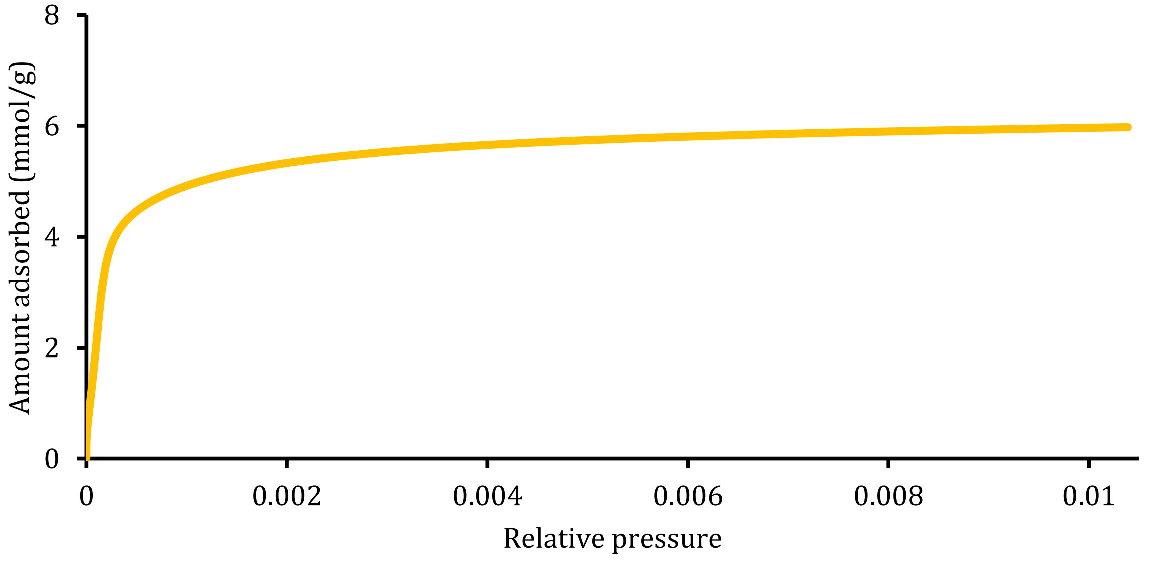
# Determining the pore size distribution of microporous solids

## Introduction

**Porous solids have a wide range of applications according to the size and shape of their pores: water purification, hydrogen storage, catalysis of chemical reactions, etc.** They are therefore commonly described by their pore size distribution, which relates the amount of pore volume for each pore diameter. In particular, micropores are defined as pores measuring up to 20 Å in width. Their size distribution is usually derived from the low pressure region of a gas adsorption isotherm, starting at $10^{-4}$ mbar or lower when the gas probe is nitrogen gas. A gas adsorption isotherm is measured from the pressure evolution as successive doses of a gas probe are sent to the solid material and are adsorbed on its surface and trapped in its pores. Beforehand each pore surface and volume must be emptied of any molecule; this is achieved through a long degassing at a temperature above 300 °C under vacuum.

## Experimental details

- Method: Analysis of micropores by gas adsorption, ISO 15901-3:2007(E) [1]
- Instrument: *Micromeritics* 3Flex
- Adsorptive gas: $N_2$ at 77 K
- Sample: reference Y Zeolite material, dried under vacuum for 8 h at 350 °C on a side furnace (unrestricted from $1.33 \cdot 10^{-2}$ mbar) then for 4 h at 300 °C at sample port
- Amount of sample: 125 mg
- Sample holder: glass tube of 12 mm outer diameter with a seal frit

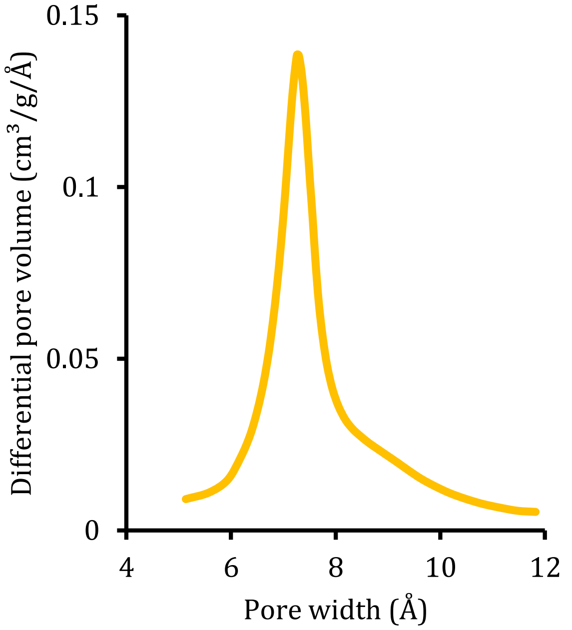



*Adsorption isotherm of the reference Y Zeolite solid. The low pressure region only is represented. According to the classification of standard physisorption isotherms (IUPAC [2]) this is a type I isotherm, as characterised by the rapid increase in the amount of gas adsorbed in the lowest pressure range. This feature is attributed to the filling of micropores. The subsequent horizontal plateau shows that the micropores are filled and no further adsorption can take place.*

# Results

The adsorption isotherm already indicates the presence of micropores. But a precise pore size distribution can be derived from it using the Horvath-Kawazoe (HK) model. It is based on the potential energy profiles of the nitrogen molecules adsorbed in the micropores and is highly dependent on the pore geometry, the nature of the adsorbent and its interaction with the adsorbed gas molecules. [1]

In the end the pore size distribution on the right is obtained (with the pores chosen cylindrical and the interaction parameter $1.68 \cdot 10^{-43}$). One peak is visible, which corresponds to the main micropore size of the distribution: 7.4 Å in diameter. The area under the peak represents the total micropore volume in the solid: 0.21 $cm^3$/g.




# Conclusion

- The distribution of pore size of a microporous solid can be extracted from the low pressure region of its adsorption isotherm using the HK model.
- The HK model is only valid for well-defined pore shapes, which can be spheres, cylinders or slits.
- The quantity needed for that experiment is typically of 150 mg and it needs to be known within 2 % error, as the results are always presented in specific units.
- Pore sizes screened by this method range from 5 Å to 20 Å in width.
- There exist various other models which calculate the micropore size distribution from the adsorption isotherm depending on the micropore geometry and the chemical nature of the adsorbent: Dubinin & Radushkevich, Saito & Foley, non-local density functional theory, etc.

[1] *Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption* — Part 3: Analysis of micropores by gas adsorption, ISO 15901-3:2007(E)

[2] Sing K.S.W., Everett D.H., Haul R.A.W., Moscou L., Pierotti R.A., Rouquérol J. and Siemieniewska T., IUPAC Recommendations 1984: Reporting Physisorption Data for Gas Solid Systems with Special Reference to the Determination of Surface Area and Porosity, *Pure & Applied Chemistry* 57, 1985, pp. 603-319