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^{13}C NMR Molecular dynamic investigation of tropical wood Angelin Pedra (*Hymenolobium paetrum*)

Marta C.J.A. Nogueira[a], Maria Inês B. Tavares[b,*], José de S. Nogueira[c]

[a]*Depto. de Arquitetura e Urbanismo/FAET/UFMT, 78060-900 Cuiabá, MT, Brazil*
[b]*IMA/UFRJ, CT, Cid. University, Ilha do Fundao, Rio de Janeiro, RJ CP 68525, Brazil*
[c]*Depto de Física/ICET/UFMT, Cuiabá, Mato Grosso, Brazil*

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Abstract

Time has shown wood as a very important material in several areas related to civil construction. Because of its organic origin, wood presents different physical and mechanical properties for different species. In consequence of these variations, there is the necessity to study chemical composition and molecular dynamic to better understand its property that will promote the use in civil construction. The focus of this work is to evaluate the Angelin Pedra wood in relation to the main chemical components, the domain type and the chemical components that constitute these domains. Solid state nuclear magnetic resonance (NMR) will be used for that, since the main advantage of NMR comparing to other techniques specially for the sample in question, is the potential of this spectroscopy to provide analysis of all functional group without pre-treatment of the sample. Some solid state NMR techniques were used and it was observed that the wood in investigation presents different packing, cells arrangements and chains ordination along the fibers in the different parts of the wood, because of the different distribution of the main wood components along the fibers.

Keywords: Wood; ^{13}C NMR; Molecular dynamics

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1. Introduction

The solid state nuclear magnetic resonance has been applied to obtain information on molecular dynamic and structure of complex materials such as wood, for example, because NMR presents a substantial support to study amorphous and heterogeneous materials [1–7]. Knowing that wood can be considered as polymer composite that is basically constituted by cellulose, hemicellulose, lignin and others minor compounds, the ^{13}C solid state NMR techniques can provide several information on this material. Cellulose is the main component of the cellular wall and it is a linear high molecular weight polysaccharide constituted by (D +) anidroglicose, which are linked by itself and glicosidic links like acetol (α 1-4), which generates chains with high polymerization degree. The cellulose chains form inter and intramolecular hydrogen linkage. The intramolecular interactions are responsible for the chain rigidy and the intermolecular interactions are responsible for the vegetal fiber formation [7–10]. Hemicelluloses are branched chains with low molecular masses comparing to cellulose, and are principally constituted by glucose, mannose, galactose, xylose and arabinose. Lignin is constituted by a branched heterogeneous aromatic polymer [7–11]. As it is very well known that wood structure is complex, its characteristics and chemical properties need to be explored. The main objective of this work was to investigate both structural and the molecular dynamic behavior of different regions of Angelim Pedra, *Hymenolobium paetrum*, specie found in the north of Mato Grosso state in Brazil. In this State, a very expressive volume of timber is produced, and chemical investigations are fundamental to generate information that allow us to rationalize the use of timber. This work is dealing with the use of different solid state NMR techniques to generate proper information of different wood regions, which will be considered as a probe to understand the total wood behavior such as: magic angle spinning (MAS),

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[*] Corresponding author. Tel.: +55-21-2562-7225; fax: +55-21-2270-1317.

E-mail address: mibt@ima.ufrj.br (M.I.B. Tavares).

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cross-polarization and magic angle spinning (CPMAS), cross-polarization and magic angle spinning with dipolar dephasing (CPMASDD) [8], variable contact time (VCT) [9], delayed contact time (DCT) [9] and the proton spin-lattice relaxation time parameter ($T_{1\rho}^{H}$) in the rotating frame. The solid state NMR techniques used were chosen because of their characteristics to generate information on molecular structure and dynamics. The MAS technique was applied in special conditions, using a very short recycle delay to detect only the mobile region of each wood region part. The CPMAS was carried out to observe the samples in general, and of course, to detect the main rigid component of each sample. CPMASDD was applied to detect the specific sample components, like carbonyls and not hydrogenated carbons. The VCT will inform on sample heterogeneity and also will give the $T_{1\rho}^{H}$ relaxation time parameter, which is intimately associated with molecular mobility. As VCT detects $T_{1\rho}^{H}$ indirectly by polarization transfer, it is not appropriate for elastomeric samples such as natural rubber. Therefore, for rigid and heterogeneous samples VCT can be used to determine the $T_{1\rho}^{H}$, because for these samples the cross polarization time is much less than relaxation time, $T_{\mathrm{CH}} \ll T_{1\rho}^{H}$. DCT is also used to measure indirectly $T_{1\rho}^{H}$, which enhances the measurement of more mobile samples. However, care needs to be taken with samples that relax very quickly, because the $T_{1\rho}^{H}$ seems to be not uniform for these type of samples.

2. Experimental

Anatomical identification at the macroscopic level was carried out considering the wood patterns presented by Mainieri and Chimell [12] (1989).

Three different wood regions were investigated and they were denominated as 7D—heartwood, 9D—zone of transition between heartwood and sapwood and 12D—sapwood.

Solid state ^{13}C NMR spectra were obtained on a Varian INOVA 300 spectrometer operating at 75.4 MHz for ^{13}C. All solid NMR experiments were done at ambient probe temperature and were performed using gated high decoupling. A zirconium oxide rotor of 7 mm diameter was used to acquire the NMR spectra at a spinning rate of 6.0 kHz. The ^{13}C NMR spectra were carried out in the cross-polarization mode with MAS. For the VCT experiment, a range of contact time was established from 200 to 8,000 μs. Proton $T_{1\rho}$ values were determined from the intensity decay of ^{13}C peaks with increasing contact-times and by DCT experiment, where the range of spin-locking was 200–8000 μs.

3. Results and dicussion

Different solid state techniques were used to generate a map of Angelin wood regions.

The first solid state NMR technique employed was MAS. Fig. 1 shows the ^{13}C MAS NMR spectra of 7D and 9D samples. The ^{13}C spectrum of 7D (considered the total sample) showed signals located at 56.6 and 62.4 ppm derived from $\mathrm{CH_2{-}OH}$, 74.7 ppm derived from CH–OH, which indicates that the heartwood region presents a mobile region and/or amorphous regions, which seems to be constituted by a unordered molecular structure of hemicelluloses with some lignin. The 9D sample presented three broad signals at 56.6, 62.4, 73.2 ppm and a broader signal located at 126.0 ppm, which probably derives from the amorphous part that may be constituted principally by lignin. Focusing the sample 12D a very poor signal at 63.4 ppm was detected, which indicates that this sample seems to be more rigid than the other two.

The second solid state NMR technique used was cross polarization CPMASDD. In this technique only rigid and non hydrogenated carbons can be detected. Fig. 2 exhibits the ^{13}C CPMASDD NMR spectra of 7D, 9D and 12D samples. However, some mobile carbons like methyl and methyl oxide are detected. 7D sample presented two signals located at 72.2 ppm (CH–OH) and 104.7 ppm (C–O–C), which probably come from the rigid domain such as cellulose. 9D sample presented six signals, as this sample showed to be more amorphous than the others, these signals probably comes from the lignin. For 12D sample only two signals located at 55.2 and 153.9 ppm were detected, these signals may be derived from lignin. The CPMASDD results confirmed the first observations obtained by ^{13}C MAS.

Fig. 3 compares the ^{13}C CPMAS NMR spectra of 7D, 9D and 12D samples. The ^{13}C CPMAS NMR spectrum of 7D sample showed twelve signals in the range of 20–180 ppm. The broadening of most signals derived from unordered molecular structure of lignin, hemicelluloses and amorphous cellulose region, which generates one type of domain. However, some sharp signals located at 106.6 ppm (C_1), 90.2 ppm (C_4) and 66.3 ppm (C_6) are derived from ordered cellulose that constituted another domain with different mobility. Sample 9D showed large signals located from 50 to 105 ppm, the broadness of these signals confirm that the sample is amorphous and heterogeneous, which is constituted by a mixture of hemicellulose and lignin. The ^{13}C CPMAS NMR spectrum of 12D sample, showed narrow signals when compared to the others two samples, which are located at 106.9 ppm (C–O–C), 90.2 ppm (CH–OH) from crystalline region, 76.6 (CH–OH), 74.3 (CH–OH) and 66.6 ($\mathrm{CH_2{-}OH}$) and is mainly constituted by hemicellulose and some crystalline cellulose. The CPMAS technique corroborates all results detected by MAS and CPMASDD techniques.

Fig. 4 shows the VCT experiment showed a series of ^{13}C CPMAS spectra decay obtained for the three different wood regions. The samples showed different behaviors for each portion of the wood, which can be partially attributed to the chains arrangements along the samples and partially to the different components compositions. In all case the samples

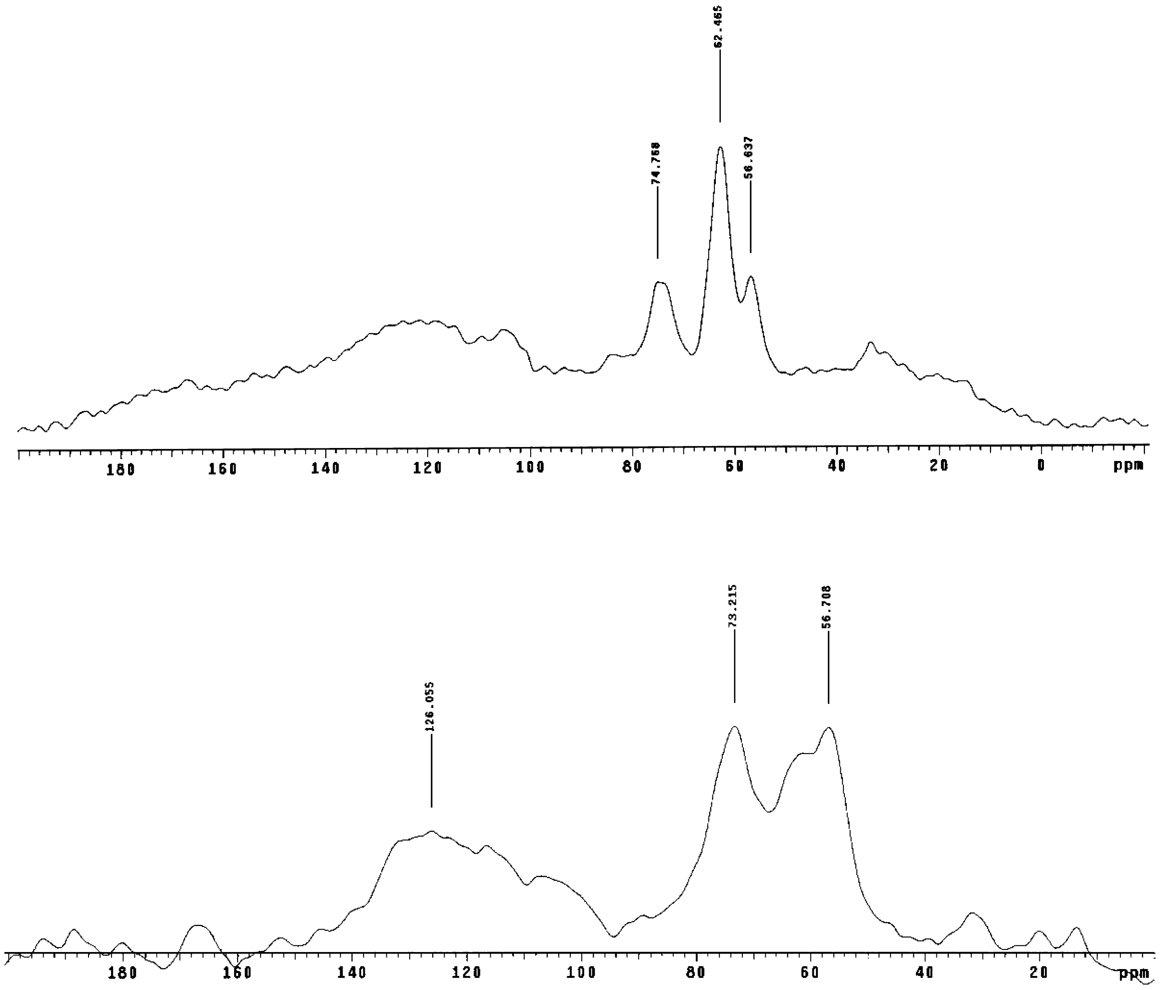

Fig. 1. ^{13}C NMR MAS spectrum of the samples 7D (top) and 9D (bottom).

decay represent a behavior of heterogeneous amorphous material.

From the VCT and also DCT experiment, proton spin-lattice relaxation times in the rotating frame for each resolved carbon were detected. Tables 1–3 show the values of $T_{1\rho}^{H}$ parameter for 7D, 9D, and 12D samples, respectively.

As expected the $T_{1\rho}^{H}$ values are non-uniform, due to the sample nature and its complexity. At least two domains with different molecular mobilities exist, one rich in unordered components dispersed in different ways and one rich in ordained chains. The $T_{1\rho}^{H}$ corroborates with the chemical information extracted by the others NMR techniques used.

For this sample, both techniques used to measure the $T_{1\rho}^{H}$ parameter, showed that it is constituted by different

Table 1
Proton spin-lattice relaxation time in the rotating frame for 7D sample, obtained by variable contact and delayed contact time experiments for all resolved carbon

$T_{1\rho}^{H}$ (ms)			
δ (ppm)	VCT	δ (ppm)	DCT
–	–	154.7	14.2
–	–	134.9	6.3
124.3	2.9	126.7	4.0
105.3	8.7	106.6	5.0
89.0	12.6	90.2	19.7
85.3	9.0	85.2	6.5
75.2	7.0	76.3	9.4
72.6	8.0	73.9	10.2
65.3	8.1	66.3	8.4
56.6	9.4	57.5	11.5
33.0	1.4	34.1	2.1

Table 2
Proton spin-lattice relaxation time in the rotating frame for 9D sample, obtained by variable contact and delayed contact time experiments for all resolved carbon

$T_{1\rho}^{H}$ (ms)			
δ (ppm)	VCT	δ (ppm)	DCT
105.3	11.3	105.3	15.0
73.4	6.2	73.4	27.9

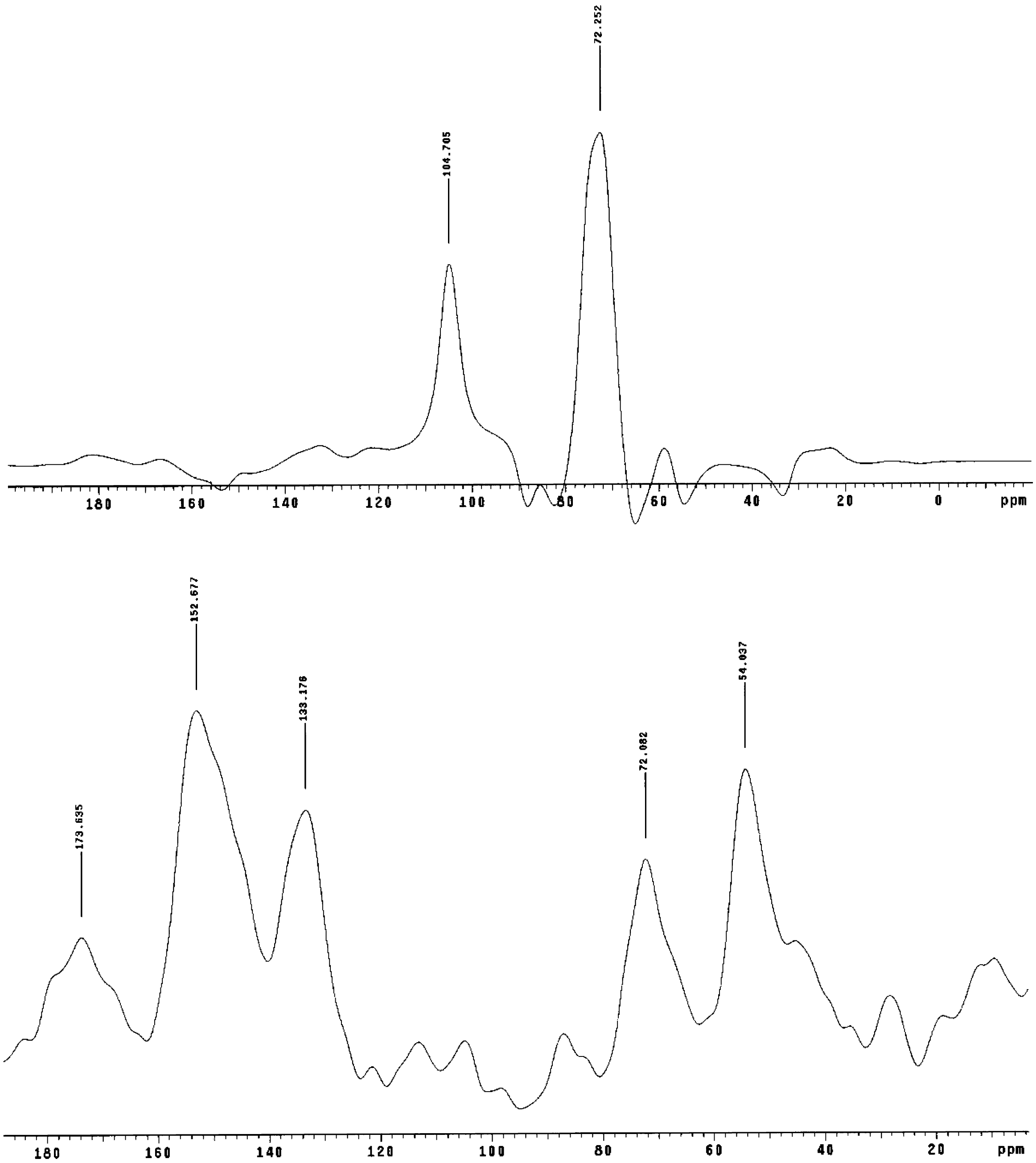

Fig. 2. ^{13}C NMR CPMASDD spectrum of the samples 7D (top) and 9D (bottom).

Table 3
Proton spin-lattice relaxation time in the rotating frame for 12D sample, obtained by variable contact and delayed contact time experiments for all resolved carbon

$T_{1\rho}^{H}$ (ms)			
δ (ppm)	VCT	δ (ppm)	DCT
106.9	nd	106.6	4.3
85.9	nd	85.2	2.4
76.6	6.8	76.3	5.4
66.6	7.8	66.6	16.0

nd-non determined.

components, which exist in distinct domains that present their own molecular mobility.

Analyzing the behavior of $T_{1\rho}^{H}$ parameter for the 12D sample, it shows that this wood region seems to be more rigid than the two others and/or can be constituted by one rigid domain that probably controls the relaxation process.

Focusing the $T_{1\rho}^{H}$ values, for all samples evaluated, it was observed that the global wood behavior as a heterogeneous amorphous material, which probably is formed by a mixture of unordered and ordered regions.

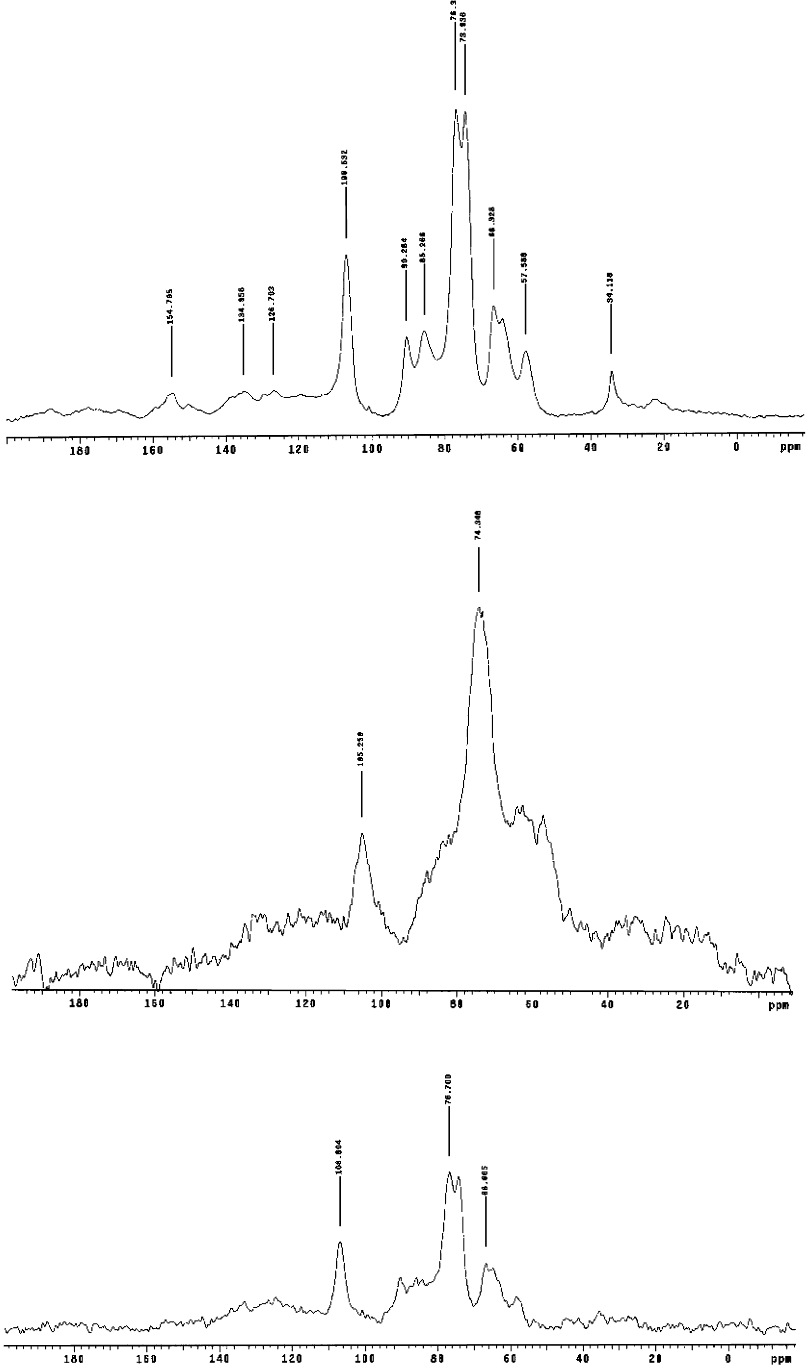

Fig. 3. ^{13}C NMR CPMAS spectrum of the samples 7D (top), 9D (middle) and 12D (bottom).

4. Conclusion

In conclusion, it was possible to obtain useful qualitative information on chemical compounds and molecular dynamic from the Angelin Pedra wood without any pre-treatment, using the chosen solid state NMR techniques. The performance of two techniques used for determining proton spin lattice relaxation time in the rotating frame rates for the different wood regions is compared. From all information described it was evaluated that this wood is a mixture of unordered and ordered regions distributed in different ways, which probably is responsible for the special characteristics like good mechanical resistance.

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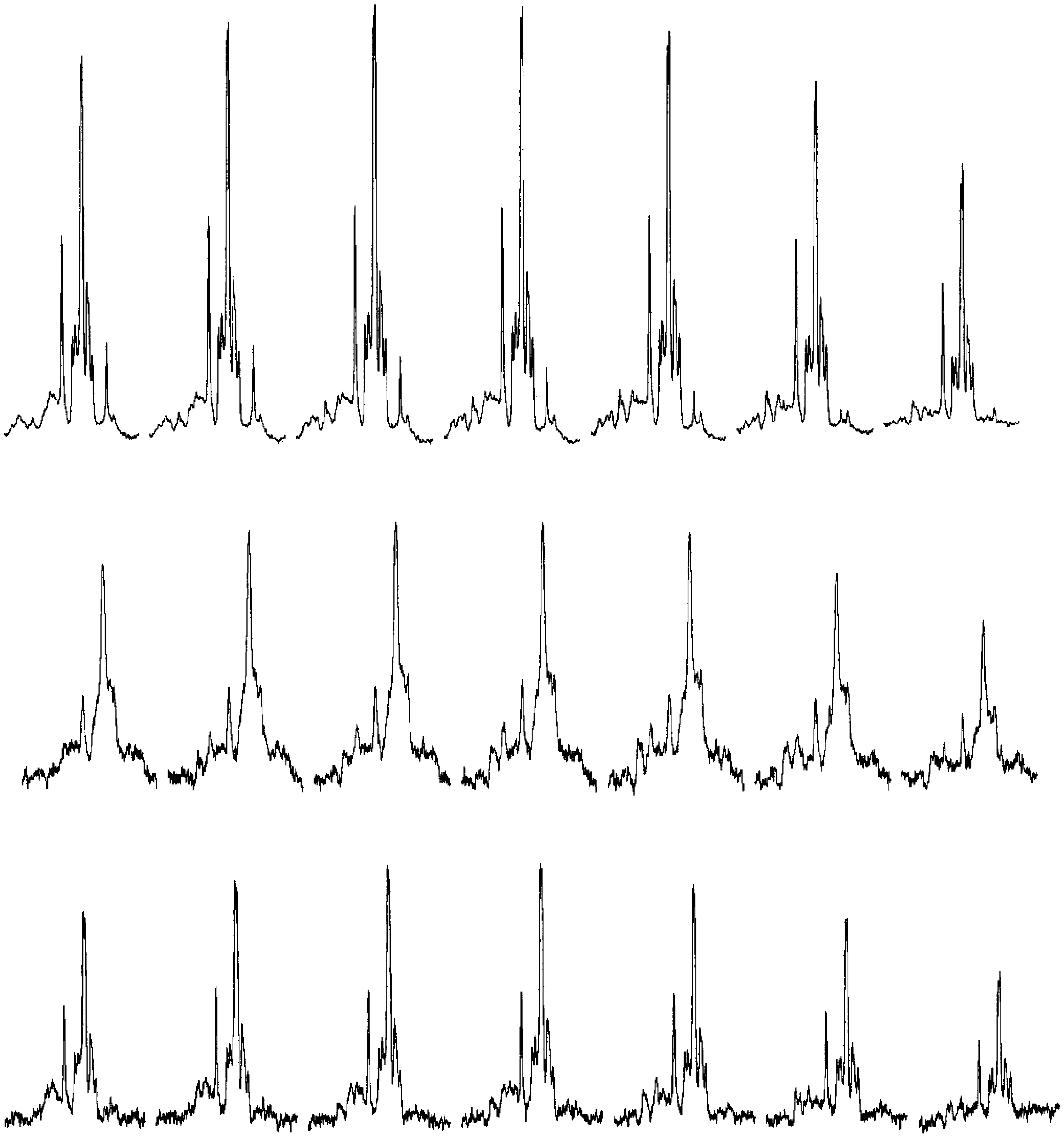

Fig. 4. VCT for the samples 7D (top), 9D (middle) and 12D (bottom).

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