COVALENT
METROLOGY

Welcome

COVALENT METROLOGY

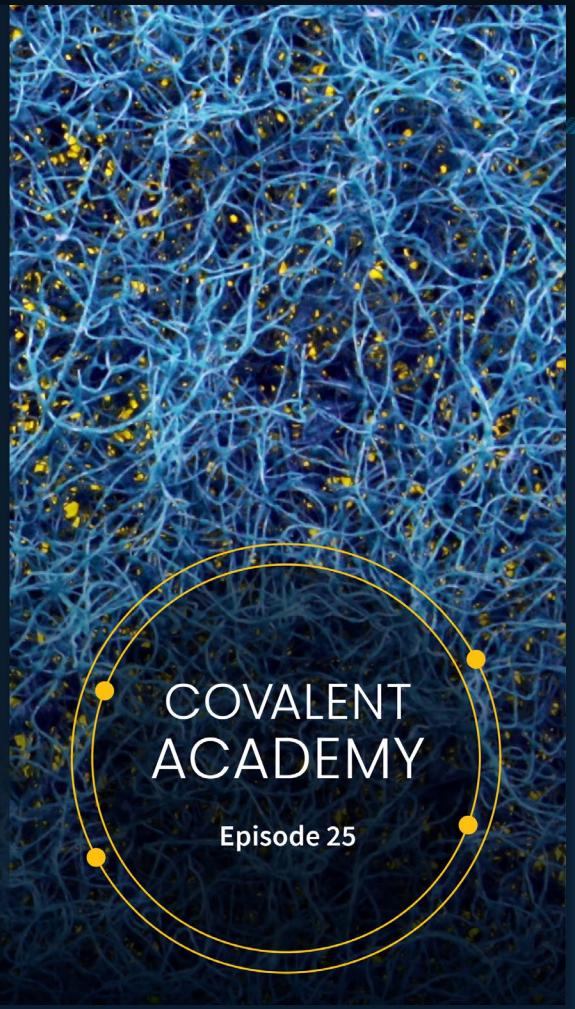
POROMETRY, POROSIMETRY, AND PYCNOMETRY: THE 3 P'S YOU NEED FOR POROUS MATERIALS CHARACTERIZATION

SPEAKER:

Nanette Jarenwattananon, PhD

Senior Manager, Material Property Testing

October 7, 2021 | 11AM PT



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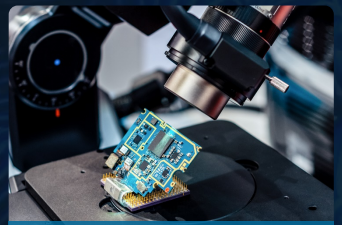
Silicon Valley-based analytical labs and platform delivering quality data and expert analysis for advanced materials and device innovation



Comprehensive Solutions Stack

50+ cutting-edge instruments, offering 100+ Techniques

Analytical Services

Advanced Modeling

Method Development

Temp. Staffing Solutions

Affordable and Fast

Fast Turnaround Times, No Expedite Fees

Volume Savings

Instant Access to Data and Reports in Secure Portal

Flexible Business Model

Custom Consulting Solutions and Certified Onsite Support

Training and Certification on Instrumentation

Co-op and Tool-Share Opportunities

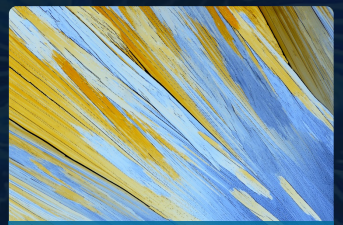
Laboratory Audits

Rich Network of Partnerships

Rigaku · J.A. Woollam · ThermoFisher Scientific · Keyence · Anton Paar · PVA TePla · Asylum Research an Oxford Instruments company · TA Instruments

Partner to World's Leading Instrument Manufacturers and Labs

Expanding Instrumentation, Lab Connections and Learning



Who We Are, Who We Serve

500 Clients + 40-60 New Clients/ Quarter

40+ People, 13 PhDs

Cutting-edge Analytical Capabilities

Lab Location: Sunnyvale, CA

Covalent Technical Groups and Organization

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PCBA, Semiconductor, and Electronic Device Metrology & Failure Analysis

- DPA / Mechanical Cross-section
- Dye & Pry Test
- EBIC / OBIC failure analysis
- Hot Spot Detection
- IR Imaging / Emission Microscopy
- NIR Imaging
- Root-Cause Failure Analysis

Electron Microscopy and Scanning Probe Microscopy

- AFM & Advanced AFM Modes (EFM, KPFM, MFM, PFM)
- Scanning Acoustic Microscopy (SAM)
- SEM (+ EDS)
- FIB-SEM (+ EDS)
- S/TEM (+ EDS / + EELS)
- Nano-indent / Nano-scratch

Optical Microscopy & Spectroscopy

- Chromatic Aberration
- Digital Optical Microscopy
- FTIR and ATR-FTIR
- Laser Scanning Confocal Microscopy
- Spectral Ellipsometry
- UV-Vis-NIR Spectroscopy
- White Light Interferometry

X-Ray Characterization

- X-Ray Diffraction (XRD)
- X-Ray Reflectometry (XRR)
- Micron-spot ED-XRF
- WDXRF
- Micro-computed X-ray Tomography (Micro-CT)
- 2D X-ray Inspection & X-ray Radiography

Elemental / Chemical Composition Analysis

- EPMA
- GD-OES
- GC-MS
- ICP-MS and LA-ICP-MS
- Raman Microscopy & Spectroscopy
- NMR (1D or 2D; solid / liquid)

Particle Analysis

- Dynamic Light Scattering (DLS)
- Laser Diffraction Particle Size Analysis (PSA)
- Particle Zeta Potential

Material Property Characterization

- DSC
- DMA & TMA
- Rheometry
- TGA
- Surface Zeta Potential
- Porometry / Porosity
- Gas Adsorption
- Gas Pycnometry / Foam Density
- Tap Density

Surface Spectroscopy Analysis

- Dynamic-SIMS
- ToF-SIMS (Static-SIMS)
- Ion Scattering Spectroscopy (ISS)
- Ultraviolet Photoelectron Spectroscopy (UPS)
- X-ray Photoelectron Spectroscopy (XPS)

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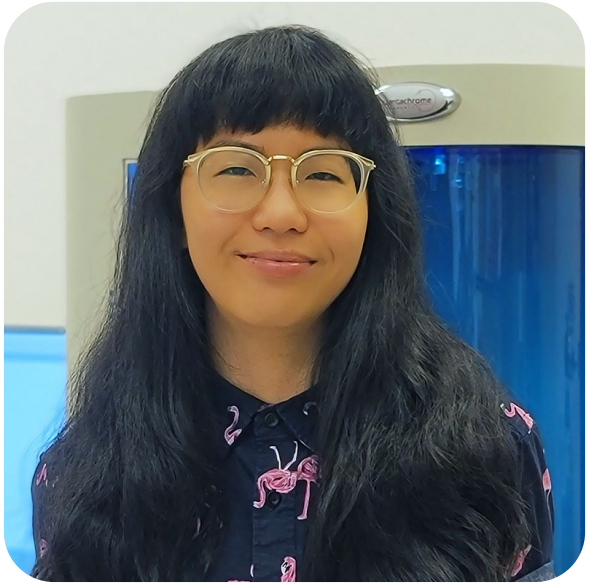
Nanette Jarenwattananon, PhD

Sr. Manager, Material Property Testing &
Analytical Chemistry Groups, Covalent Metrology

- Materials analyst and chemist with experience in spectroscopic techniques, developing tailored methods for novel analytical applications in both industrial & academic research
- Nanette leads both the Material Property Testing and Analytical Chemistry groups at Covalent Metrology
- PhD, Physical Chemistry, UCLA
- BA, Chemistry, Barnard College, Columbia University



Agenda

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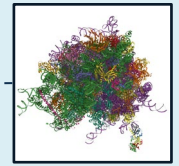
1. Definitions - Types of Pores
2. Capillary Flow Porometry – Differentiating Two Filtration Media
3. Gas Porosimetry – Why does PTFE Seal Well?
4. Gas Pycnometry – Determination of Percent Solids in Battery Slurries

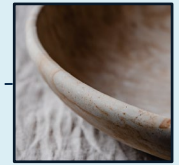
Why are porous materials important?

- Porous materials are everywhere and important for a wide variety of processes and industries.
  - Pores in catalysts increase the surface area for reactions to occur. Reactants and products flow to/from active sites in the porous structure.
  - With filtration membranes and masks, the maximum size of particle that can be removed from the fluid stream is limited by the size of pores that go through the layer.
  - Battery separators must be able to hold enough liquid electrolyte for efficient ionic conductivity.
  - Carbon capture materials must have enough surface area and large enough pores to capture greenhouse gas emissions.
  - In pharmaceutical tablets, pore size is directly related to their dissolution rate.

Catalysts

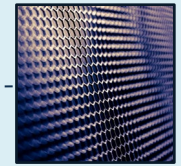


Ceramics



Energy

Carbon



Pharmaceuticals

What is a Pore?

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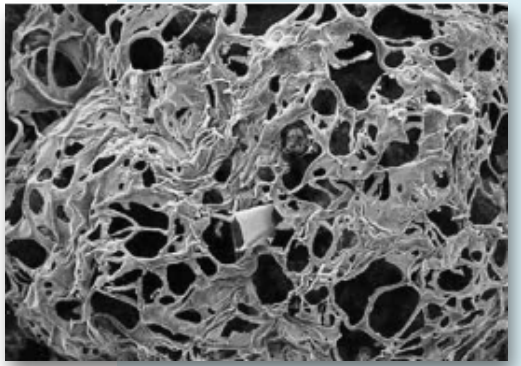
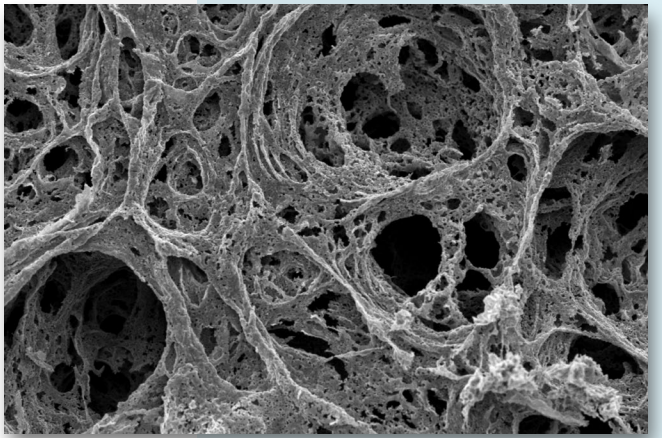
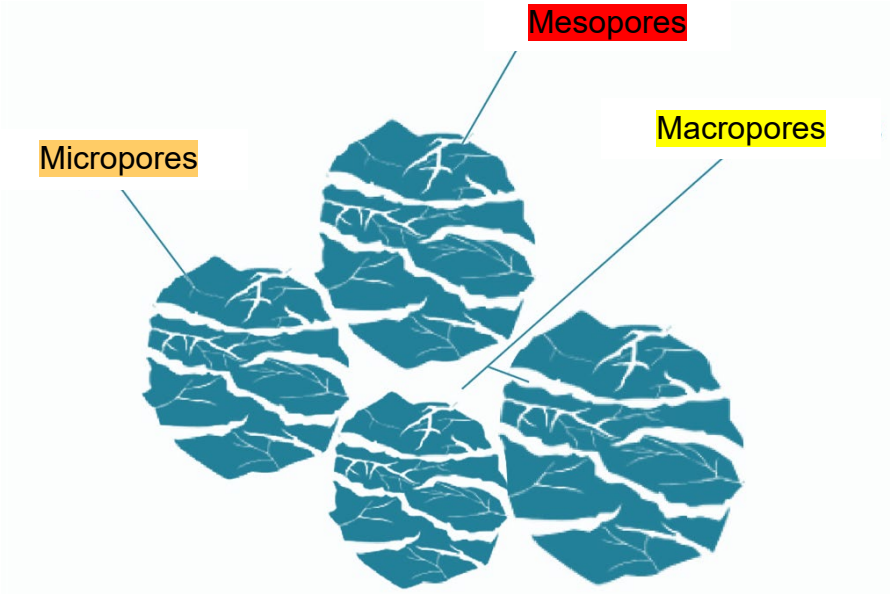
- A **porous material** or **porous medium** is a material containing pores.
- **Pores** are openings in solid surfaces in which gases, liquids, or other solid particles can occupy.
- The skeletal part of the material is the **matrix** or **frame**.
- Porous media are created bottom-up as an architectural process (COFs, MOFs) or top-down which builds pores from non-porous materials (leaching, etching, sintering, steam reforming).
- Pore type(s) determines the characterization method or methods.



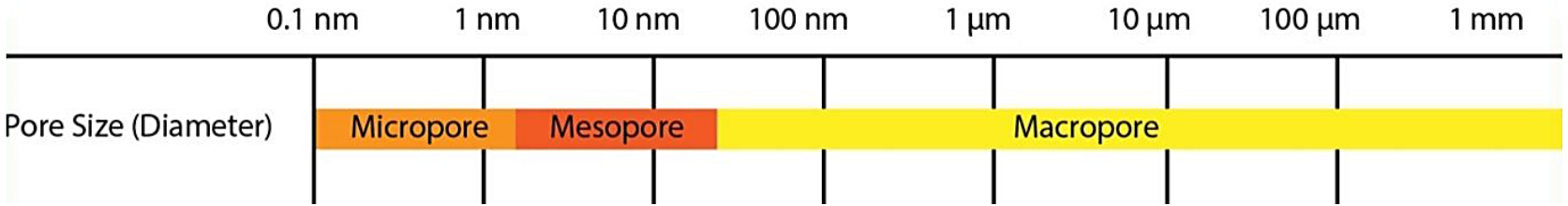


Pores are described by their size/width

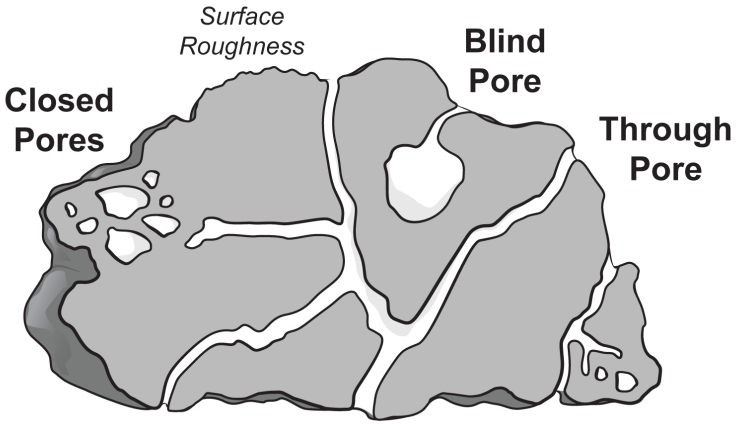


IUPAC definition of pores is based on width:

- Macropores > 50 nm
- Mesopores 2-50 nm
- Micropores < 2 nm
  - Wide micropores 0.7 -2 nm
  - Narrow micropores < 0.7 nm



Pores are also described by accessibility to material's surface



1. **Closed Pore** completely isolated from any surrounding fluid
2. **Open Pore** has access to the surface of the material
   - **Blind Pore** an open pore that connects to only one external surface
   - **Through Pore** an open pore that directly connects two external surfaces of a solid

- **Limiting Pore Size** the smallest wall-to-wall dimension within a through pore

How do we measure pore sizes?

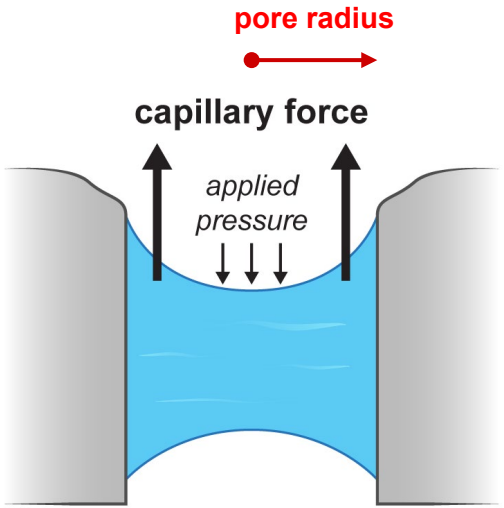
1. **Porometry** – pore size distribution of through pores
   - Apply inert gas at increasing pressure to displace a fluid from pores
   - Pore size distribution of through pores: minimum, maximum (first bubble point), and mean pore size
   - Can extract **permeability** information – how well fluids pass through the pores

2. **Porosimetry** – surface area, pore size distribution and pore volume of blind and through pores
   - Gas adsorption (non-destructive) and mercury intrusion (destructive)

3. **Pycnometry** – estimates the pore volume within a material
   - Can extract **porosity** information– the ratio of void volume to the total volume
   - No pore size distribution

Capillary Flow Porometry for through-pore measurements

- In porometry, we measure **gas flow** vs **gas pressure** through a dry sample and a wet sample.
  - In dry analysis we push a gas through.
  - In wet analysis we soak the sample with a wetting fluid first.



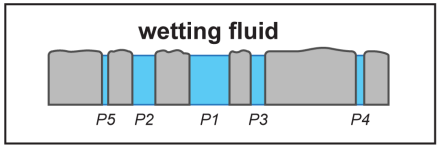
A. Completely wet sample

B. Gas pressure is applied from upstream to downstream

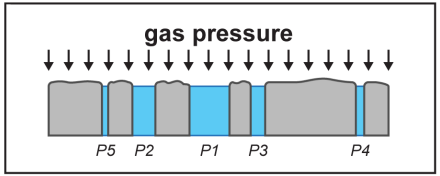
C. Gas pressure forces wetting fluid from larger pores (P1) first

D. As pressure increases, the gas forces the wetting fluid from smaller pores (P2, P3, P4, P5)

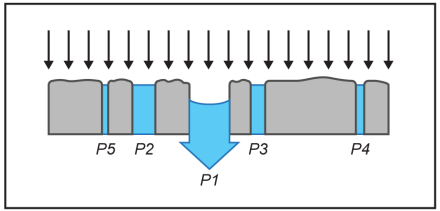
A.



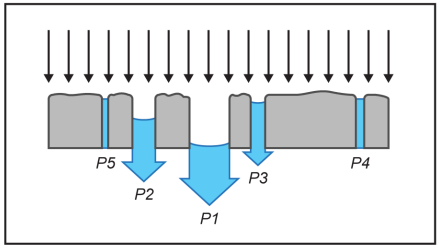
B.



C.

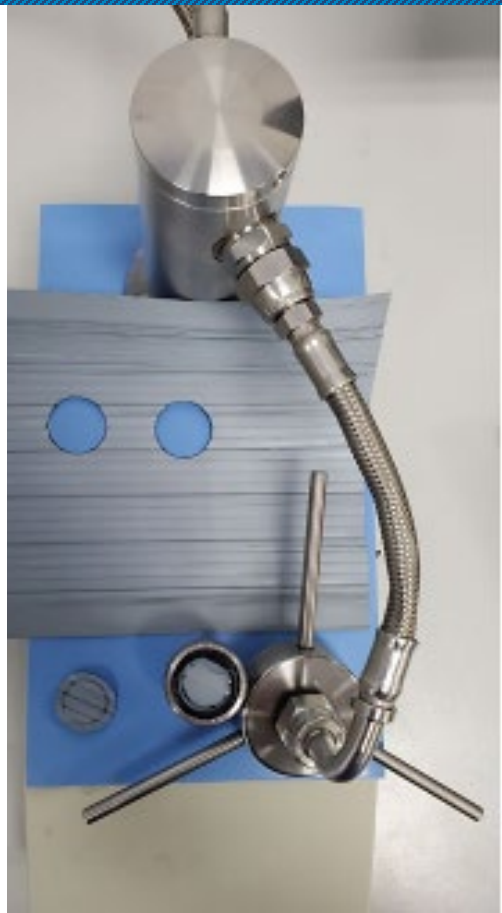


D.



Anton Paar Porometer 3G zh for Capillary Flow Porometry

Pore Size: < 0.02 to 500 microns



Porometry uses experimentally measured flow and pressure to calculate pore size

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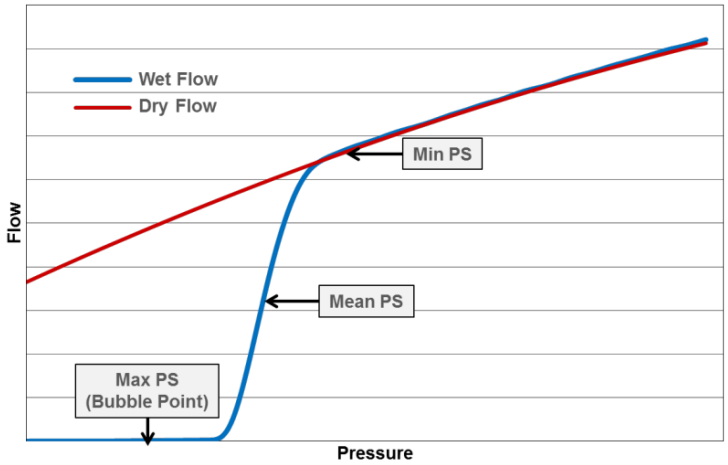
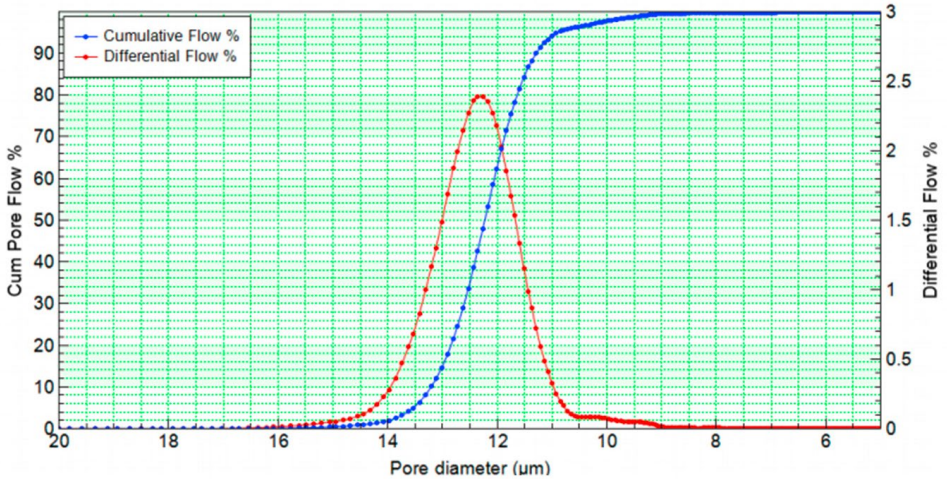
Experimental Data



Calculate pore size via the Washburne equation:

$$d = \frac{4y\cos\theta}{P}$$



d = pore diameter

P = pressure

y = surface tension of wetting liquid

θ = contact angle of wetting fluid

Case Study 1: Even though two filters look similar, they have different physical properties

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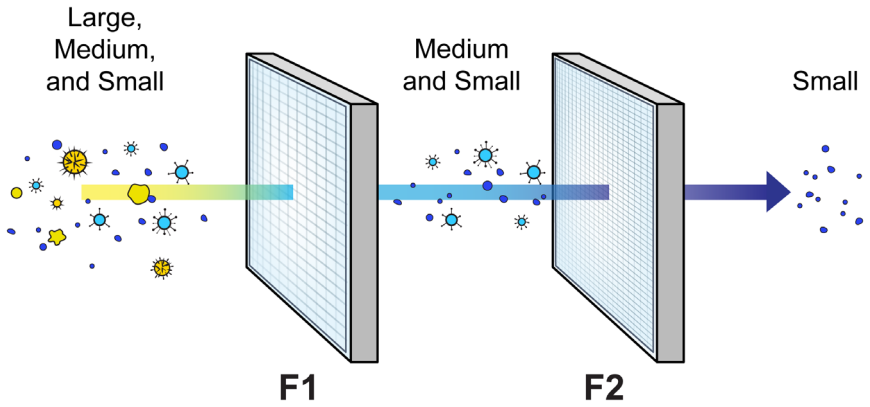

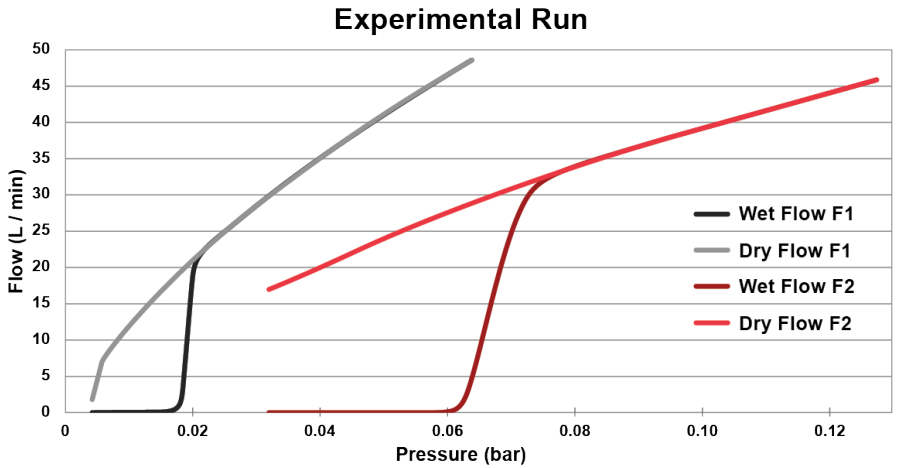

	F1	F2
Bubble Point Pressure	0.02 bar	0.06 bar
Maximum Pore Size	38 um	10.6 um
Minimum Pore Size	26 um	8.2 um
Mean Pore Size	33 um	9.5 um

CS1: Pore size and density can distinguish two similar filters

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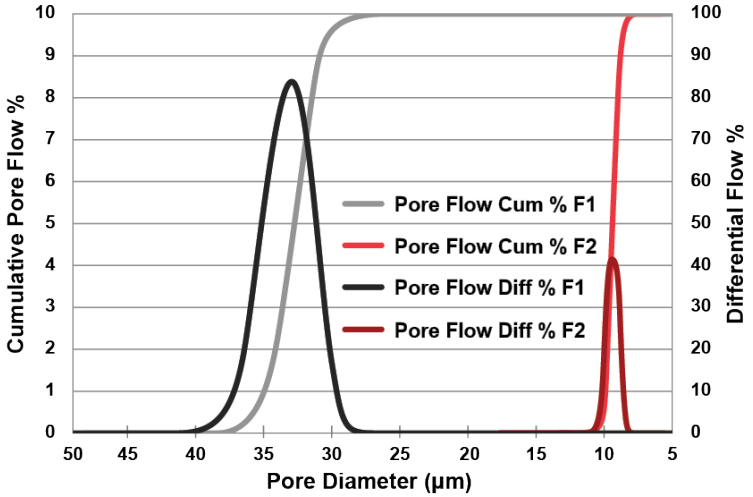

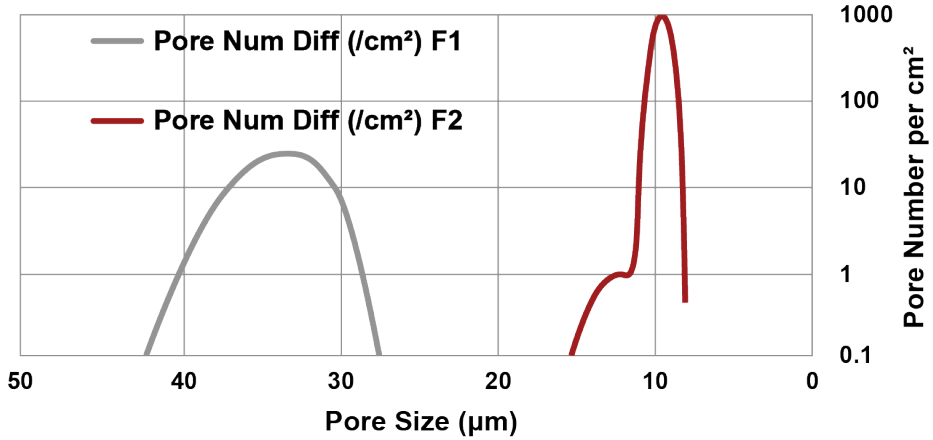

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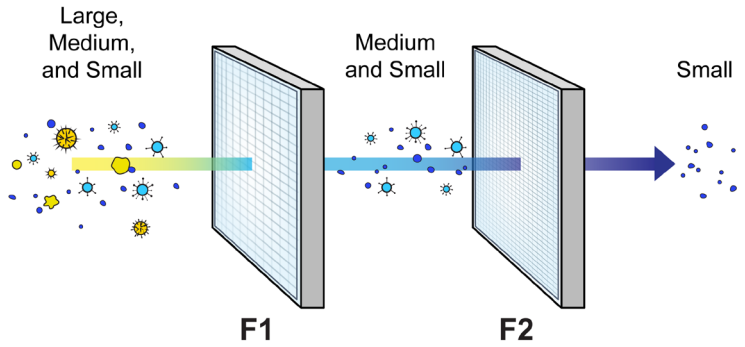

Gas adsorption measurements provide surface area, pore size distribution, and pore volume

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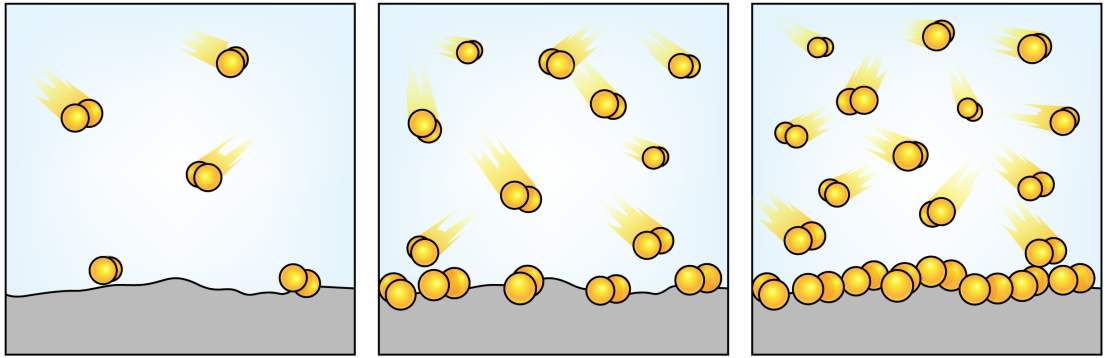
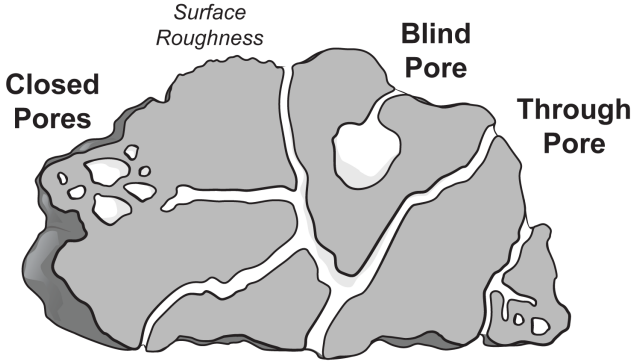
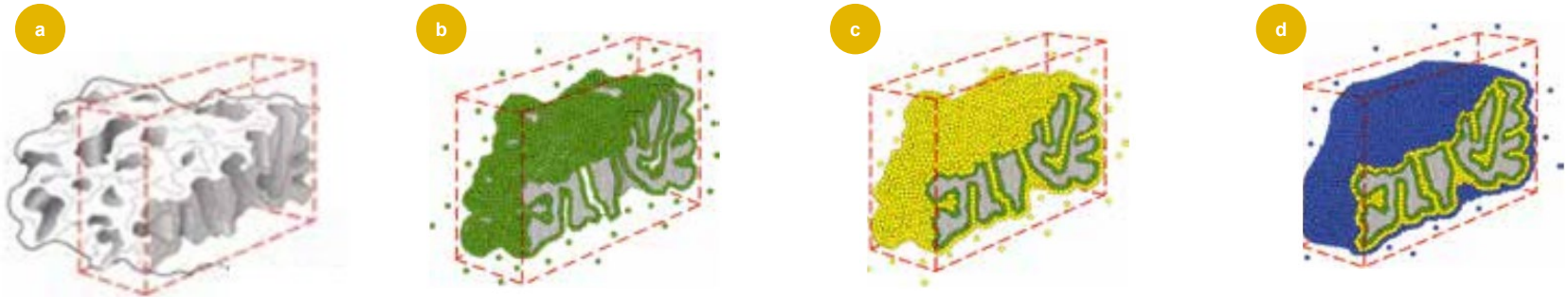
- Gas sorption experiments are a way to quantify **surface area** of a solid, **pore size**, and **pore volume distribution**.
- Unlike porometry, gas porosimetry can provide information about blind pores and roughness.
- Physical adsorption (**physisorption**) is the process by which gas molecules are adsorbed onto the surface of a solid.





Gas sorption process



a) Start by cleaning the sample (degassing).

b) Dose with adsorbing gas. Gas molecules stick to the surface of the material, forming a thin monolayer. Can use BET theory to estimate the sample's surface area.

c) As more gas is added, multiple layers stack on top of each other. Experimental isotherms of adsorbed gas volume vs. relative pressure can be converted to pore size distributions.

d) Total pore volume filling occurs at 100% saturation. Knowing the density of the gas, we can calculate the volume it occupies and thus get the total pore volume.

We can reverse this process to get the desorption isotherm.

Adsorption isotherm is used to calculate pore size, pore volume and surface area

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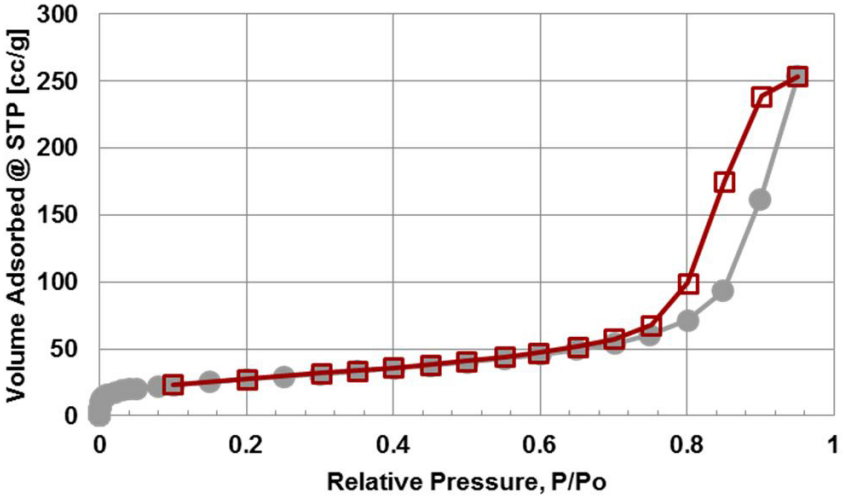

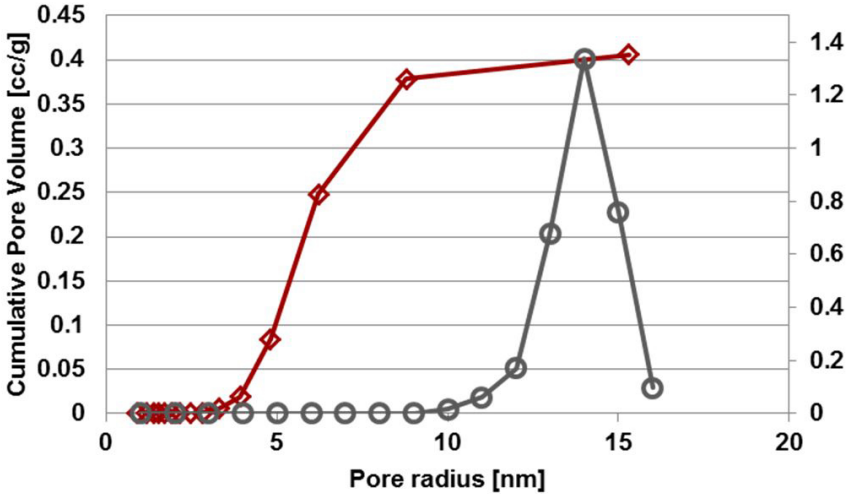

Anton Paar NOVAtouch LX^2 for Gas Porosimetry

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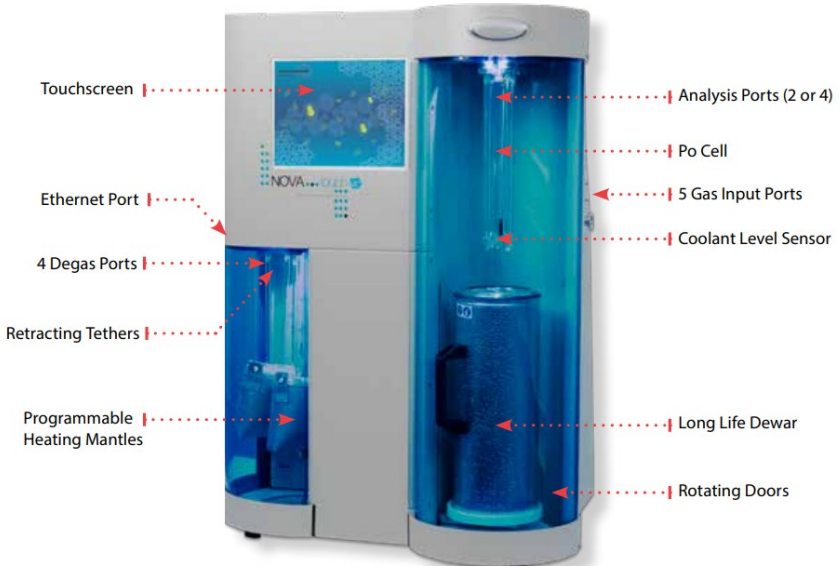

Pore Size: 3.5 - 5000 Å (0.35 – 500 nm)

Surface Area: 0.01 m^2/g and higher

Chemisorption

Anton Paar Autosorb iQ

Choosing the right gas for physisorption measurements

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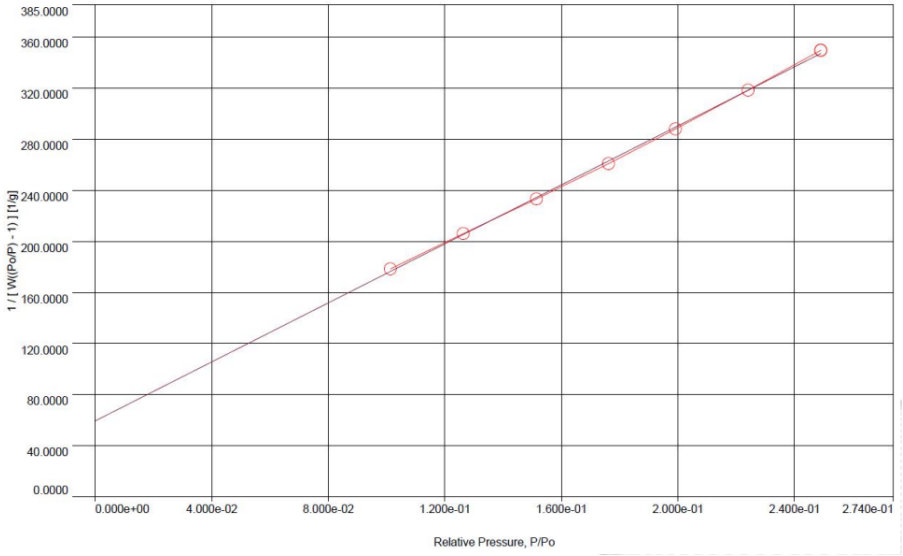
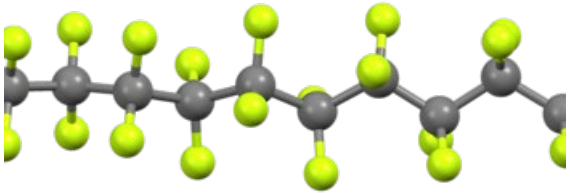
Gas	Temperature	Surface Area	Micropore Size Distribution	Mesopore Size Distribution	Total Pore Volume
Nitrogen	77 K	✓	Not recommended	✓	✓
Argon	87 K	✓	IUPAC Recommended	✓	✓
Carbon Dioxide	273 K	-	✓	-	-
Krypton	77 K	✓ low surface area	-	-	-
Krypton	87 K	✓ thin films	✓ thin films	✓ up to 10 nm	-

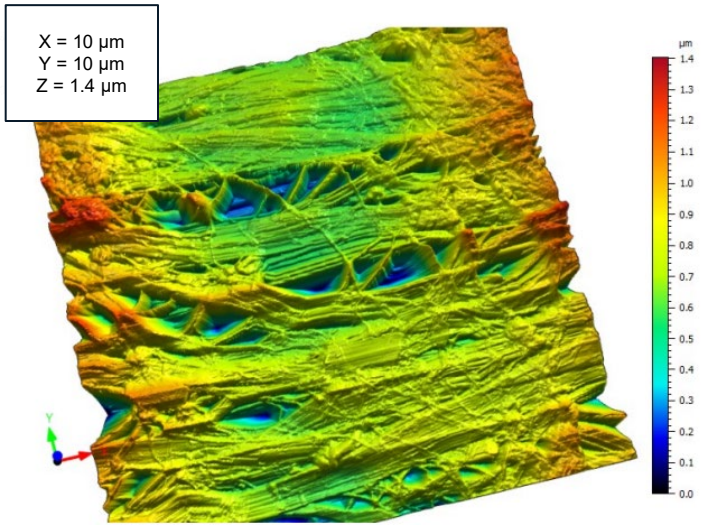
Case Study 2: PTFE's low surface area helps it seal leaks

- Good sealing materials are typically low porosity – low surface area values (<10 m^2/g) and provide a non-porous barrier to gas or liquid.



BET surface area of PTFE powder: 2.59 m^2/g

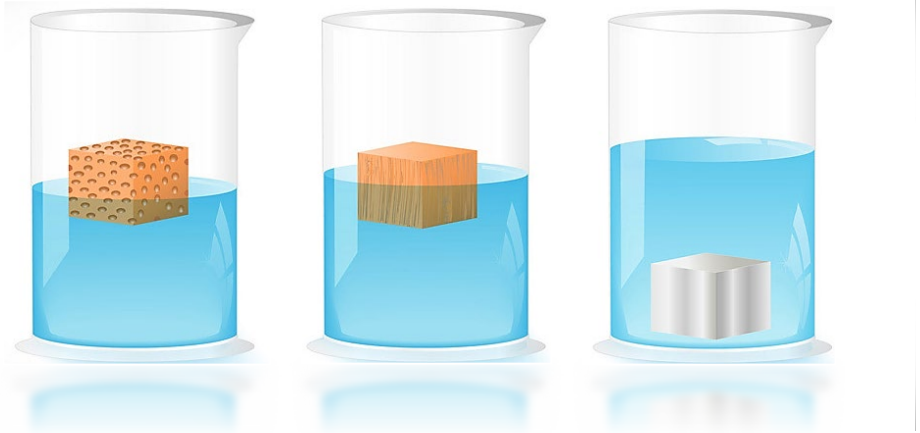




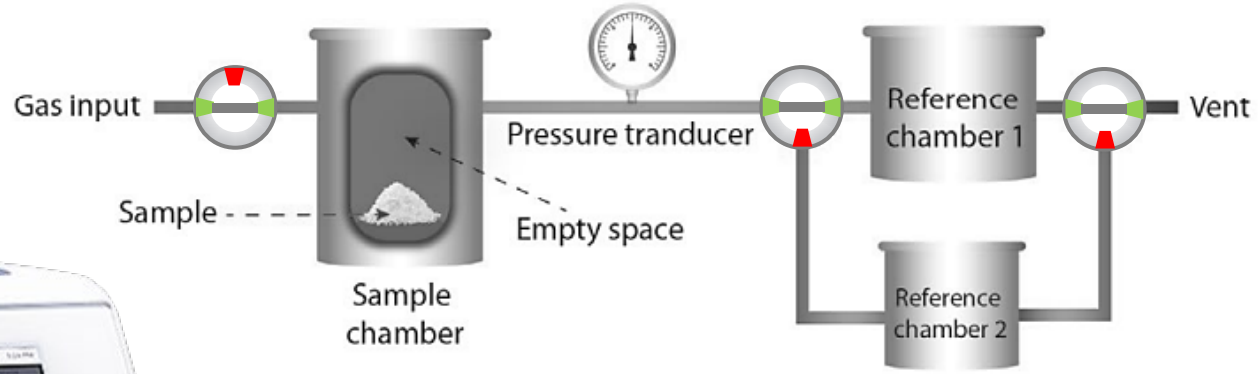
Gas pycnometry is a pressure measurement

- Pycnometry is from “*pyknos*,” meaning “dense.”
- In pycnometry, the Archimedes principle of fluid displacement is used to measure the volume occupied by an irregular shape.
- Use of inert gases such as helium, penetrates even the smallest pores and eliminates surface chemistry effects.

- Boyle’s Law $P_1V_1 = P_2V_2$
- Assumes constant temperature



Anton Paar Ultrapyc 500 for Gas Pycnometry



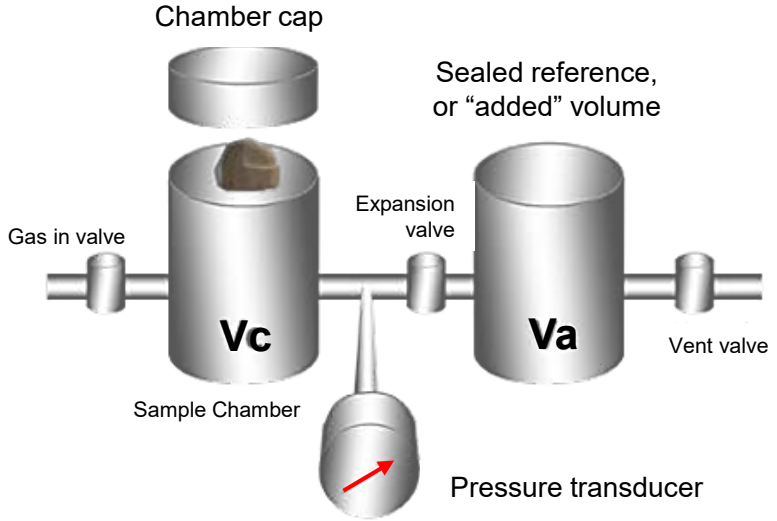
Pycnometry works by measuring pressure drop

1) Fill sample chamber of known volume with a gas at a specific pressure.
   - The gas fills all the empty space inside the sample chamber, including sample pores.
   - Wait for pressure to stabilize and record value.

2) Open valve, which allows gas to expand into a known reference chamber.
   - Wait for pressure to stabilize and record value.

3) Compare pressure drop between an empty sample chamber and full sample chamber to calculate pycnometric volume (V_{sample}) occupied by sample.

$$V_{sample} = V_{cell} - V_{exp}\left(\frac{P_2}{P_1 - P_2}\right)$$



V_{sample} = calculated sample volume

V_{cell} = calibrated sample chamber volume

V_{exp} = calibrated expansion volume

P_1 = gas pressure when only sample cell is pressurized

P_2 = gas pressure after expansion

Case Study 3: measuring solid content in battery electrode slurries via gas pycnometry

- Four steps to determine the solid content percentage of an organic slurry:
  1) Measure density of dry Si powder, ρ_s
  2) Measure density of Si/organic solvent slurry, ρ_y
  3) Measure density of organic solvent, ρ_L
  4) Calculate the percentage of solids in the slurry

$$\%\ \text{solids} = \left(1 - \frac{\rho_L}{\rho_y}\right) \times \left(\frac{\rho_s}{\rho_s - \rho_L}\right) \times 100$$

- Good agreement between formulated values and calculated values.

Material	Density (g/cm³)	Percent of Solids
Si	2.33 (ρ_s)	-
Organic Solvent	0.789 (ρ_L)	-
Slurry A	0.842 (ρ_y)	9.5%
Slurry B	0.904 (ρ_y)	19.2%

All 3 P's in One Case Study

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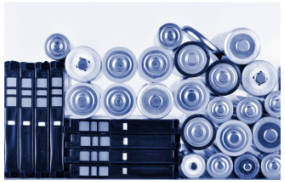
Anton Paar

Structural Characterization of Battery Components

Relevant for: anode, cathode, battery separator, supercapacitors, battery industry, energy industry

Structural properties, such as surface area, pore size and density, of battery components can be characterized using a variety of different techniques. Examples of gas sorption, mercury intrusion, and capillary flow porometry for anode, cathode, and separator materials, among others, are discussed.



1 Introduction

Research and development professionals in the battery industry are always in search of the most efficient and safest battery technologies to fuel the energy needs of our world today and into the future. In order to optimize their design efforts, battery developers rely on accurate physical property characterization for battery components such as the anode, cathode, or separator. Important properties that guide design include surface area, pore size and pore volume, porosity (% open space), and density.

1.1 Surface Area

Surface area is a critical property for anode, cathode, and even separator materials. Surface area differences affect performance variables such as capacity, impedance, discharge rate capability, and charging rates. Deviations from expected surface area can
also indicate impurities or undesirable particle size for component manufacturers. BET surface area measurements are routinely used to evaluate the accessible surface area of battery components all the way down to very low surface area materials, even less than 0.01 m^2/g, and is measured using manometric or flow physisorption techniques.

1.2 Pore Size and Volume

The determination of pore volume and pore size is also of interest for battery materials. For example, changes in the pore size distribution of an electrode material could indicate phase transformations or structural changes in the material over the course of its practical use. These measurements can also be used to determine the correlation between a material's compression and annealing temperature and its resulting pore size distribution. Pore volume is also an important property. For example, in a battery separator this volume must be able to host a sufficient amount of liquid electrolyte for efficient ionic conductivity. Mercury intrusion porosimetry and gas sorption are routinely used to assess these properties.

The choice of technique is dictated by the pore size range within the material, with gas sorption being used for micropores (< 2 nm) and mesopores (2-50 nm) and mercury intrusion being used for large mesopores (> 5 nm) and macropores (> 50 nm).

1.2.1 Through-Pore Size and Permeability

For battery separators, the through-pore (pore that starts at one end and empties out the other) size distribution may be more important for a given application than a total pore size distribution. Characterization of the through pores can be done using capillary flow porometry. Permeability analyses can also be performed in order to get a sense of the structural nature of the pores. As an example, a tortuous pathway helps to isolate the positive electrode particles from the negative electrode material, but increases the effective resistance caused by the separator, thereby reducing battery efficiency and lifetime.

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1.3 Density

Volumetric capacity is a crucial property of battery devices that operate in limited spaces. Understanding the volume occupied by the electrode material itself, as well as the open spaces within the matrix, often referred to as the material's porosity, is necessary for predicting performance.

Tapped density analyzers provide mass per volume information, including the spaces within and between particles, of the powders used to manufacture electrode components. Gas pycnometry is used to measure the true or skeletal density of a material and excludes the influence of any pores accessible from the exterior of the sample. For a regular shaped sample, where the dimensions can be measured, % porosity can be calculated directly from the gas pycnometry data. In the case of powders or irregular shaped samples, volume and density measurements from gas pycnometry are often combined with other techniques such as gas sorption or mercury intrusion, which can give total pore volume information, in order to determine the % porosity of a material.

2 Examples

2.1 Surface Area of Anode and Cathode

Graphite anode and $LiNiCoMnO_2$ cathode materials were characterized using N_2 at 77 K gas sorption measurements in the linear BET surface area range (P/P_0 = 0.05-0.3). The resulting BET surface area plots are shown in Figure 1 and calculations give a surface area of 2.5 m^2/g for the anode and 1.5 m^2/g for the cathode.

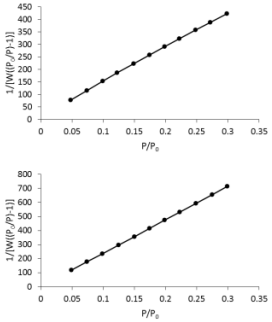

Figure 1: BET surface area plots derived from the N_2 (77 K) adsorption isotherms for graphite (anode, top) and $LiNiCoMnO_2$ (cathode, bottom) measured on a NovaTouch.

2.2 Surface Area and Pore Size of Separator

A battery separator comprised of polyvinylidine fluoride (PVDF) was characterized using mercury intrusion porosimetry for pore size and volume (Figure 2). The pore size distribution from mercury intrusion represents the distribution of all large meso- (2 to 50 nm) and macropores (> 50 nm) within the separator, regardless of whether they are through-pores are closed on one end (dead end). Porosity information can be obtained by combining the intruded pore volume from mercury with the skeletal density from helium pycnometry measurements.

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How do I choose which “P” I want?

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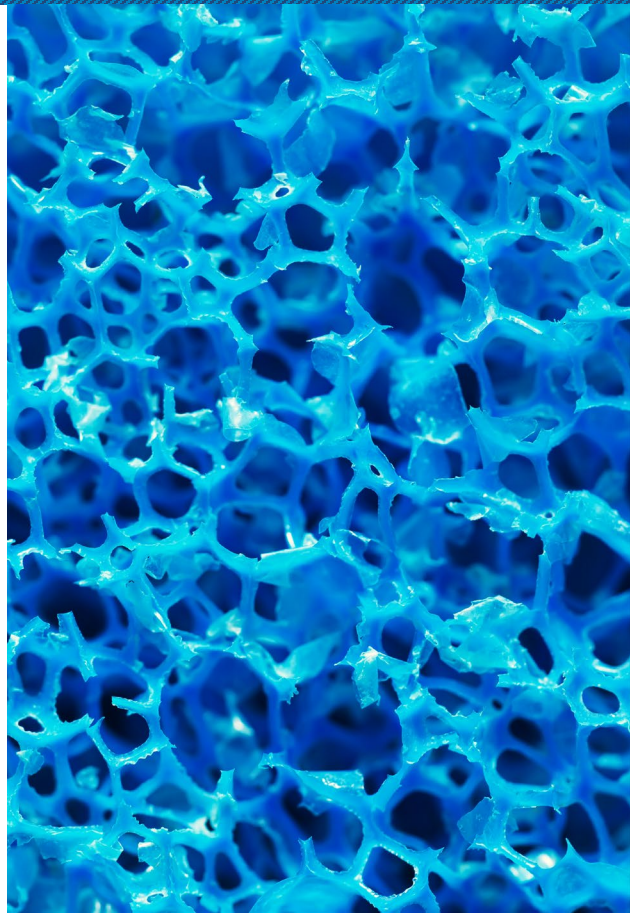
1. **Closed porosity**
   → use pycnometry to compare true density results with expected values

2. **Through-pores**
   → use capilliary flow porometry

3. **Blind pores and full pore characterization**
   → use porosimetry



Porous Media Characterization Capabilities @ Covalent

- Capillary Flow
- Porometry
- Through Pores
- Permeability

Anton Paar Quantachrome Porometer 3G zH

- Pore Size: < 0.018 - 500 µm
- Flow rate: 0.01 - 200 L/min

- Pore Size Analysis
- Gas Adsorption
- BET Surface Area

Anton Paar Quantachrome NOVAtouch XL2

- N_2, Ar ,CO_2, He & inert gases
- Pore Size: 3.5 - 5000 Å
  (0.35 – 500 nm)
- Surface Area: 0.01 m^2/g to no known upper limit
- Pressure: 0 – 0.13 Mpa
  (0 – 1000 Torr)

- True Density
- Skeletal Density
- Pycnometry

Anton Paar Quantachrome Ultrapyc 5000 Micro

- Volume: 0.25 - 4.5 cm^3
- Controlled Temp: 15 - 50 ºC

Porous Media Characterization Capabilities @ Covalent

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NEWLY INSTALLED

- **Extended Range Physisorption**
- **Chemisorption**
- **BET Surface Area**
- **For challenging non-porous, mesoporous & microporous materials**

Anton Paar Quantachrome Autosorb iQ C-XR-XR

- N_2, Ar ,CO_2, He, O_2, Kr, & other gases
- Minimum Pore Size: 0.35 nm (3.5 Å)
- Minimum Surface Area: < 0.01 m^2/g
- Chemisorption Furnace: up to 1100C

Closing

- Thank you, Covalent Metrology Team, with special thanks to those in the MatChem group!

- Special thanks to our partner, Anton Paar!

Coming Up…

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32

UPGRADING METROLOGY SERVICES WITH MOUNTAINS™ 9: IMPROVED AUTOMATION, VISUALIZATION, AND ANALYSIS

Cyrille Charles
Key Account Manager
Digital Surf

October 21, 2021 | 11am PT

Digital Surf

COVALENT METROLOGY

MODERNIZING MICROSCOPY METHODS: CAPABILITIES AND APPLICATIONS OF TEM/STEM SYSTEMS

SPEAKER:

Dr. Jan Ringnalda
Principal Scientist, Materials and Structural Analysis
Thermo Fisher Scientific

November 11, 2021 | 11am PT

ThermoFisher SCIENTIFIC

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Want to learn more about Covalent's

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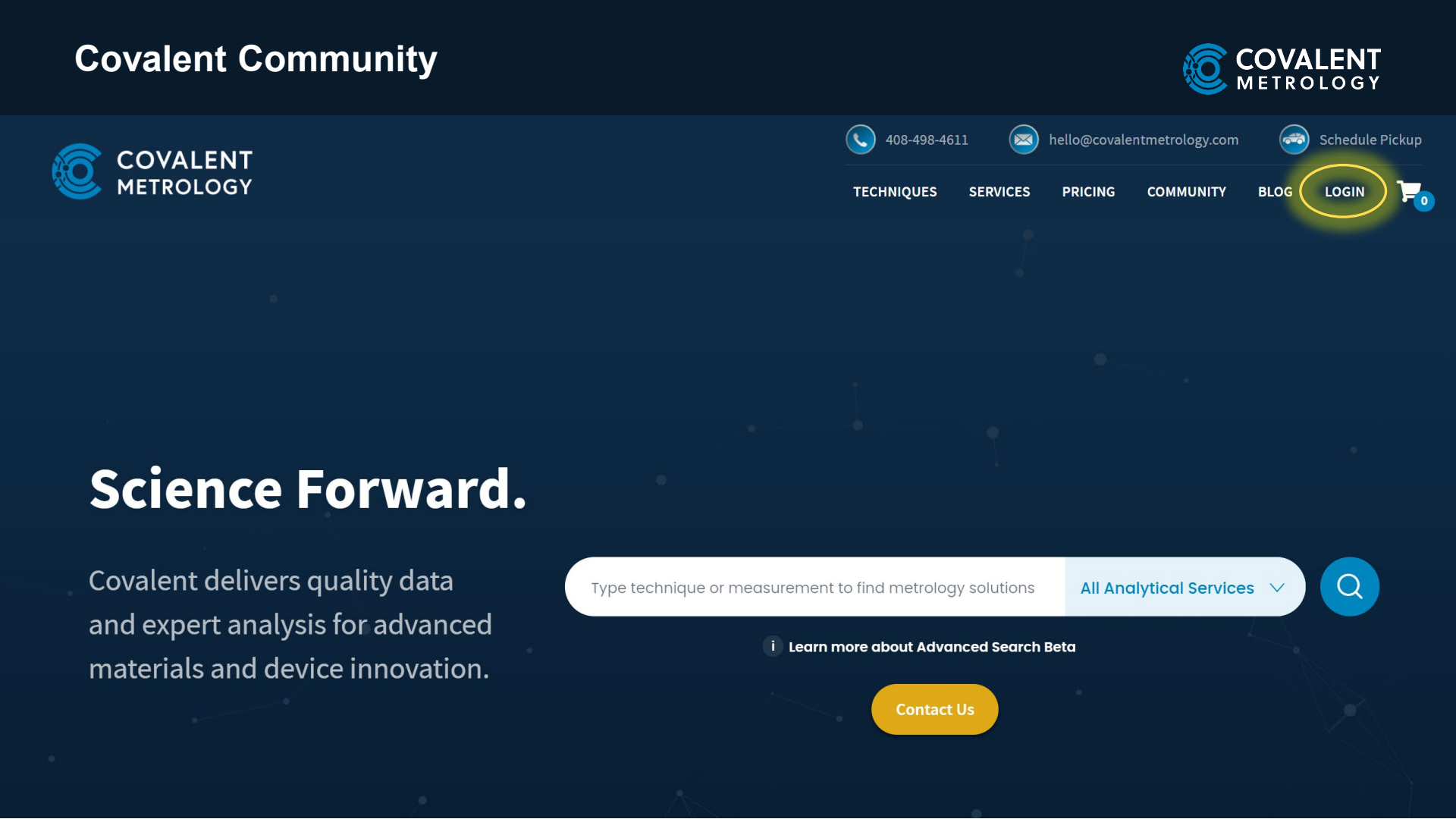
- link is in the chat -

Covalent Community



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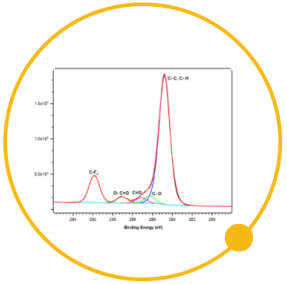

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Q & A Session

Thank you