Determining the pore size distribution of wet porous solids

Introduction

Pore size distribution of porous solid materials describes the amount of pore volume for each pore diameter. It is usually derived from a gas adsorption isotherm. However, the material’s surface must be dry and clean so that the gas probe has full access to it. For materials which cannot undergo a drying process, because their microstructure would change upon water molecules removal (e.g., hornification of cellulose), a wet technique must be used: thermoporometry.

Experimental details

- **Method**: water thermoporometry in melting using DSC, as described in [2]
- **Instrument**: Setaram microSC, calibrated by Joule effect from −20 °C to 180 °C
- **Thermal profile**: cooling down to -25 °C at 1 K/min, followed by a heating ramp at 0.05 K/min from -25 °C to 1 °C
- **Sample**: reference silica-alumina porous material, soaked in purified water in excess before loading in the cell
- **Amount of sample**: around 100 mg of solid in 150 mg of water
- **Sample holder**: standard 1 mL Hastelloy cells; the measurement cell contains the sample and the reference cell is empty

Thermoporometry experiment by DSC on porous silica-alumina filled with ice. Upon heating a peak appears from −15 °C, due to the melting of ice trapped in the pores. A subsequent peak starting at 0 °C corresponds to the melting of ice remained out of the pores (free ice).
**Results**

The DSC curve above is transformed into pore size distribution, by first converting the temperature $T$ into pore diameter $D$:

$$D = \frac{4\gamma}{\rho_s \cdot \Delta_f H \cdot \ln \frac{T_0}{T}}$$

with $\gamma$ the surface tension between solid and liquid water [3]; $\rho_s$ the volumic mass of ice [4]; $\Delta_f H$ the massic enthalpy of fusion of ice [5]; $T_0$ the melting temperature of free ice as obtained from the DSC curve (here 0.4 °C).

Secondly the heat flow $\Phi$ is converted into differential pore volume per amount of porous solid $dV/dD$:

$$\frac{dV}{dD} = \frac{-\Phi}{\beta \cdot \rho_s \cdot \Delta_f H \cdot m_p \cdot \frac{dT}{dD}}$$

with $\beta$ the scanning rate (here 0.05 K/min); $m_p$ the mass of dry porous solid; $dT/dD$ numerically derived from the first equation. Thermodynamic parameters all depend on the temperature. [1, 2]

In the end the pore size distribution below is obtained. One peak appears, corresponding to the melting peak of trapped ice observed in the DSC curve. By integration of this peak the pore dimensions are evaluated: average pore diameter of 9.9 nm, total pore volume of 0.54 cm³/g, both similar to the reference material specifications: 12.1 ± 1.5 nm and 0.61 ± 0.08 cm³/g respectively.

![Pore size distribution graph](image)

**Conclusion**

- Thermoporometry is a technique using DSC to evaluate pore size distributions. Water is the probe molecule as its melting point depression depends on the pore size.
- This technique needs a small heating rate, in order to guarantee a thermodynamic equilibrium at each temperature, and a high sensitivity in terms of heat flow; both requirements are met with the instrument used here: Setaram microSC.
- This technique can be applied to any porous solid with a porosity range from a few nm to 150 nm, as long as there is no interaction of water with the solid (e.g. swelling). Liquids other than water can also be used, such as benzene or cyclohexane.