Sensitivity enhancement and quantitative aspects of ^{29}Si solid state NMR spectra

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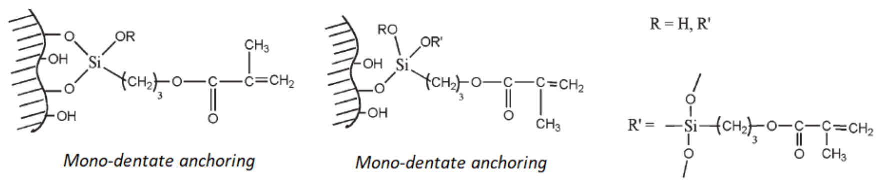
Introduction

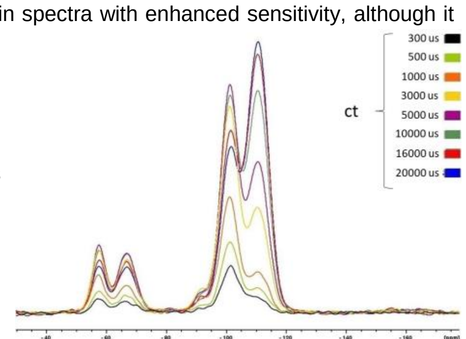
^{29}Si solid state NMR spectroscopy (SSNMR) has proven to be a valuable tool for the characterization of silicon-based materials [1,2]. The utility of ^{29}Si SSNMR arises from the extreme sensitivity of ^{29}Si chemical shift to the local chemical environment, and in particular to the number of bridging oxygens and OX groups (X = H, R) bonded to the observed ^{29}Si nucleus. Unfortunately, ^{29}Si NMR presents some inherent downsides, mainly related to the scarce natural isotopic abundance (4.67%) of ^{29}Si nuclei and to their long spin-lattice relaxation times T_1. The purpose of this work is to compare some solid state NMR ^{29}Si techniques in terms of quantitativity and sensitivity. In particular, results from Direct Excitation (DE), Cross Polarization (CP) and from the innovative Multiple Cross Polarization (MultiCP) [3] techniques are discussed and compared. All the above-mentioned techniques have been tested on a sample of silica functionalized with 3-(trimethoxysilyl)propyl methacrylate (SiO_2-TSPM).



Cross Polarization

Cross Polarization (CP) is commonly used to obtain spectra with enhanced sensitivity, although it presents the drawback of being non quantitative.

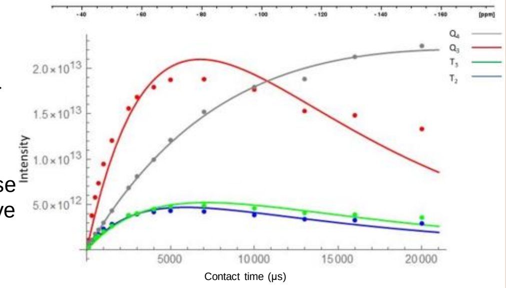
CP spectra with variable contact time (ct) were considered in order to obtain CP dynamic curves for all the ^{29}Si signals.



The CP dynamic curves of each signal were fitted by the equation:

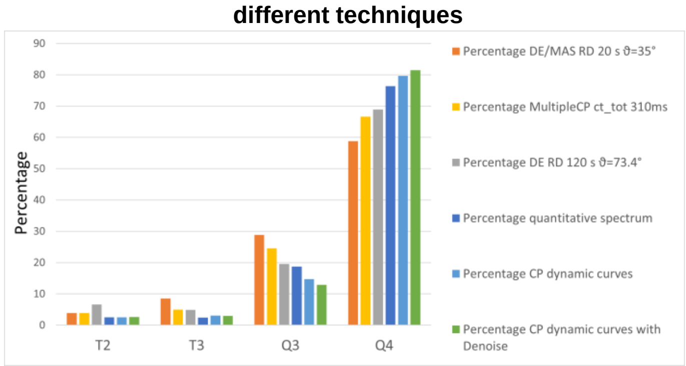
$$I_S(t) = I_{0,S}\frac{1}{1-T_{IS}/T^I_{1\rho}}\{e^{(-t/T^I_{1\rho})} - e^{(-t/T_{IS})}\}$$

$I_{0,S}$ is related to the number of nuclei giving rise to the signal thus providing quantitative information.



Quantitativity and Sensitivity Comparison

Comparison of the percentages of the ^{29}Si signals obtained by the different techniques



Comparison of the sensitivity of the different techniques

	S/R	t (h)	k
Quantitative Spectra	52.0	91.34	5.44
DE/MAS RD 20 s ϑ=35	67.5	10.00	21.3
DE/MAS RD 120 s ϑ=73.4	109.7	26.67	21.2
Multi CP ct_tot 310 ms	215.1	2.72	130.4
CP ct 20 ms	127.3	1.29	112.0
MultiCP ct_tot 20 ms	122.1	0.28	230.0

Sensitivity Factor (k) [6,7]

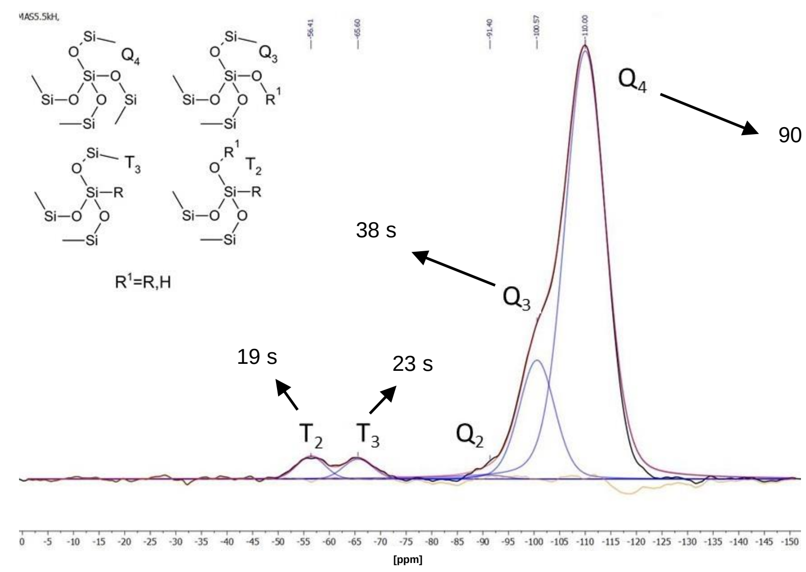
$$k = \frac{1}{\sqrt{t}}\frac{S}{R}$$

References: [1] S. Borsacchi, et al., *J. Mater. Chem.* **16**, 4581-4591 (2006) [2] M. Tonelli, et al., *Dalton Trans.* **45**, 3294-3304 (2016) [3] R. L. Johnson, K. Schmidt-Rohr *J. Magn. Reson.* **239**, 44-49 (2014) [4] S. Smet, et al., *Magn. Reson. Chem.* **57**, 224-229 (2019) [5] R. Francischello, et al., *NMR in Biomedicine* **34**, e4285 (2021) [6] Freeman R, Hill HDW, *J. Chem. Phys.* **54**, 3367–337 (1971) [7] Yan C, et al., *RSC Adv.* **10**, 23016–23023 (2020)

CISUP (Centre for Instrument Sharing-University of Pisa) is acknowledged for the use of the Bruker Avance NEO 500 solid-state NMR spectrometer.

^{29}Si DE/MAS

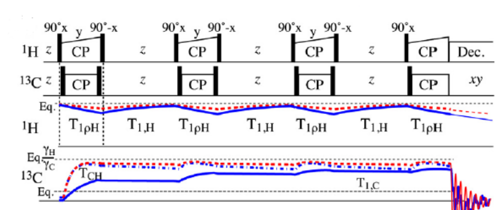
Direct Excitation (DE) techniques were used to acquire both quantitative and non quantitative spectra. In the figure a quantitative spectrum acquired with a long recycle delay of 600 s is shown; longitudinal spin-lattice relaxation times (T_1, s) measured by DE experiments at variable recycle delays are reported on top of each signal.



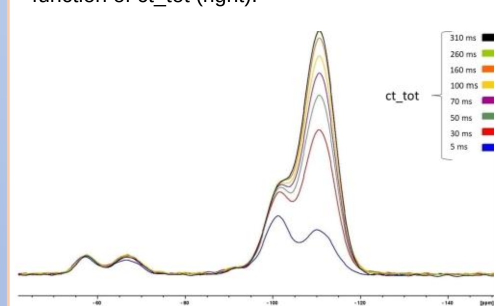
Multiple Cross Polarization

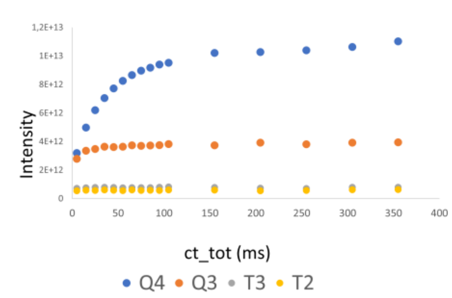
The recently developed Multiple Cross Polarization (MultiCP) technique was tested. This technique already proved to be successful in providing high-sensitivity quantitative ^{13}C spectra [3], but its application to ^{29}Si is still quite limited [4].

MultiCP pulse sequence [3]
It is composed by a series of CP blocks separated by a delay t_z, during which ^{1}H longitudinal magnetization returns to equilibrium while the magnetization of ^{29}Si nuclei is stored along the z axis.



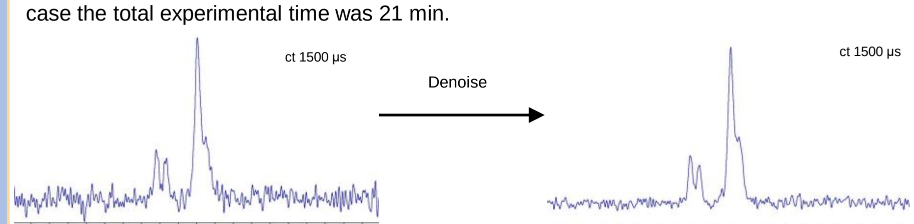
Below, MultiCP spectra at variable total contact time (ct_tot), given by the sum of the durations of all the CP blocks, are reported (left) together with the curves of the intensity of each signal as a function of ct_tot (right).





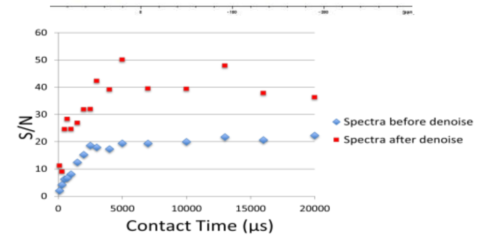
Application of denoise techniques on CP spectra

Noise reduction techniques [5] have been tested on ^{29}Si CP spectra acquired with very few scans (40 scans) at the same contact times used to build the CP dynamic curves shown above. In this case the total experimental time was 21 min.



A significat increase of S/N is obtained after application of denoise techniques.

The analysis of the CP dynamics curves obtained from these spectra provided similar results to those obtained from the CP spectra recorded with 2000 scans (total experimental time 16.7 h).



Conclusions

In this work, the results from ^{29}Si DE, CP and MultiCP experiments have been compared in terms of sensitivity and capability to provide qualitative data. ^{29}Si MultiCP experiments provided nearly quantitative spectra with a significant signal enhancement. Promising results were obtained by applying noise reduction techniques on ^{29}Si CP spectra, allowing to strikingly shorten the experimental time to acquire CP dynamics curves.