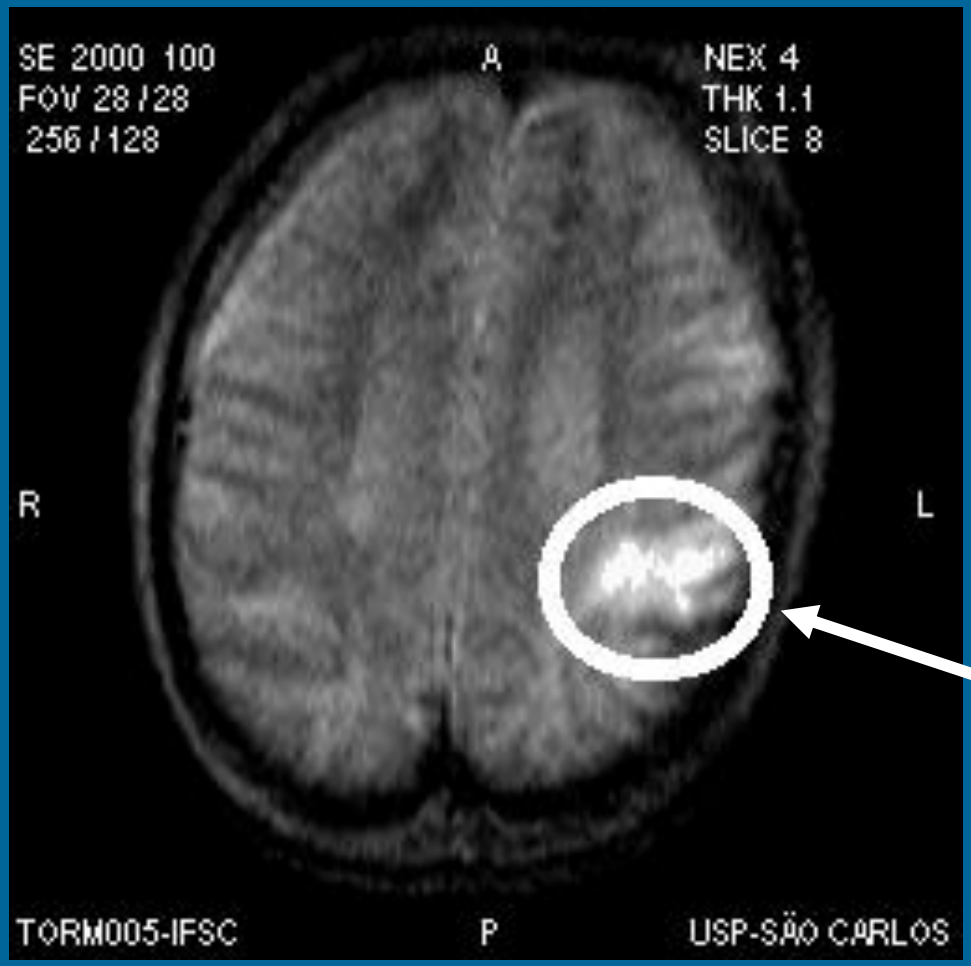
Exemplo de contraste por T_2



(corte transversal)

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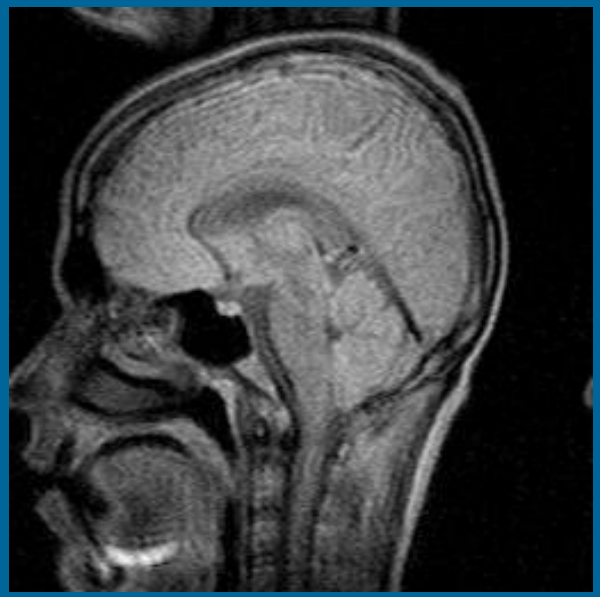
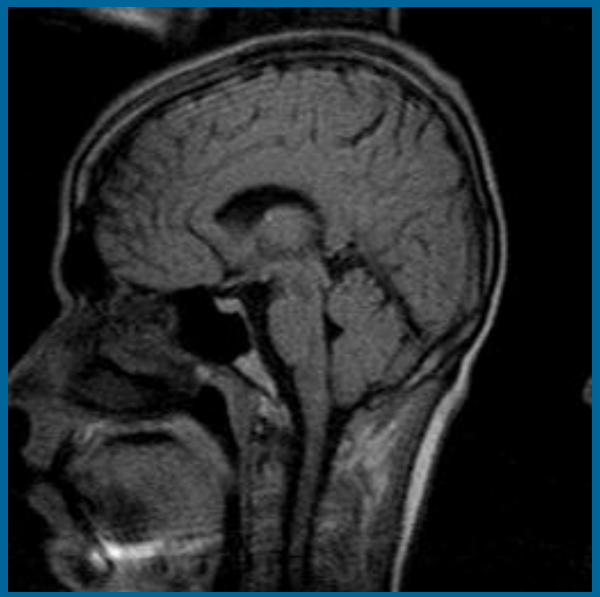
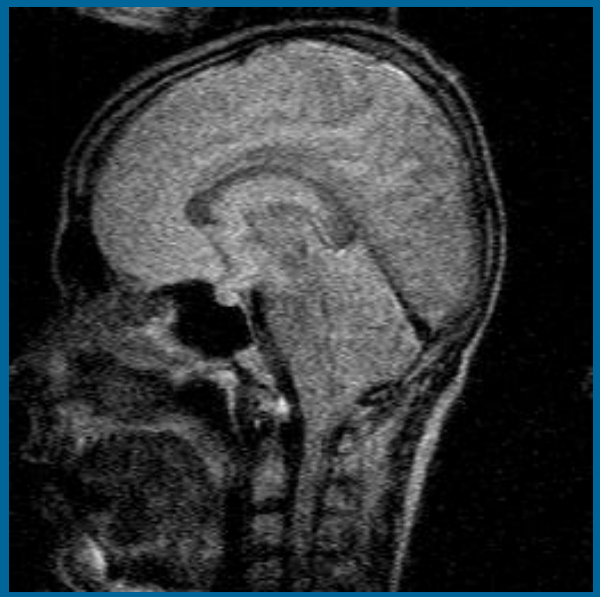
Comparação entre diferentes contrastes

Densidade T_1 T_2

http://mri.if.sc.usp.br

MRI aplicada ao estudo de fármacos

Visualising Tablet Dissolution

Measurement of Hydration and Drug Release

Reprint from G.I.T. Laboratory Journal 9-10/2008, pp 42–43, GIT VERLAG GmbH & Co. KG, Darmstadt, Germany, www.gitverlag.com

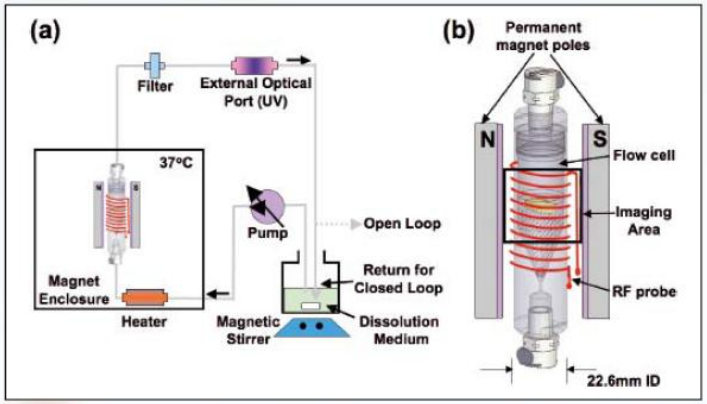


Fig. 1: (a) Schematic diagram of the PharmaSense, low field Magnetic Resonance Imager combined with USP 4 apparatus, and (b) expanded view inside magnet enclosure

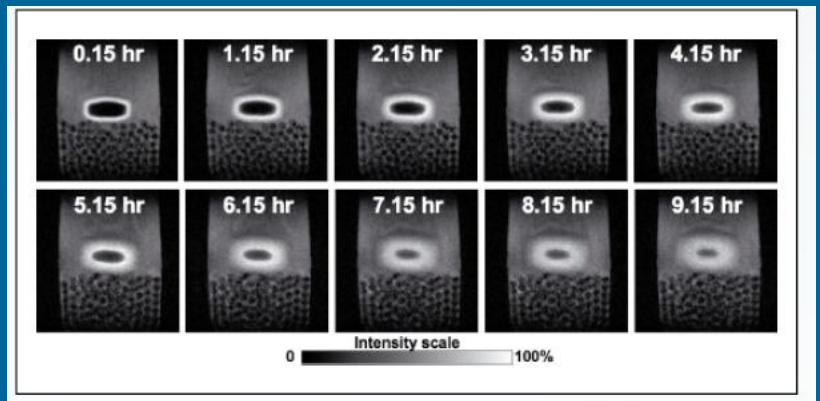
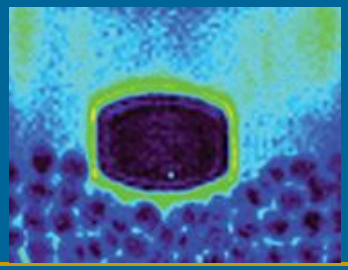
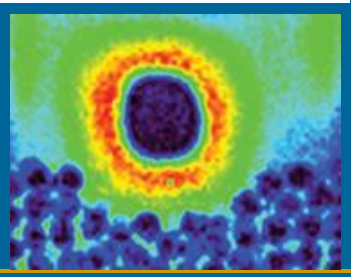


Fig. 2: A set of images acquired during dissolution of a Chlorpheniramine Maleate, USP standard tablet in water flowing at 16 ml/min at 37°C in a closed loop configuration. Time stated is the start of a 4.3 min scan. 250 µm isometric pixel resolution and 3 mm slice (Other image parameters: 12 ms echo time, 1 s repetition time and 2 averages).

Oxford Instruments Molecular Biotools Ltd. (OIMBL)
Tubney Woods, Abingdon, Oxon OX13 5QX
Tel: +44 (0) 1865 393 200
Fax: +44 (0) 1865 393 333
E-mail: molecularbiotools@oxinst.com
www.oxford-instruments.com





Aplicações ao estudo de alimentos

- Presença de poros em queijos.
- Determinação da fração cristalina em margarinas.
- Existência de defeitos em frutas e legumes.
- Difusão e retenção de água em géis (especialmente em leites e derivados).
- Processos de transformação em produtos alimentares (fritura, congelamento, etc.).
- Determinação de teores de gordura em sementes, carnes, etc.

RMN aplicada ao estudo de alimentos

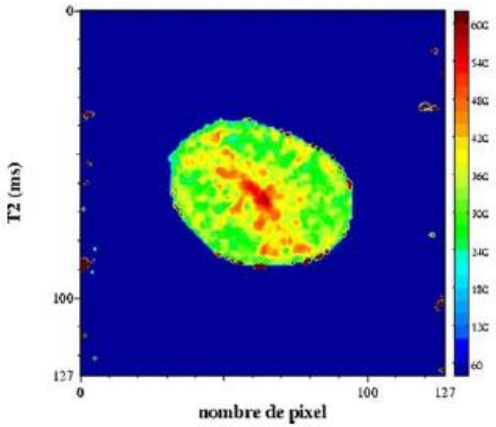


Fig. 9. Cartographie T_2 d'une pomme de terre crue. Séquence multi-écho $n \times T_E = 17$, nombre d'échos, $n = 24$, $T_R = 1500$ ms, acquise à 0,2 T (Magnetom Open, Siemens). L'épaisseur de coupe était de 3 mm et la résolution de 1,2 mm [50].

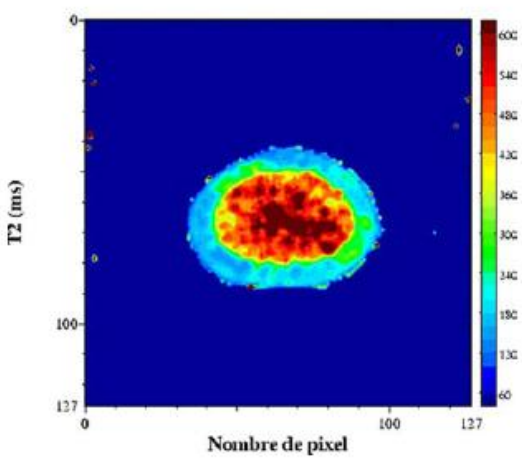


Fig. 10. Cartographie T_2 d'une pomme de terre frite (1 min). Séquence multi-écho $n \times$ TE = 17, nombre d'échos, n = 24, T_R = 1500 ms). L'épaisseur de coupe était de 3 mm et la résolution de 1,2 mm [50].

Tableau 2
Temps de relaxation (ms) et amplitude (%) calculés à partir de la courbe de relaxation spin–spin d'une pomme de terre crue [50]. Les écarts types sont calculés avec cinq répétitions

Composante de relaxation	T_{2i} (ms)	A_i (%)
Eau dans le grain d'amidon	4 ± 1	12 ± 4
Eau dans le cytoplasme	184 ± 32	27 ± 13
Eau dans la vacuole	563 ± 51	61 ± 17

F. Mariette / C. R. Chimie 7 (2004) 221–232

RMN aplicada ao estudo de alimentos

Um novo método de Ressonância Magnética Nuclear para análise da gordura intramuscular de carne bovina

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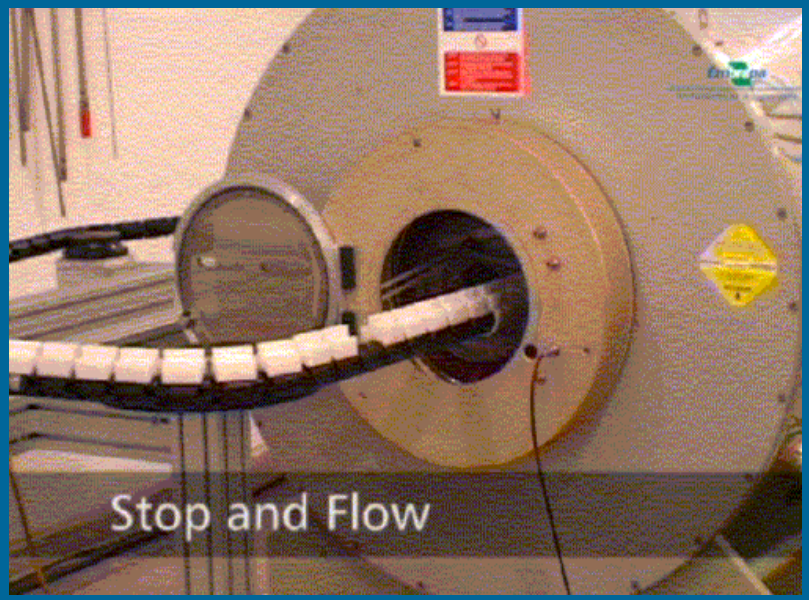

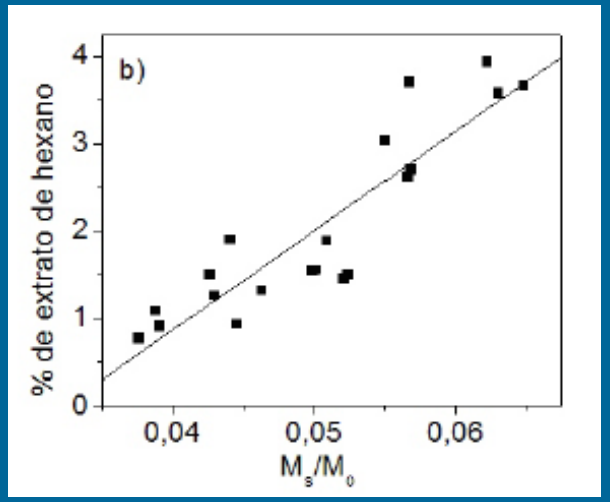

O CWFP permite analisar cerca de 20 amostras embaladas (~ 1kg) separadas por 20 cm em aproximadamente 1 minuto. Isso representa um potencial para se analisar mais de 1000 amostras por hora.

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Determination of Oil and Moisture Content in Fish Feed

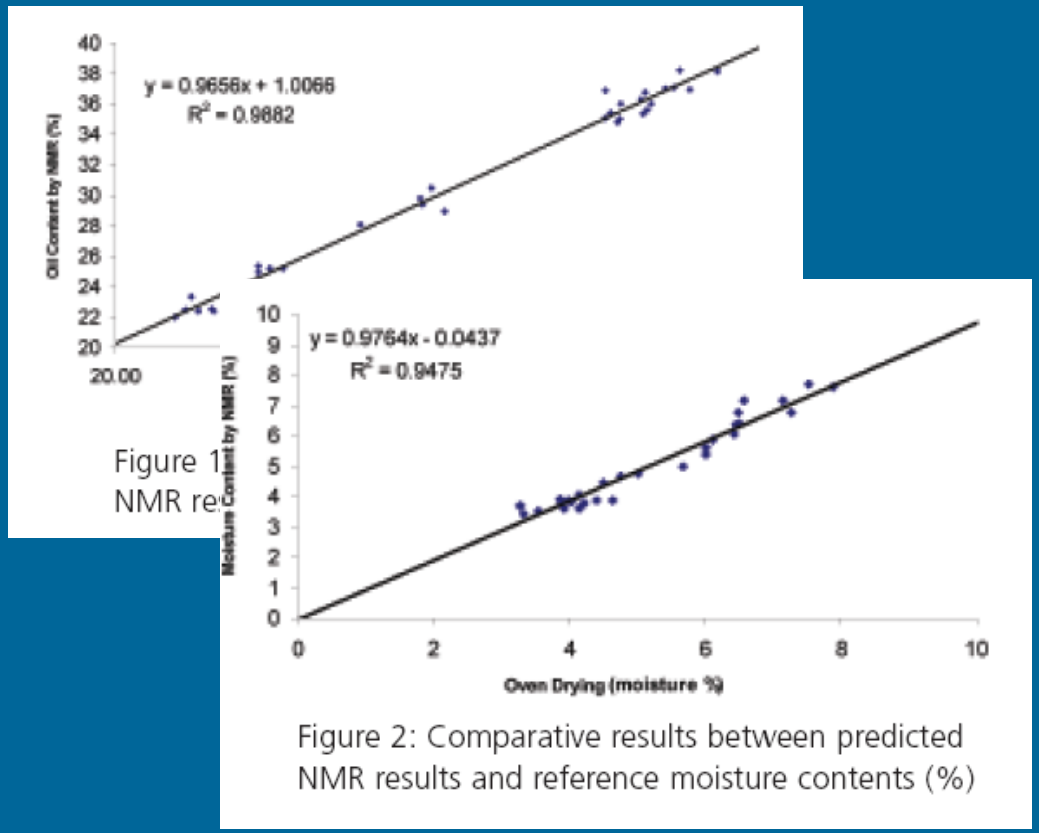

Figure 1
NMR re

Figure 2: Comparative results between predicted NMR results and reference moisture contents (%)

Application Note 4

OXFORD INSTRUMENTS

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