Getting Particular about Particles and Porosity

Measuring micro-, meso-, and macropores

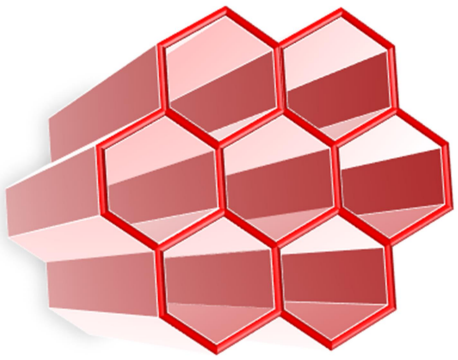

Figure 1: Pores are the pathways into and throughout porous materials as depicted here with hexagonal cylinder-like pores.

The specific needs of researchers, quality assurance departments, and production facilities for particle characterization vary by material, material property, and application. The most obvious characteristics that describe a particle include its size and shape, as well as its chemical composition. Another property, the *surface area* or total exposed surface better describes how a particle interacts with its surroundings. When a material is solid with no discernible pores, the surface area is easily derived from the geometric shape of the particles. Particle sizing techniques are often sufficient to give a clear picture of the particle characteristics and behavior. Anton Paar's PSA particle size analyzers are often chosen to investigate the characteristics of non-porous materials.

However, the introduction of porosity into the material (either intra- or inter-particle porosity) creates additional properties of interest. Surface area, in particular, is affected by the presence of pores. Instead of simply measuring the external dimensions of a particle, several types of pores must be taken into account and included in the surface area calculation. The presence of pores, and even undulations and step edges formed by a surface's roughness, can add a staggering amount of surface area to a particle. In fact, porous materials that have a significant volume of very small pores might exhibit a surface area larger than a football field – several thousand square meters per gram.

Why does porosity matter and how does porosity dictate which characterization method is best for different materials? Let's find out by examining porosity and pore sizes from largest to smallest.

1 Porosity

Porous materials are found throughout nature and are important for a multitude of industrial, medical, and natural processes. For example, the pores within catalysts increase the available surface for reactions to occur. In addition, reactants and products are directed to and from active sites through the porous structure. The size of the pores present in pharmaceutical tablets directly relates to their dissolution rate. The pores that travel through a filtration membrane define the size of particles which can physically pass through and those that will be removed from an influent.

Pores are the openings in solid surfaces which gases, liquids, or even foreign microscopic particles can occupy. Pores come in a variety of sizes defined in a set of standards approved by IUPAC based on different size widths:[1]

- Micropores have an internal width of less than 2 nm
- Mesopores have an internal width between 2 nm and 50 nm
- Macropores have an internal width larger than 50 nm (Refer to Figures 1 and 2).

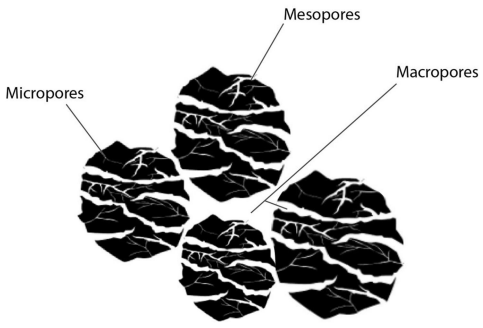

Figure 2: A visual representation of micro- and mesopores arranged within a particle and macropores formed between particle packing known as interparticle pores.

Knowing the discrete pore size of porous materials is beneficial for many reasons and often the pore size is a contributing factor in the selection of a porous material for a certain application – whether the intended application is filtration and particle rejection, selective adsorption, or catalysis.

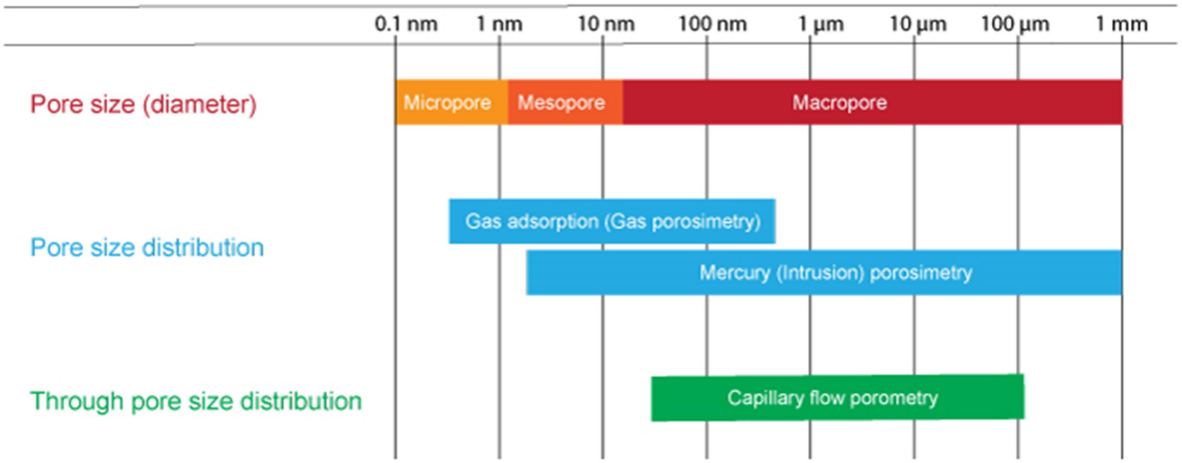

Figure 3: Pore sizes and the techniques used to measure them.

1.1 Macroporous Particles

As noted previously, macroporous particles have pore sizes larger than 50 nm in diameter. Common materials of this pore size include concretes, ceramics, pharmaceutical materials, in addition to filters and membranes. Interparticle porosity is also typically macroporous.

Techniques such as gas adsorption, mercury intrusion porosimetry, and capillary flow porometry can help characterize different aspects of macroporous materials. Surface area should be characterized with gas adsorption. Pore size and pore volume for through and blind pores are better characterized by mercury intrusion porosimetry. Capillary flow porometry is most often used to characterize specifically the pore size distribution of through pores in materials such as filters or membranes.

Mecury intrusion porosimetry is based on the physical principle that a non-reactive, non-wetting liquid will not penetrate pores until sufficient pressure is applied to force its entrance. The Anton Paar *PoreMaster* series is known for accuracy, operational convenience, and reliable performance when characterizing macroporous particles using mercury intrusion porosimetry. The instruments apply pressure to a sample and, as pressure increases, the intrusion volume of mercury is detected by the change in capacitance between the mercury column and a metal sheath surrounding the stem of the sample cell. As the mercury column shortens, the pressure and volume data are continuously acquired and displayed. The *PoreMaster* instruments feature:

- Computer-guided volume calibration to ensure reliable data consistent with ISO 9000 and other quality standards.
- Automatic mercury transfer from reservoir to low-pressure ports, eliminating operator exposure to mercury.
- Multiple data reduction parameters including mercury surface tension and contact angle for consistency with existing databases and research applications.
- Automatic repeat intrusion/extrusion cycles for research on hysteresis phenomena.
- Simultaneous high- and low-pressure operation for maximum productivity.

Capillary flow porometry involves applying an increasing pressure to one side of a wetted porous sample while measuring the amount of flow downstream of the sample. At first this flow will be zero. Once the pressure is increased to the bubble point (associated with the largest through pore size present) an initial flow through the sample will be detected. As the pressure is increased, the pores in the sample are progressively emptied (largest through pore first, then smaller ones). The flow rate through the emptied pores is recorded and used together with the pressure to provide information such as the maximum pore size, the mean flow pore size, and full pore size distributions.

The *Porometer 3G* instruments from Anton Paar measure the bubble point, pore size distribution, permeability, and other related information about through pores in membranes and other filtration media. Developers and

manufacturers of filter media around the world use these instruments to measure the bubble point and through pore size distribution of their track-etched membranes, woven or non-woven fabrics, hollow fibers, papers, or ceramic monoliths. They understand that these properties are crucial predictors of the materials ultimate filtration and separation performance.

1.2 Mesoporous Particles

Metal oxide powders, silicas, aluminas, and some carbons exemplify mesoporous particles, typically having pore sizes of 2 nm to 50 nm. Gas adsorption is the preferred characterization method for these particles because it yields both surface area *and* pore size and can be done with nitrogen, the well-established, inexpensive, and well-suited gas adsorbate.

The gas sorption process starts when clean, dry samples are brought to a constant temperature and small amounts of a gas (usually nitrogen) are admitted in steps into an evacuated sample chamber. The gas molecules quickly find their way to the surface of every pore in the adsorbent. Gas molecules adsorb to the surface and the monolayer amount is used to calculate surface area, often using the BET[i] method, and pore size is calculated from pore filling pressures.

The Anton Paar *NOVAtouch* instrument is an ideal choice for high-speed surface area and pore size analyses of mesoporous materials. Designed with 2 or 4 analysis stations, 4 sample prep stations, and including multiple data reduction methods, the *NOVAtouch* delivers rapid BET surface area and mesopore size distributions. The *NOVAtouch's* intelligent design and unique touchscreen interface saves bench space and enables intuitive user interaction.

1.3 Microporous Particles

Zeolites, carbons, and metal and covalent organic frameworks (MOFs/COFs) belong in the microporous particle category because they generally have pore sizes of 2 nm or below. This classification brings with it unique properties such as a high surface area that allows these microporous materials to be used in applications such as catalysis, adsorption, filtration, separation, and others.

Characterizing the physical properties of microporous materials is generally achieved using the gas sorption technique. Because pore filling of micropores occurs at such low relative pressures, an instrument typically needs a turbo-molecular vacuum pump and low-pressure transducers. However, argon has benefits over nitrogen adsorption experiments by providing faster analysis time (because the pore filling steps shift to slightly higher pressures) and kinetics at liquid argon temperature. In addition, argon lacks nitrogen's quadrapole moment, which means that argon does not interact significantly with the surface chemistry of the adsorbent, therefore the pore filling pressure with argon is directly related to the pore size to improve the measurement accuracy. These attributes of argon combine to significantly speed up analysis time. Another option for gas adsorption experiments, specifically for carbons, is carbon dioxide which results in rapid micropore size analysis.

The Anton Paar *autosorb iQ* is specifically designed with this in mind. Metal-to-metal (VCR) fittings employed in the measurement manifold(s) for extremely low leak rate allow high-quality micropore size measurements using 0.1 torr or 1 torr transducers. Multiple physisorption analysis stations are served by dedicated measurement manifold and transducer sets. A dedicated P_o (saturation pressure) transducer, and a long-life dewar (90+ hours) are all standard features. This is a highly sophisticated gas sorption analyzer with up to three micropore analysis stations and four dedicated built-in sample preparation (degas) ports. Metal organic frameworks (MOFs), activated carbons, and zeolites – indeed any type of microporous particle – can be analyzed with an extensive suite of density functional theory (DFT) pore size calculations and a wide range of sample cell types.

1.4 Comparison of Pore Size Analysis Technologies

	Gas Sorption	Mercury Intrusion Porsimetry	Capillary Flow Porsimetry
Pore Size [nm]	0.3 to 500	3.5 to 1,000,000	20 to 500,000
Pore dimensions by IUPAC definition[ii]: Micropores <2 nm; Mesopores 2 nm to 50 nm; Macropores >50 nm			
Pore Type	All pores accessible from external surface	All pores accessible from external surface	Through pores only
Anton Paar Instrument	autosorb iQ & NOVAtouch	PoreMaster series	Porometer 3G series
Mean Pore Size	Yes	Yes	Yes
Pore Size Distribution	Yes	Yes	Yes
Pore Volume	Yes	Yes	No
% Porosity	No	Yes	No
Surface Area	Yes	Yes	No
Typical Applications	▪ Carbons ▪ Zeolites ▪ Catalysts ▪ MOFs/COFs ▪ Silicas ▪ Aluminas ▪ Pharmaceuticals ▪ Polymers ▪ Battery components	▪ Ceramics ▪ Catalysts ▪ Pellets ▪ Pharma ▪ Tablets ▪ Concrete ▪ Core samples ▪ Chromatography media	▪ Filters ▪ Membranes ▪ Woven & non-woven textiles ▪ Hollow fibers ▪ Papers

Table 1: Comparison of pore size analysis technologies

2 Conclusion

Porous materials are important in many industrial, medical, catalytic, and natural processes. Anton Paar offers instruments that implement gas adsorption, mercury intrusion porosimetry, and capillary flow porometry techniques to characterize different physical and chemical properties of porous materials:

- Surface area of macroporous materials should be characterized with gas adsorption.
- Pore size and pore volume for through and blind meso- and macroporous materials are better characterized by mercury intrusion porosimetry.
- Capillary flow porometry is most often used to characterize specifically the pore size distribution of through pores in materials such as filters or membranes.
- Gas adsorption is the preferred characterization method for meso- and microporous particles because it yields both surface area *and* pore size.

[i] Brunauer, S. et al. (1938). Adsorption of Gases in Multimolecular Layers. Journal of the American Chemical Society, pp. 309–319.
[ii] Thommes, M. et al. (2015). Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure and Applied Chemistry, pp. 1051–1069.