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PROCESSING OF TIME DOMAIN NMR SIGNALS WITH FILTER AND KRYLOV DIAGONALIZATION METHODS

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Abstract: Time-Domain Nuclear Magnetic Resonance (TD-NMR) has been used in non-destructive and non-invasive analysis of agri-food products. In these measurements, the multiexponential relaxation times T_1 and T_2 are commonly used, often analyzed through uni- or multivariate methods. The univariate analyses are simple and requires less data than the multivariate ones but it demands the decomposition of the multiexponential signals in the relaxation times values and respective amplitudes. This is an ill-posed problem as it is extremely susceptive to small variation in signal to noise ratio. In the last three decades several algorithms have been proposed to minimize this error and they are generalized known as Inverse Laplace Transform (ILT). Here we are evaluating the use of the Filter Diagonalization Method (FDM) and the Krylov Basis Diagonalization Method (KBDM) as alternative methods. These methods have been applied to simulated signals, varying the number of exponentials, amplitudes, signal-to-noise ratio, and other parameters. The results shows that both methods present similar results to the ones obtained with ILT algorithms even when the data is processed without any regularization procedure.

Keywords: TD-NMR, signal processing, ILT, FDM, KBDM.

PROCESSAMENTO DE SINAIS DE RMN NO DOMÍNIO DO TEMPO USANDO OS MÉTODOS DE DIAGONALIZAÇÃO FILTRADA E DE KRILOV

Resumo: A Ressonância Magnética Nuclear no Domínio do Tempo (RMN-TD) tem sido utilizada em análises não destrutivas e não invasivas de produtos agroalimentares. Os tempos de relaxação multiexponencial T_1 e T_2 da amostra são amplamente utilizados nessas análises, utilizando análises uni e multivariadas. A análise univariada é simples e requer menos dados do que a multivariada, mas exige a decomposição dos sinais multiexponenciais nos valores dos tempos de relaxação e respectivas amplitudes. Este processo é um problema mal posto, pois é extremamente suscetível a pequenas variações na relação sinal-ruído. Nas últimas três décadas, vários algoritmos foram propostos para minimizar esse erro e são generalizados, conhecidos como Transformada de Laplace Inversa (ILT). Aqui, estamos avaliando o uso do Método de Diagonalização de Diagonalização Filtrada (FDM) e do Método de Diagonalização da Base de Krylov (KBDM) como uma alternativa aos métodos atuais. Esses métodos foram aplicados a sinais simulados, variando o número de exponenciais, amplitudes, relação sinal-ruído e outros fatores. Os resultados mostram que ambos os métodos apresentam resultados semelhantes aos obtidos com algoritmos ILT mesmo quando os dados são processados

sem nenhum procedimento de regularização

Palavras-chave: RMN-DT, processamento de sinais, ILT, FDM, KBDM.

1. Introduction

Nuclear Magnetic Resonance (NMR) has been widely employed as an analytical technique, with applications ranging from the analysis of molecular structure and dynamics to the generation of images of living organisms, such as those used in medical imaging. In chemical analyses, NMR is applied through spectroscopy, which is divided into two main approaches: High-Resolution Nuclear Magnetic Resonance Spectroscopy and Time-Domain NMR (TD-NMR) (Nordon et al., 2001).

The initial applications of TD-NMR, in the late 1960s, were in industrial quality control, where quantitative analyses of one or two components were performed using the signal intensities from the Free Induction Decay (FID), spin echo, or both (Nordon et al., 2001). Over the past three decades, TD-NMR analyses have evolved to determine longitudinal (T_1) and transverse (T_2) relaxation times, which has significantly expanded the range of applications of the technique, enabling the extraction of new information about various physical and chemical properties of materials (Azeredo et al., 2000; Corrêa et al., 2009). A common issue encountered in relaxation analyses involving multiexponential decay is the determination of the relaxation times (time constants of the exponentials, T_1 or T_2) and their respective amplitudes when two or more components are present. This occurs because it is an ill-posed mathematical problem, meaning that there is no unique exact solution. The first methods used to determine T_1 were based on discrete multiexponential fitting, where the signal is fitted with up to three discrete exponentials (a number defined by the operator). A solution that has been increasingly adopted in recent years, including for multidimensional signal processing, is the method known as the Inverse Laplace Transform (ILT) (Gil & Geraldes, 1987).

One of the advantages of the ILT is that it does not require prior knowledge of the number of exponentials to be fitted and provides a continuous distribution signal, a spectrum of relaxation times, sometimes referred to as a relaxogram. However, since it is an ill-posed problem that is highly sensitive to signal-to-noise ratio, signal offset, and other parameters, the processing requires regularization parameters to achieve an acceptable result. Therefore, this work evaluates signal processing methods for relaxation, data based on the Krylov Basis Diagonalization Method (KBDM) and Filter Diagonalization Method (FDM) (Moraes, 2021). Precision, accuracy, and other parameters were assessed using both simulated and experimental signals with varying numbers of exponentials, amplitudes, signal-to-noise ratios, and other conditions. The aim is to determine the advantages and limitations of each method (FDM and KBDM) compared to conventional approaches such as discrete exponential fitting and the ILT.

2. Materials and Methods

Initially, theoretical CPMG signals were simulated using a MATLAB routine developed in MATLAB software version R2015a. The generated data were based on a log-normal distribution of exponential decays, following the methodology described in (Moraes, 2021). Signals were simulated with various decay constants, amplitudes, and different noise levels in the order of magnitude of samples of biological materials and food.

Discrete fitting of the decay curves from both simulated and experimental CPMG signals was performed using Origin 8.5 software, applying mono-, bi-, and tri-exponential functions.

The decay curves of both experimental and simulated CPMG signals were also processed using an Inverse Laplace Transform (ILT) routine developed in Python, which incorporates Tikhonov regularization, and was implemented within the Origin 8.5 software according to (Moraes, 2021).Data processing using the FDM method was performed in Origin 8.5 software using a routine developed by Prof. Claudio José Magon from the Institute of Physics of São Carlos – University of São Paulo (IFSC–USP), as described in (Magon, 2007; Maria et al., 2012; Moraes, 2021).

3. Results and Discussion

Simulated decay curves with signals containing three T_2 components were analyzed. The results from the tri-exponential discrete fitting, ILT, and FDM processing of simulated CPMG signals with three T_2 components - 100, 300, and 500 ms, with amplitudes of 1:2:1, respectively—and with 0%, 1%, 2%, and 5% white noise are shown in Table 1. Figure 1 displays the CPMG signals and the ILT results for the simulated signals with three components.

Table 1: Results of the tri-exponential discrete fitting, ILT, FDM, and KBDM methods applied to a simulated CPMG signal containing three T_2 components of 100, 300, and 500 ms with amplitudes of 1:2:1, respectively, and white noise levels of 0%, 1%, 2%, and 5%.

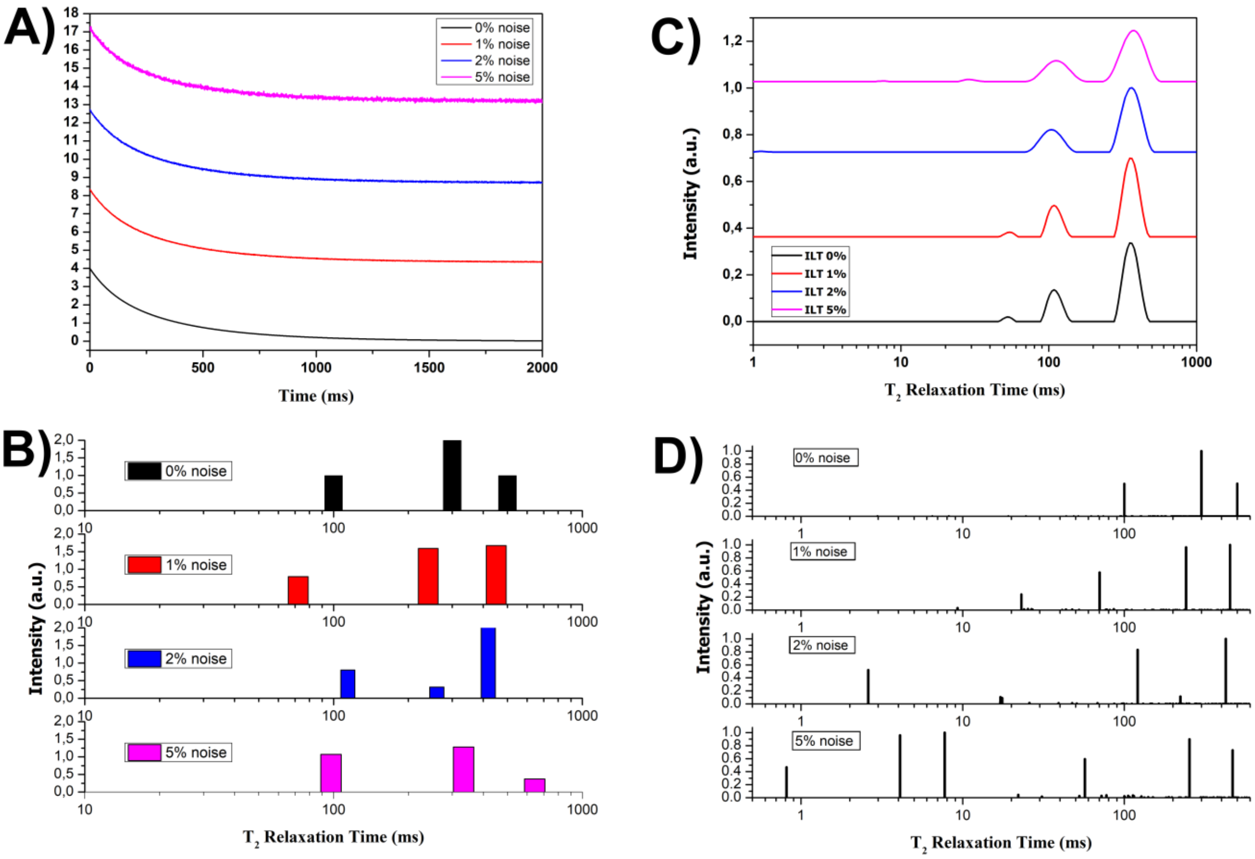
% of noise	tri-exponencial fitting		ILT		FDM		KBDM	
	T_2 (ms)	Area	T_2 (ms)	Area	T_2 (ms)	Area	T_2 (ms)	Area
0%	99.99±2.00	0.99	109.41±2.19	0.36	100.00±2.00	0.99	101.01±2.02	0.50
	299.76±5.99	1.99	359.59±7.19	1	300.01±6.00	1.99	298.55±5.97	1.00
	499.49±9.99	1.00			500.02±10.00	0.99	501.06±10.02	0.50
1%	99.84±1.99	0.99	109.46±2.19	0.35	72.12±1.44	0.79	70.03±1.40	0.58
	299.16±5.98	2.00	-	-	240.15±4.80	1.59	241.51±4.83	0.96
	502.90±10.06	1.00	359.66±7.19	1	450.83±9.02	1.67	455.01±9.10	1.00
2%	97.76±1.96	0.97	104.13±2.08	0.38	114.16±2.28	0.80	120.30±2.41	0.84
	303.43±6.07	2.16	-	-	260.11±5.20	0.32	-	-
	518.54 ± 10.37	0.86	362.05±7.24	1	418.74±8.37	2.29	437.47±8.75	1.00
5%	131.43 ± 2.63	1.30	112.35±2.25	0.42	97.61±1.95	1.07	-	-
	-	-	-	-	333.12±6.66	1.28	-	-
	392.46±7.85	2.55	372.04±7.44	1	643.5512.87	0.37	-	-

As can be observed, the ability to obtain accurate values decreases as the complexity of the signals and the noise level increase. Using tri-exponential fitting, CPMG signals with three components yield values very close to the simulated ones in the absence of noise. However, with the introduction of noise, the accuracy of the fits—both for T_2 values and their respective amplitudes—gradually decreases. With 5% noise, the tri-exponential fitting did not converge, resulting in the detection of only two T_2 components. Similarly, ILT produced highly inaccurate results for both T_2 values and their corresponding amplitudes under noisy conditions.

In contrast, the processing of CPMG signals with three components using the FDM method delivered the best results. In the absence of noise, both T_2 values and areas were highly accurate. From 1% noise onwards, the method exhibited increasing errors proportional to the noise level; however, it still performed better than the other two methods under all conditions.

Using the KBDM technique, values close to the expected ones can be observed when the signal has low noise; however, with 5% noise, it is not possible to obtain accurate results. In this technique, it is also noticeable that the area of each signal does not closely match the expected response of the actual signal.

Figure 1: Comparison of the results obtained using different CPMG signal processing methods. A) CPMG signal; B) result obtained using the ILT technique; C) result obtained using the FDM technique; D) result obtained using the KBDM technique.



4. Conclusions

In general, the processing of CPMG signals with up to three components without noise yields satisfactory results using the methods described above. However, these methods still present limitations when the signal contains more than three components or has a high noise level.

The multi-exponential fitting tool available in Origin 8.5 produces reliable and satisfactory results for signals with up to three components and low noise levels. However, it does not perform well for signals with more than three components or with high noise levels (above 5%).

The ILT method, on the other hand, shows larger errors compared to the other methods. Nevertheless, it has the significant advantage of being applicable to unknown samples, where the number of components is not known in advance. ILT can achieve greater precision under these conditions and enables the generation of relaxation time distribution

spectra, which expands the possibilities for analyzing these types of signals.
The FDM and KBDM techniques yield good results for exponential signals with low noise levels and offer a significant advantage when no prior information about the sample is available. This is because the outcomes obtained using these techniques are not influenced by analyst intervention in parameter selection during signal processing. However, the KBDM technique has the drawback of requiring a longer processing time to generate results.

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