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# Application of trilinear SLICING to analyse a single relaxation curve

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**Abstract**

Determining the time constants and amplitudes of exponential decays from relaxation data is a common task in LF-NMR. In this communication, we present an application of the SLICING algorithm to evaluate its possibilities for solving this problem. The method, originally introduced to compare different samples, is applied here to analyse a single relaxation curve, using the embedding technique. To test this procedure, we acquired data sets from samples of liquids properly separated, and characterized by different relaxation times. The results show a good estimation of parameters, comparable with those obtained applying Marquardt's algorithm, when the components have sufficiently different relaxation times.


*Keywords:* SLICING; LF-NMR; Exponential decay; Curve fitting; Transverse relaxation time $T_2$

## 1. Introduction

The transversal relaxation time data obtained by low field nuclear magnetic resonance (LF-NMR) are elaborated traditionally by multiexponential fitting, but, often, problems such as ill-conditioning, and local minima are found. SLICING [1] is a procedure, based on a particular class of multidimensional analysis, called multi-way analysis, recently proposed to compare and classify different samples, analysing directly the relaxation curves [2,3].

In this article, as an alternative to classic multiexponential fitting, we evaluate the possibilities of SLICING to estimate the relaxation times of the different components, taking into account a single sample each time. In particular, we intend to verify the method applicability limits in comparison to those of Marquardt's algorithm [4].

SLICING for this purpose is possible by the use of an embedding procedure, which we have previously used in the analysis of temporal series by other algorithms, such as recurrence analysis [5,6]. By this procedure a bidimensional array can be built starting from a monodimensional temporal series.

In practice, the embedding space is constructed by the method of delays [7]: the space is generated by the construction of a multivariate matrix having as rows the original series shifted by a fixed lag consecutively applied to the series. The embedding dimension equals the number of rows of the matrix. Example: given the series: 10, 11, 21, 32, 41, ... the corresponding three-dimensional embedding space at lag = 1 is:

| | | | | | |
|---|---|---|---|---|---|
| 10 | 11 | 21 | 32 | 41 | ... |
| 11 | 21 | 32 | 41 | ... | ... |
| 21 | 32 | 41 | ... | ... | ... |

In our case, we used a dimension of embedding equal to 3, greater than the number of expected components.

In the context of nonstationarity (relaxation), the notion of a "correct" embedding, or delay is inappropriate. Instead, it becomes important to remember that a sufficiently large embedding be chosen which will "contain" the relevant dynamics (as it may change from one dimension to another) as well as account for the effects of noise, which tend to inflate dimension. There are no clear guidelines relative to this question, except from what can be inferred from studies of noise. In this

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respect, investigators have indicated that noise will tend to require higher dimensions, even in the case of stationary dynamics. Given that the actual relaxation occurs in a three-dimensional space, an embedding of three was chosen. Embedding higher than this serves only to amplify noise.

Choice of lag is governed by similar considerations. As a system changes from one dimension to another the effects of the lag are perforce changed. Thus, a so-called "optimal" lag in one embedding, becomes less so as the relevant dimension changes. Although there have been numerous proposals for choice of lag, chief among them the first local minimum of the autocorrelation or mutual information, they all are presented with the assumption of stationarity. What would appear to be more important is an understanding of how the data is acquired, as well as the system studied. Because, again, the data are nonstationary and nonlinear, resorting to autocorrelations is questionable given its basis in linear theory. Choice of a lag of one suffices according to theory, and standardizes the procedure [8].

Relative to how SLICING works we refer to the original article, recently published on this journal [1]. The SLICING method can give different results depending on the meta-parameters lag and slab used in the fit. (Note that the SLICING "lag" is different from the one used to embed the original data). Concerning this, in a recent article Engelsen and Bro suggest an optimization of the parameters' values and called this particular procedure PowerSlicing (contained in the library used for these calculations) [9]. In this case, the SLICING lag does not have a constant value, but is lag $= 2^x$, with $x = 1,2,\ldots,N$, where $N$ has a value such that $2^N \leqslant J/2$, where $J$ is the number of bins on the time axis. With regard to the value of the slab parameter, PowerSlicing takes always a number as high as possible. The authors report that this particular form of the SLICING procedure provides the most accurate $T_2$-estimates for both theoretical and experimental data and recommend its use [9]. In our particular case $N = 11$, so we have a slab of 12.

The samples are characterized by two classes of water different for their transversal relaxation times, $T_2$. Changing the paramagnetic ion concentration difference, we verified that the relaxation time values of the two components, obtained by Marquardt's algorithm or SLICING procedure, are consistent with those measured separately.

As a first step, we measured the four copper sulphate solutions one at a time. In Table 1 the intensity values, arbitrary units (a.u.), and the transversal relaxation times, ms, obtained by the analysis of the data with the two methods, are reported. The intensities of the different components, in the case of the SLICING procedure, are obtained multiplying the score value of the component by the first point of the corresponding loading vector. For each sample, the model error, squared sum of errors (SSE), has been calculated according to the equation:

Table 1
$T_2$ fit parameters for the four copper sulphate solutions[a]

| | $I$ (a.u.) | $T_2$ (ms) | Model error |
|---|---|---|---|
| Solution 1 ($CuSO_4$, 27 mM) | | | |
| Marquardt | $82.19 \pm 0.03$ | $55.90 \pm 0.03$ | — |
| Slicing | 78.79 | 55.92 | 10.30 |
| Solution 2 ($CuSO_4$, 60 mM) | | | |
| Marquardt | $68.82 \pm 0.04$ | $28.65 \pm 0.03$ | — |
| Slicing | 64.07 | 28.17 | 8.60 |
| Solution 3 ($CuSO_4$, 5.5 mM) | | | |
| Marquardt | $95.55 \pm 0.04$ | $188.1 \pm 0.1$ | — |
| Slicing | 94.2829 | 191.09 | 24.70 |
| Solution 4 ($CuSO_4$, 0.49 mM) | | | |
| Marquardt | $74.06 \pm 0.03$ | $399.8 \pm 0.2$ | — |
| Slicing | 73.7376 | 402.5665 | 25.07290 |

[a] Intensity values, measured in arbitrary units (a.u.), and transversal relaxation times, in ms, obtained by the analysis of the data with Marquardt's algorithm [4], and by the SLICING procedure (PowerSlicing [9]). For SLICING the model error is calculated by Eq. (1), the fitted parameters obtained by Marquardt's algorithm are reported $\pm$ SE.

$$\mathrm{SSE} = ||X - T^* P^T||_F^2, \tag{1}$$

where $X$ is the data matrix, $T$ and $P$ contain, respectively the scores, and the loading vectors obtained by SLICING and F implies the Frobenius norm [1].

Subsequently, we performed the measures on samples containing combined solutions. In Figs. 1A, 2A and 3A the plots of the relaxation curves of the transversal magnetization vs. time are reported for the samples containing, respectively the copper sulphate solutions, 1–2, 1–3, and 1–4.

In Figs. 1B, 2B, and 3B the plots of the loading vectors, associated with the three factors obtained by the SLICING procedure, vs. time are reported. Note that the three curves are exponential, with one of these characterized by a very long relaxation time, and indicates a constant offset.

In Figs. 1C, 2C, and 3C the plots of the residuals, associated with the SLICING procedure, vs. time are reported. Note that these curves are centred on an offset.

In Tables 2–4 the intensity values, arbitrary units (a.u.), and the transversal relaxation times, ms, obtained by the analysis of the data with the two methods, are reported with respect to the measures made on the samples containing, respectively the copper sulphate solutions, 1–2, 1–3, and 1–4.

As can be noted from the tables, the results show a good agreement among the relaxation parameters values obtained by the two different approaches. It can be further noted, however, that for the samples containing the copper sulphate solutions 1–2 and 1–3, the relaxa-

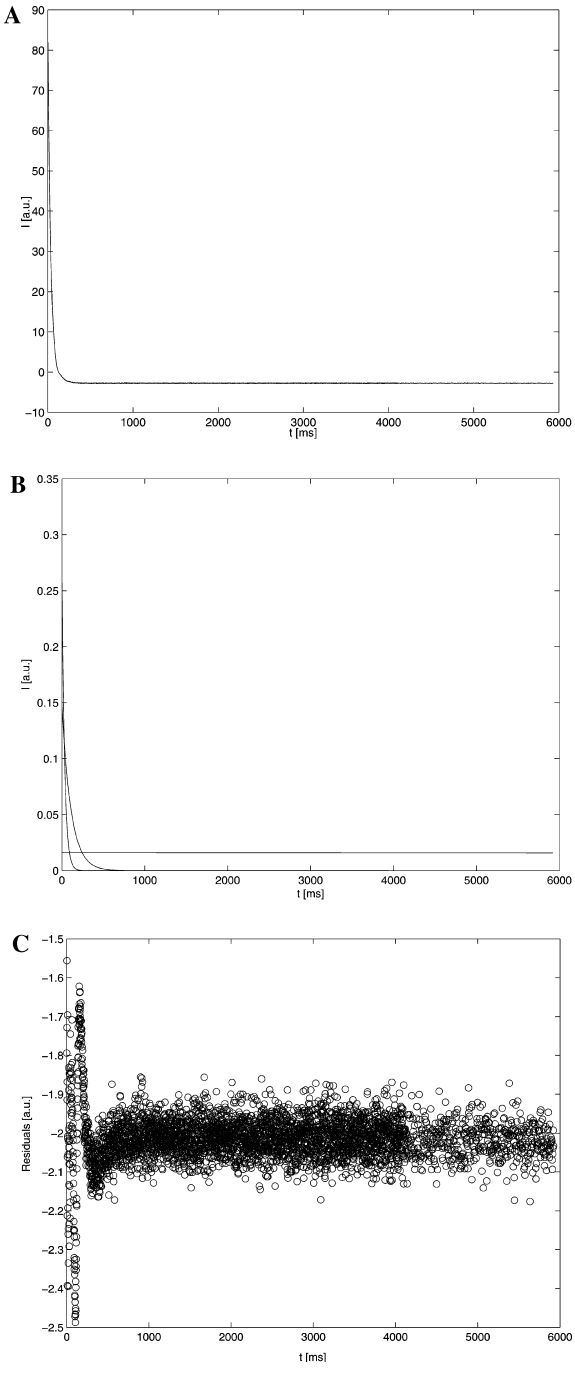


Fig. 1. (A) Plot of the relaxation curves of the transversal magnetization vs. time, for the samples containing the copper sulphate solutions 1–2. (B) Plots of loading vectors, associated to the three factors obtained by the SLICING procedure, vs. time. (C) Plots of the residuals, associated with the SLICING procedure, vs. time. Note that these curves are centred on an offset.

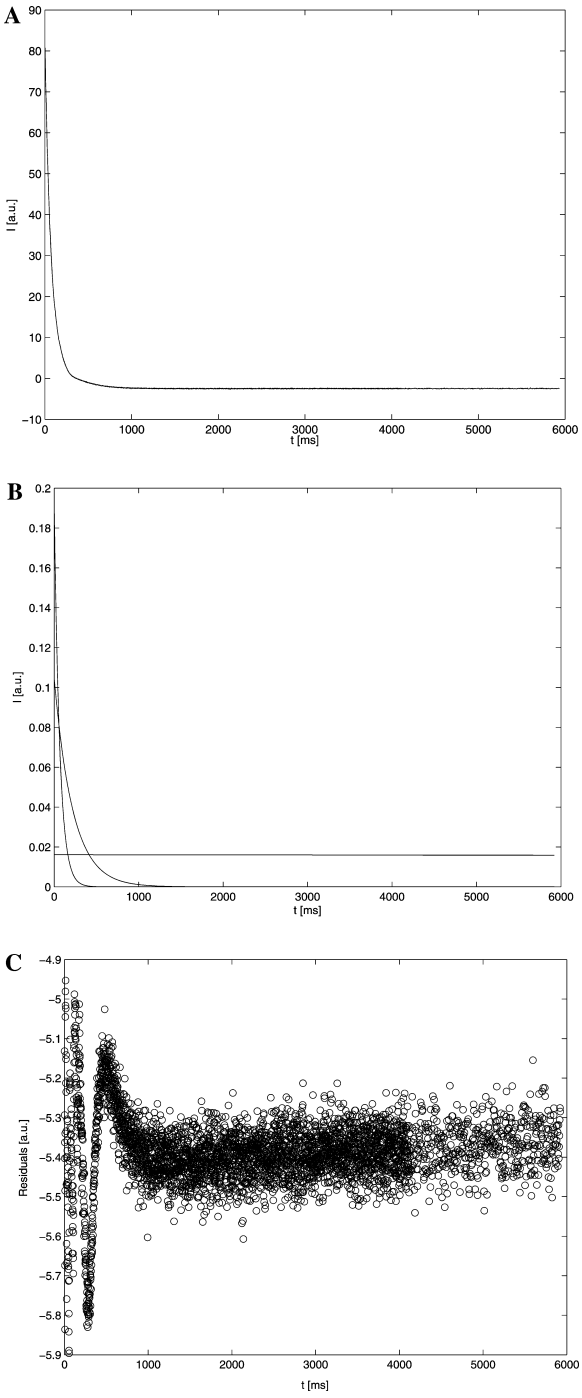


Fig. 2. (A) Plot of the relaxation curves of the transversal magnetization vs. time, for the samples containing the copper sulphate solutions 1–3. (B) Plots of loading vectors, associated with the three factors obtained by the SLICING procedure, vs. time. (C) Plots of the residuals, associated with the SLICING procedure, vs. time. Note that these curves are centred on an offset.

tion time values are different from those of the solutions analysed one at a time, while for the samples containing the solutions 1–4, there is a good agreement with the relaxation time values obtained for the same solutions singularly analysed. These results reassert the importance of a minimum difference among the $T_2$ values in order to achieve a separation of the different components that contribute to the signal [10].

This difference clearly changes with the variation of the signal to noise ratio. For example, in the case of simulated samples reported by Engelsen and Bro [9], the

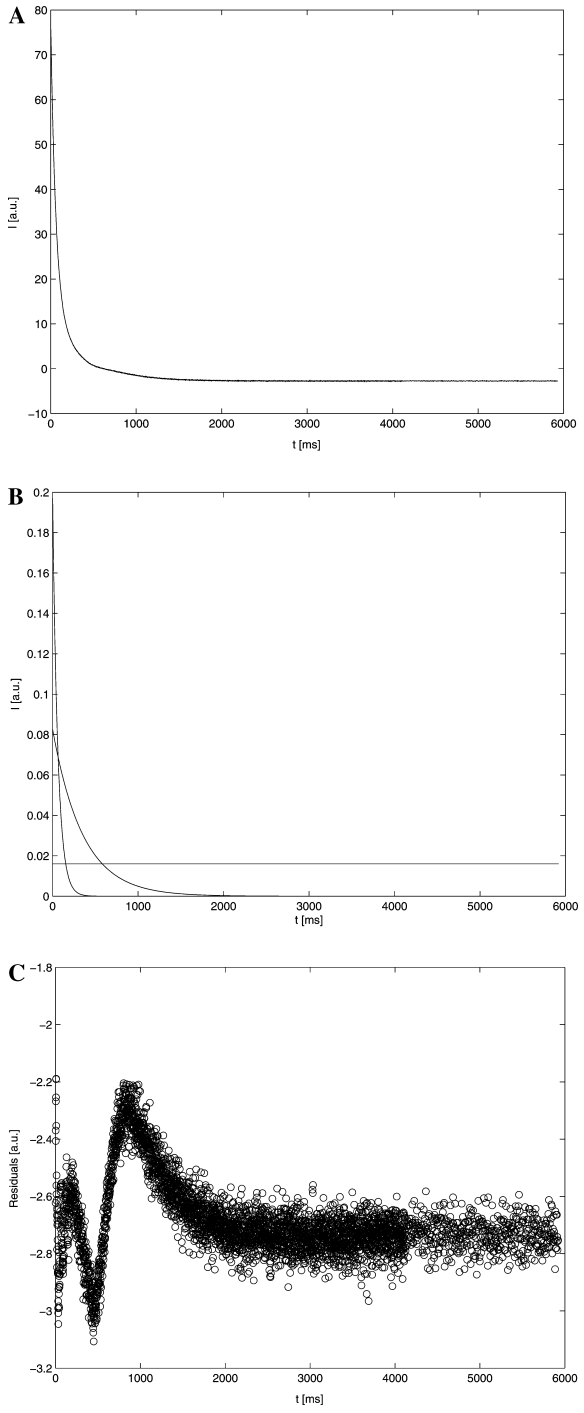


Fig. 3. (A) Plot of the relaxation curves of the transversal magnetization vs. time, for the samples containing the copper sulphate solutions 1–4. (B) Plots of loading vectors, associated to the three factors obtained by the SLICING procedure, vs. time. (C) Plots of the residuals, associated with the SLICING procedure, vs. time. Note that these curves are centred on an offset.

signal to noise ratio was 0.5% and they managed to separate the different components, even with an order of magnitude closer than one.

In conclusion, the SLICING procedure appears as an alternative to Marquardt's algorithm, when there is the suspicion that the intrinsic limits of the multiexponential fitting [10,11] have questioned the analysis results. We recall, in fact, that SLICING describes the relaxation curves with independent vectors, in a way that excludes the high correlation among the fitting parameters of the different components, obtained by Marquardt's algorithm. This is an important consideration, in that independence obviates at least some of the traditional problems associated with Marquardt's algorithm. Clearly, further evaluation is necessary.

Table 2
$T_2$ fit parameters for the sample of solutions 1–2

| | $I$ (a.u.) | $T_{2,1}$ (ms) | $I$ (a.u.) | $T_{2,2}$ (ms) | Model error |
|---|---|---|---|---|---|
| Marquardt | $86.9 \pm 0.1$ | $31.94 \pm 0.05$ | $4.2 \pm 0.1$ | $103 \pm 1$ | — |
| Slicing | 81.0184 | 32.33 | 3.4 | 109 | 7.25 |

Table 3
$T_2$ fit parameters for the sample of solutions 1–3

| | $I$ (a.u.) | $T_{2,1}$ (ms) | $I$ (a.u.) | $T_{2,2}$ (ms) | Model error |
|---|---|---|---|---|---|
| Marquardt | $76.21 \pm 0.09$ | $67.12 \pm 0.09$ | $9.33 \pm 0.09$ | $251 \pm 2$ | — |
| Slicing | 71.61 | 65.39 | 11.33 | 220 | 10.09 |

Table 4
$T_2$ fit parameters for the sample of solutions 1–4

| | $I$ (a.u.) | $T_{2,1}$ (ms) | $I$ (a.u.) | $T_{2,2}$ (ms) | Model error |
|---|---|---|---|---|---|
| Marquardt | $67.57 \pm 0.04$ | $63.79 \pm 0.08$ | $12.96 \pm 0.04$ | $407 \pm 1$ | — |
| Slicing | 63.38 | 61.18 | 14.87 | 354 | 15.30 |

## 2. Experimental

We chose to make the LF-NMR measures on concentric tubes (a 5 mm NMR tube put in a 10 mm NMR tube) containing copper sulphate solutions with known concentrations.

All measures were made using a NMS 120 Minispec (Bruker BioSpin S.r.l. Italy), operating at 20 MHz, at a temperature of 40.0 °C $\pm$ 0.1. The relaxation measurements were performed using CPMG sequence [12] ($\tau = 0.30$ ms, 3900 data points and 128 experiments).

For the measurements requiring phase information, quadrature detection was used. For any sample, the detection angle and the magnetic field offset have been adjusted optimally, then the real component was at a maximum and the imaginary component was zero, and only the real component was measured.

We used Marquardt's algorithm [4] to fit the relaxation curves, implemented on the software SigmaPlot 8.0-SPSS Inc.

Concerning the SLICING procedure, we applied it using the library provided by the authors: www.models.kvl.dk/source/lfnmr and was implemented on Matlab v 6.5.0, using the particular option PowerSlicing [9].

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