NMR CRYOPOROMETRY vs NMR RELAXOMETRY -A COMPARATIVE STUDY-

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Introduction

Low-field Nuclear Magnetic Resonance (NMR) is a technique widely used both in industries and academia for product/material/substance characterization and quality control. It is used in food industries (fish, meat, dairy products) for the quantification of total fat and solid-to-fat ratio, building material industries (cement, wood) and in petrophysics for porous media characterization in terms of pore size distribution and porous matrix properties, such as wettability, permeability, porosity [1].
In this work the authors wanted to focus on

- **NMR cryoporometry**, which is a technique for the characterization of porous media through the evaluation of the alteration of thermodynamic properties of a confined liquid (the main observed effect is the depression of melting point), being a suitable technique for pore size distribution determination between nano and micro scale (sub-nm to about 2µm) [1, 2, 3];

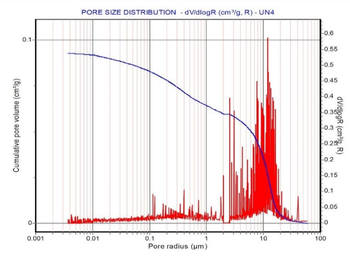
in comparison with

- **NMR Porous Media Relaxometry**, which involves the determination of longitudinal and transversal relaxation times distribution by observing the magnetization relaxation once it has been perturbed. This method relies on the relation between the surface-to-volume ratio, the relaxation times and the surface relaxivity [4, 5, 6, 7].

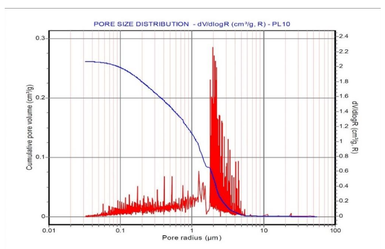
in order to highlight strengths and weaknesses of both the techniques. Mercury Intrusion Porosimetry (MIP) have been used to determine pore size distribution and to validate the results obtained with NMR.

Mercury Intrusion Porosimetry (MIP)

Uncastillo sandstone



Lecce stone



NMR Cryoporometry

Josiah Willard Gibbs and three different Thomsons (James Thomson, William Thomson, later Lord Kelvin, and J.J. Thomson) applied experiment, thermodynamics and generalised dynamics to produce an equation that well describes the phase-change behaviour of liquids in confined geometry; the Gibbs–Thomson equation for the melting point depression, ΔT_m, for a small isolated spherical crystal, of diameter *x*, in its own liquid, may be expressed as:

$$\Delta T_m = T_m^{\infty} - T_m(x) = \frac{4\sigma_{sl} T_m^{\infty}}{x \Delta H_f \rho_s}$$

A development of the Gibbs–Thomson equation has been discussed that relates these phase changes the pore area a_p and volume v_p :

$$\Delta T_m \approx \frac{a_p}{v_p} \cdot \frac{\sigma_{sl} T_m \cos\phi}{\Delta H_f \rho_s} \approx \frac{k_d \sigma_{sl} T_m}{x \Delta H_f \rho_s}$$

For many purposes this may be simplified so that the pore diameter *x* is related to a melting point depression:

$$\Delta T_m = \frac{kGT}{x}$$

where we are grouping all the thermodynamic terms into a single constant, *kGT* [K, Å] - the Gibbs-Thomson coefficient - usually established by experiment.

NMR Porous Media Relaxometry

There are several experiments showing that the pore size distribution curve obtained by mercury injection is very similar to the NMR relaxation time distribution curve [7]. NMR measures the pore body, whereas the MIP measures the pore throat, and, although this is not always stated explicitly, a pore model is assumed, usually a well-connected network of cylindrical tubes. Therefore, such similarity is not universal.
If it possible to assume that there is a consistent factor between the pore throat and the pore body, and the **average surface relaxivity ρ** is constant over the whole pore scale, then the pore size distribution determined by MIP can be similar to the NMR relaxation time distribution [7].
The comparison between the two curves (MIP pore size distribution and NMR relaxation distribution times) is not an easy task, and to avoid subjectivity we implement a **convolution method** that permits to obtain the best overlap of the two curves.
Then, supposing to use a cylindrical model for pores, one has that:

$$\frac{S}{V} = \frac{2\pi r h}{\pi r^2 h} = \frac{2}{r}$$

Assuming also the relaxation bulk term can be neglected, therefore only the surface effects are accounted, it is possible to obtain the effective relaxivity $\boldsymbol{\rho_e}$ (that accounts for the fact that NMR responds to pore "body" size whereas MIP is controlled by the sizes of pore "throats"):

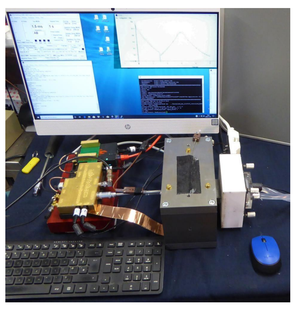
$$\rho_{1e} = R_1 \frac{V}{S} = \frac{1}{T_1} \frac{r_{throat}}{2} = \frac{d_{throat}}{4T_1} \qquad (*)$$

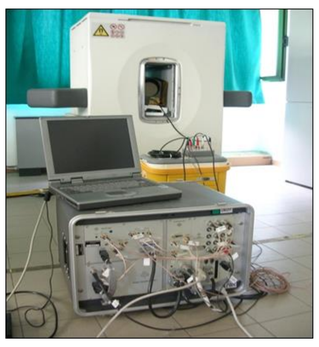
Then, assuming $\boldsymbol{\rho_{1e}}$ is fairly constant all over the sample, it is possible to scale the T_1 axis of the NMR distribution, and therefore move from an NMR relaxation time distribution to a NMR pore size distribution, using the following expression:

$$d_{throat} = 4\rho_{1e} T_1$$

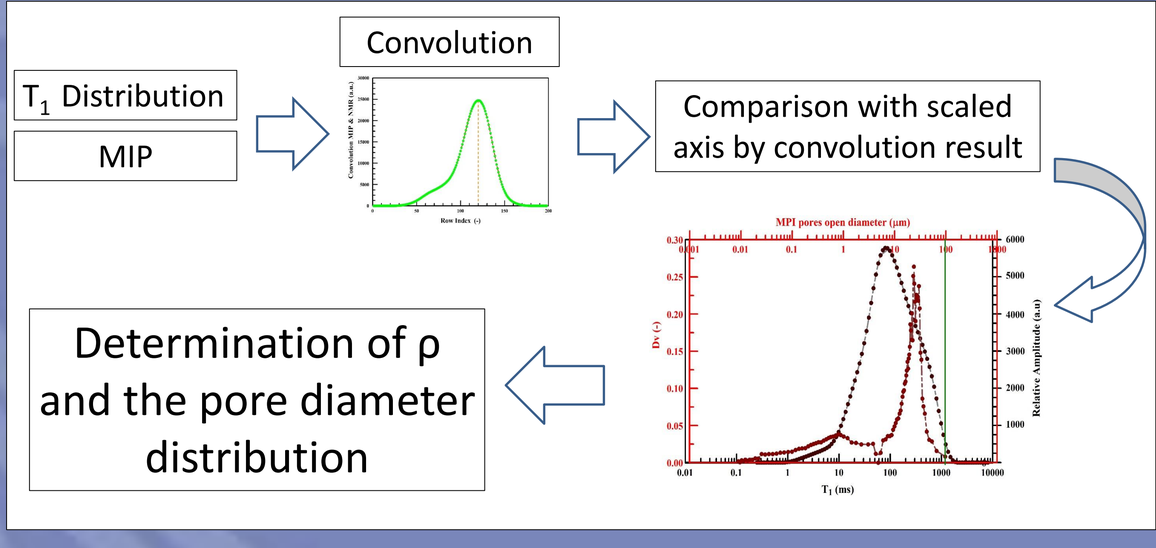
Materials and Methods

Cryoporometry: Samples were prepared by diamond slicing 2.5 mm diameter rock "sticks" to fit inside 3 mm OD NMR tubes. The aim was to reduce voids as would be present between rock grains, giving false porosity. The small sample size enables the sample to be isothermal, and so extend the pore measurement capability into the micron region. In the picture on the right, the cryoporosimeter apparatus by LabTool.

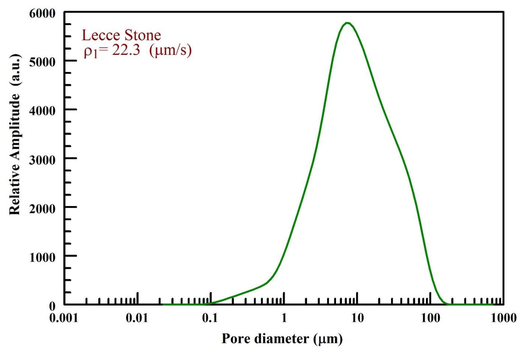


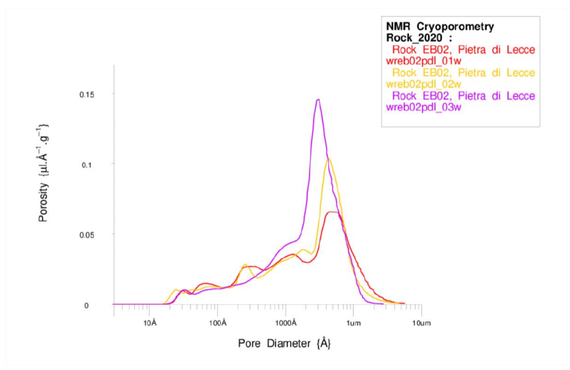


NMR Porous Media Relaxometry: sample were measured using a permanent magnet (0.8 T) and the analogical Console by Stelar (see picture on the left). The T_1 distributions have been obtained by acquiring IR curves and using UpenWin [8] for the inversion of the data. In the right picture: the samples, which were cored as 20 mm diameter and measured using an home made 25.4 mm diameter coil: Lecce stone (up) and Uncastillo sandstone (down).

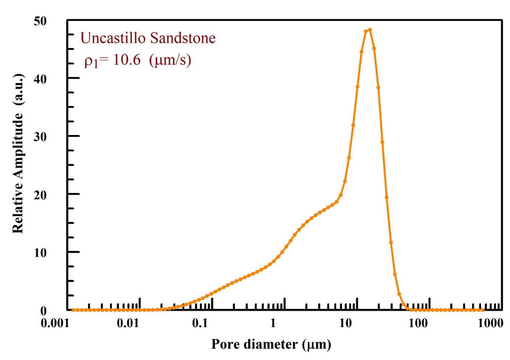


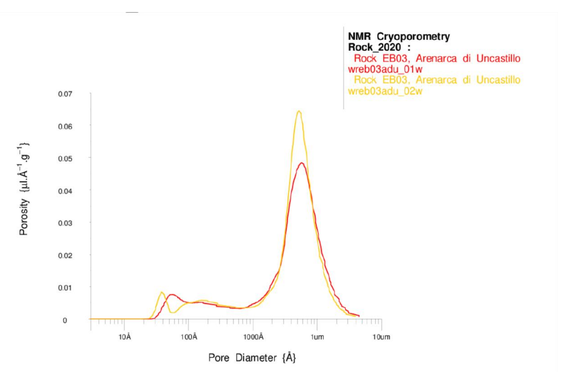
Results: Lecce Stone





Results: Uncastillo Sandstone





Conclusion

- The comparison of the pore diameter distribution shows that the results obtained are in **agreement and complementary**: while NMR cryioporometry allows the exploration of pore dimension down to sub-nm scale, NMR porous media relaxometry complete the scale up to about 100 µm. The upper limits of NMR cryioporometry is due to the reduced dimension of the sample (for hardware reason) and the lower limit of NMR porous media relaxometry depends on the MIP, with which the relaxivity is calibrated.
- From this point of view the authors deduced that for a proper porous media characterization, both technique have to be used.
- The convolution approach for T_1 distribution and MIP comparison gives values of relaxivity, using the equation (*), that are in agreement with the literature data.

References
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