The **Lab-Tools Mk3 NMR Relaxation Spectrometer** may be used to study sub-nanometer to over 2 micron pore-size distributions in many materials. It can also measure the quantities and dynamics / mobility / stiffness / viscosity / rigidity of hydrocarbons and polymers both in the bulk and deep in pores.

Nuclear magnetic resonance cryoporometry - NMRC

NMRC is a recent technique (originated in 1992) for measuring total porosity and pore size distributions. It makes use of the Gibbs–Thomson effect: small crystals of a liquid in the pores melt at a lower temperature than the bulk liquid : The melting point depression is inversely proportional to the pore size. The technique is closely related to that of use of gas adsorption to measure pore sizes but uses the Gibbs–Thomson equation rather than the Kelvin equation. They are both particular cases of the Gibbs Equations (Josiah Willard Gibbs): the Kelvin equation is the constant temperature case, and the Gibbs–Thomson equation is the constant pressure case.

Nuclear magnetic resonance (NMR) may be used as a convenient method of measuring the quantity of liquid that has melted, as a function of temperature, making use of the fact that the relaxation time in a frozen material is usually much shorter than that in a mobile liquid. To make the measurement it is common to just measure the amplitude of an NMR echo at a few milliseconds delay, to ensure that all the signal from the solid has decayed. The technique was developed at the University of Kent in the UK, by Prof. John H. Strange.

The Lab-Tools Mk3 NMR Relaxation Spectrometer with digital RF processing makes a highly stable instrument suitable for making extended NMR Cryoporometric measurements. A new version of the Lab-Tools Peltier thermoelectric cooled variable temperature NMR probe (US Patent 14/416,409) is now also available, with optional additional gas cooling and electrical heating if needed. This exhibits extremely well controlled warming rates, as needed by NMRC near the bulk melting point.

To make a NMR cryoporometry measurement, a liquid is imbibed into the porous sample, the sample cooled until all the liquid is frozen, and then warmed slowly, while measuring the quantity of the liquid that is liquid.

Fig. 1. Lab-Tools NMR Relaxation Spectrometer.

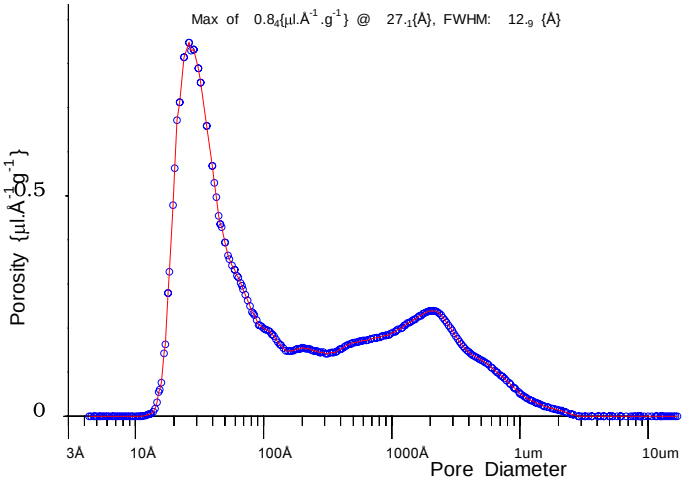


Fig. 2. An NMRC pore-size distribution for a porous carbon biochar, measured using dodecane as the probe liquid.

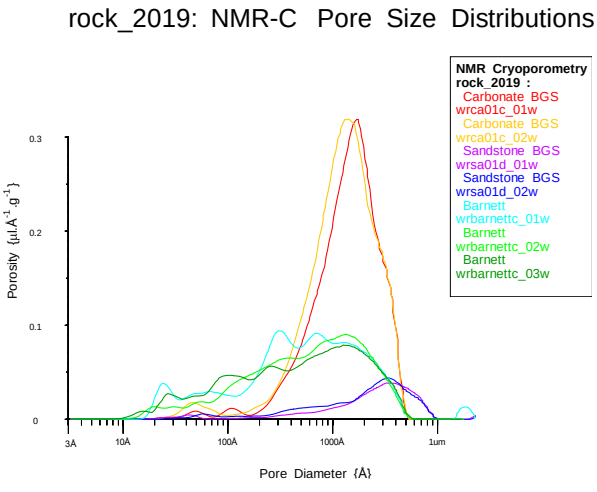


Fig.3. Repeated NMRC pore size distributions for Sandstone, Shale & Carbonate porous rocks.

Nuclear magnetic resonance cryoporometry – NMRC (cont.)

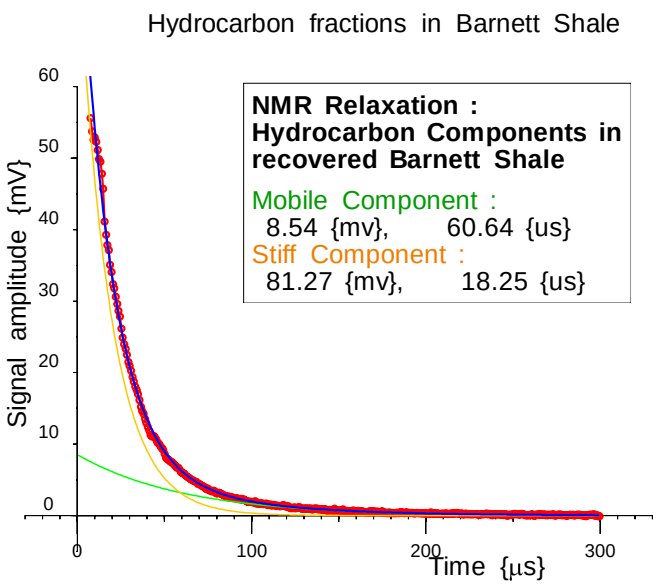
NMRC is based on two equations, the Gibbs–Thomson equation, that maps the melting point depression to pore size, and the Strange–Rahman–Smith equation that maps the melted signal amplitude at a particular temperature to pore volume.

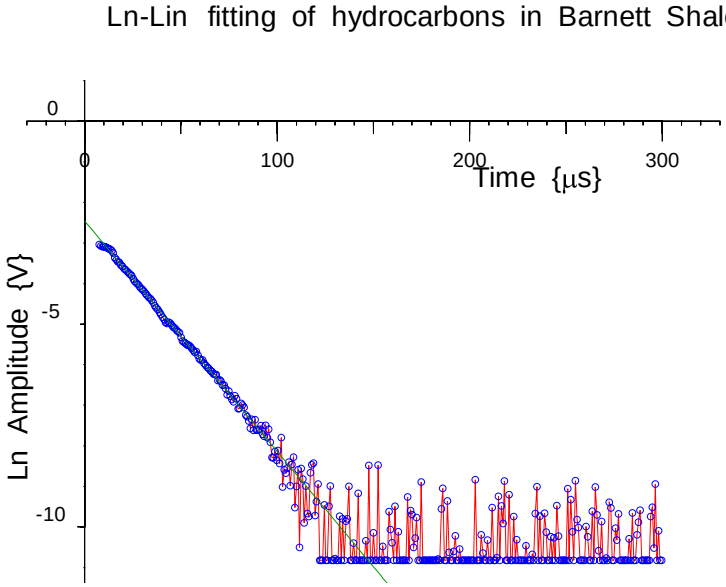
Thus NMRC cryoporometry is similar to DSC thermoporosimetry, but has higher resolution, as the signal detection does not rely on transient heat flows, and the measurement can be made arbitrarily slowly. Volume calibration of the total porosity and pore-size can be good, just involving ratioing the NMR signal amplitude at a particular pore diameter to the amplitude when all the liquid (of known mass) is melted. NMRC is suitable for measuring pore diameters in the range sub-1 nm to over 2 μm.

NMR Relaxation Material Science measurements.

The Lab-Tools Mk3 NMR Relaxation Spectrometer has fast recovery and so is very suitable to measure both the quantities and the mobility / dynamics / stiffness / viscosity / rigidity of hydrocarbons and polymers, both in the bulk and in sub-nano- to micrometer sized pores. This technique is suitable for making measurements in a range of porous materials including both porous rocks (oil/tars) and biochar (labile carbon).

For some porous materials, short T_2 components are likely to be present, from tar, resin or even amber like components. Other components may be longer, suggesting the mobility is similar to perhaps a candle wax. Oils will then give FIDs and/or echoes with even longer T_2s. Figure 4 shows a double-exponential fit to a two component decay in a porous rock. By subtracting the longer component from the data, and performing a log-lin plot, it is clear that the second, shorter, component is also a single exponential.





References

1. *Nuclear Magnetic Resonance Cryoporometry* J. Mitchell, J. Beau W. Webber and J.H. Strange. Physics Reports, 461, 1-36, 2008. DOI: 10.1016/j.physrep.2008.02.001
2. *An NMR study of porous rock and biochar containing organic material.* J. Beau W. Webber, Patrick Corbett, Kirk T. Semple, Uchenna Ogbonnaya, Wayne S. Teel, Carrie A. Masiello, Quentin J. Fisher, John J Valenza II, Yi-Qiao Song, Qinhong Hu. Proceedings of the 11th International Bologna Conference on Magnetic Resonance in Porous Media (MRPM11), University of Surrey, 2012. Microporous and Mesoporous Materials, 178, 94-98, 2013. DOI: 10.1016/j.micromeso.2013.04.004

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