"Extending Performance/Selection Criteria of Wide Pore Silica Substrates"

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Abstract

- Many varieties of silica exist in the market place. Every manufacturer's silica is different from its competitors. Particle size and distribution, surface area, total pore volume, pore size and distribution, and metals content differ for every manufacturer. The greatest factors influencing selectivity of the phase are the surface area, pore volume, and the distribution of the porosity profile. The pore distribution of these materials may have a profound impact of upon the selectivity of the system.

- Various average pore size classifications of silica have been analyzed by gas porosimetry and their pore distribution properties compared to one another.
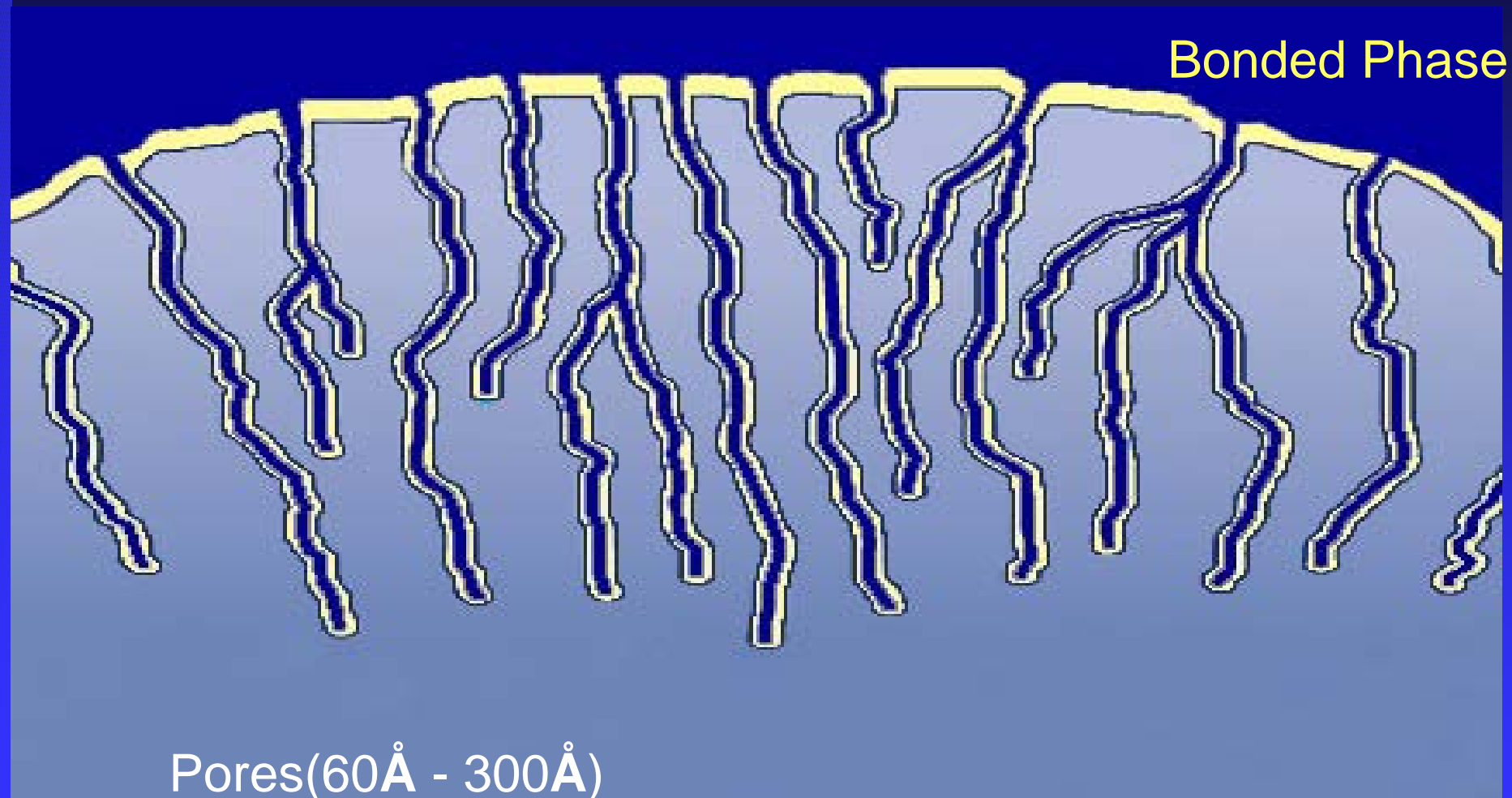
SEM Photo of Silica Particles
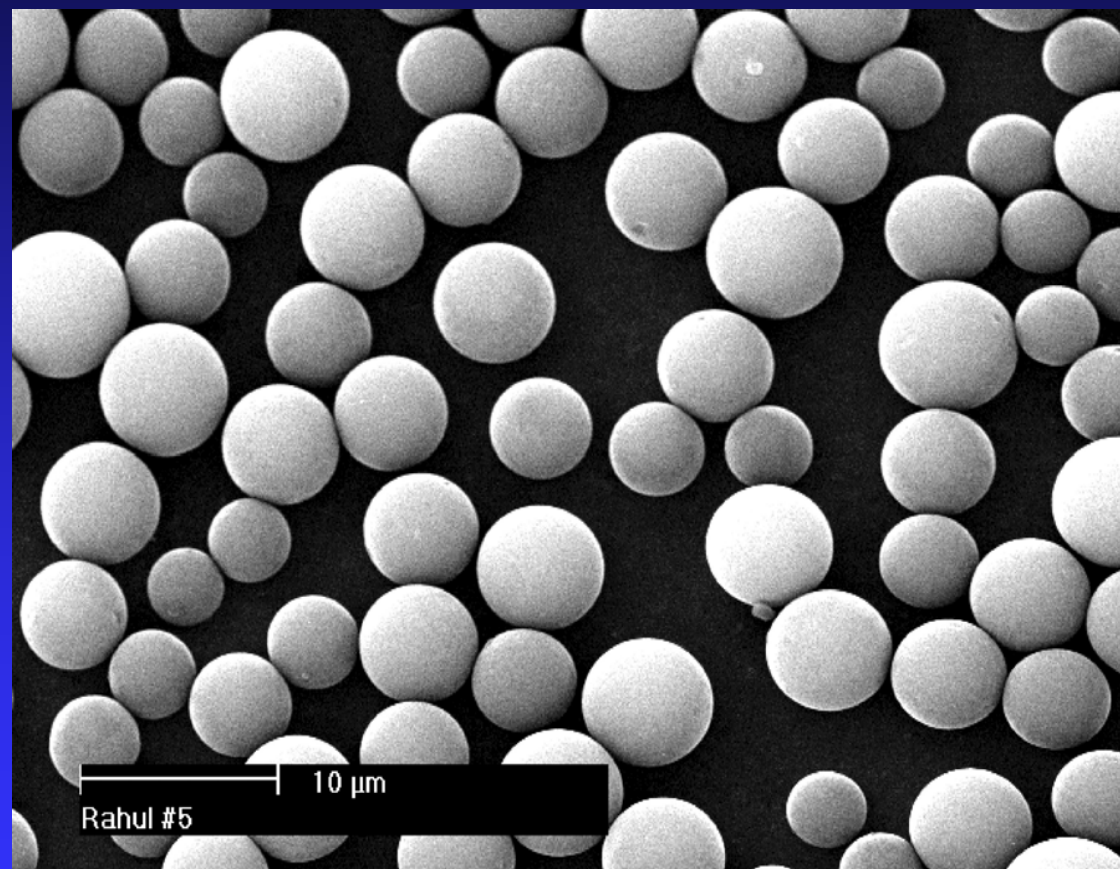
SEM Photo of Single Porous Silica Particle

Typical Illustration of a Silica Substrate

Bonded Phase

Pores(60Å - 300Å)

General Properties of Silica

➢   As the number of pores increase, the overall surface area increases.

➢   As the pore size increases, pore volume increases.

➢ Given a fixed pore volume, the materials having the smallest pores will have the largest available surface area.

Pore Size Versus Available Surface Area

Pore Size/Diam. (Å)	Surface Area (m^2/g)
60	300-600
100	150-300
200	75-150
300	50-75
500	30-40
1,000	20-30

Recommended Pore Sizes for Molecular Weight Ranges

Pore Size (Å)	MW* Range
50	< 1000
100	< 3000
500	500 - 20,000
1000	1,000 - 40,000
10,000	4,000 - 400,000
100,000	40,000 - 4,000,000
1,000,000	400,000 - 40,000,000
Mixed	500 - 10,000,000

*MW based on linear molecule

Gas Adsorption Analysis

- Mesoporous silica for HPLC exhibits a Type IV Isotherm and has pores in the range of 20 Å to 500 Å.

- Nitrogen gas is first adsorbed in the first cycle, then desorbed in the second cycle at liquid nitrogen temperatures (77.35K, 1 ATM)

- Nitrogen gas porosimetry is capable of providing information regarding surface area, pore volume, and pore size distributions to a limit of 16.2 Å² when using nitrogen gas at liquid nitrogen temperatures.
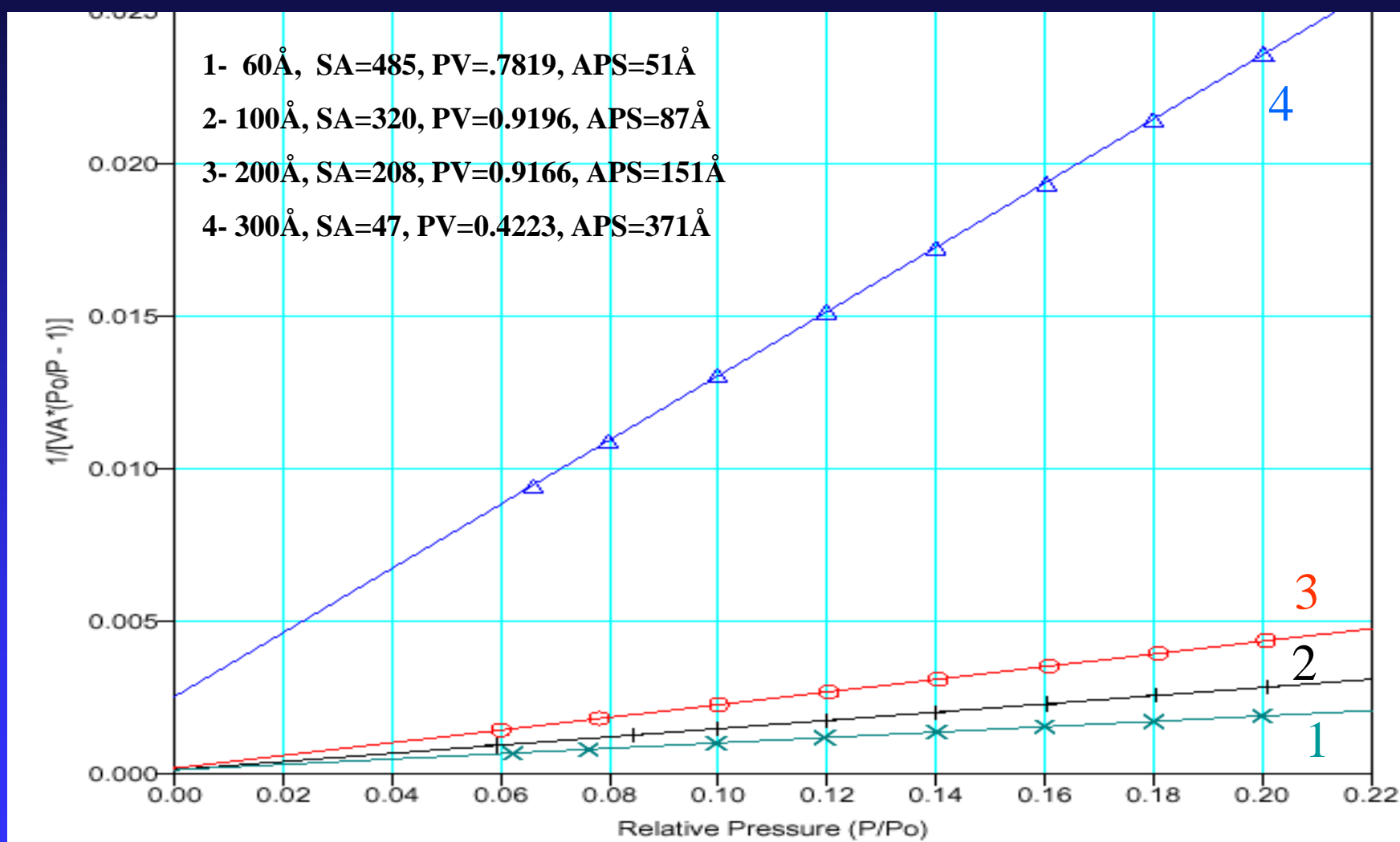
Isotherm absorption/desorption profiles of various silicas

1- 60Å, SA=485, PV=.7819, APS=51Å

2- 100Å, SA=320, PV=0.9196, APS=87Å

3- 200Å, SA=208, PV=0.9166, APS=151Å

4- 300Å, SA=47, PV=0.4223, APS=371Å
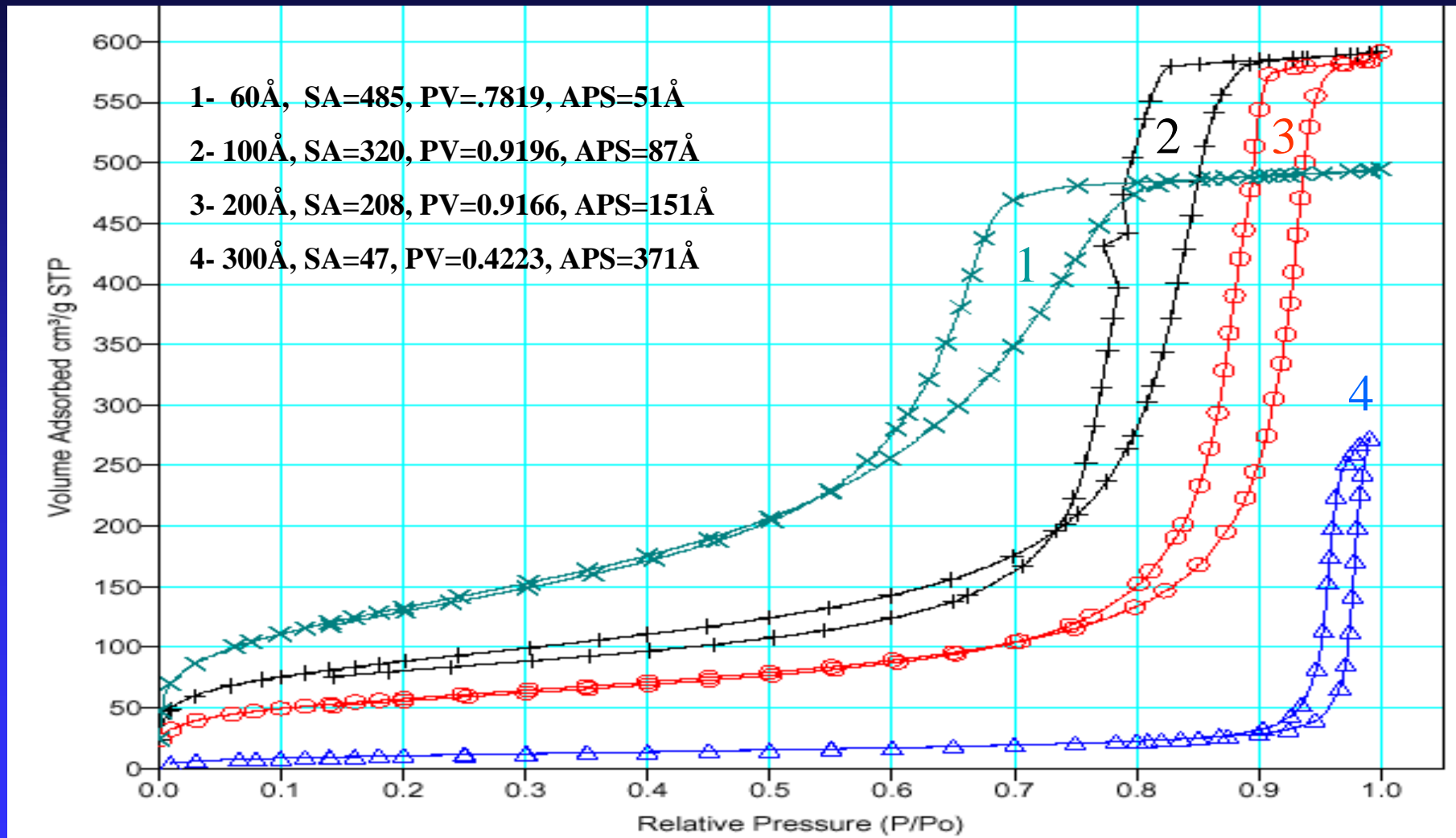
Isotherm Profile Analysis

- Hysteresis occurs because condensation (adsorption) and evaporation (desorption) within the pores are different processes.

- The great rise/fall in the slope of each curve indicates a large adsorption/desorption by pores of a specific size.

- A slow rise indicates a few pores are present, while a flat line reveals essentially no pores are present in the region.

- Pores fill from the smallest to the largest during the adsorption phase, and empty from the largest to the smallest during the desorption phase.

- The material having the largest pore volume, will have the tallest isotherm.

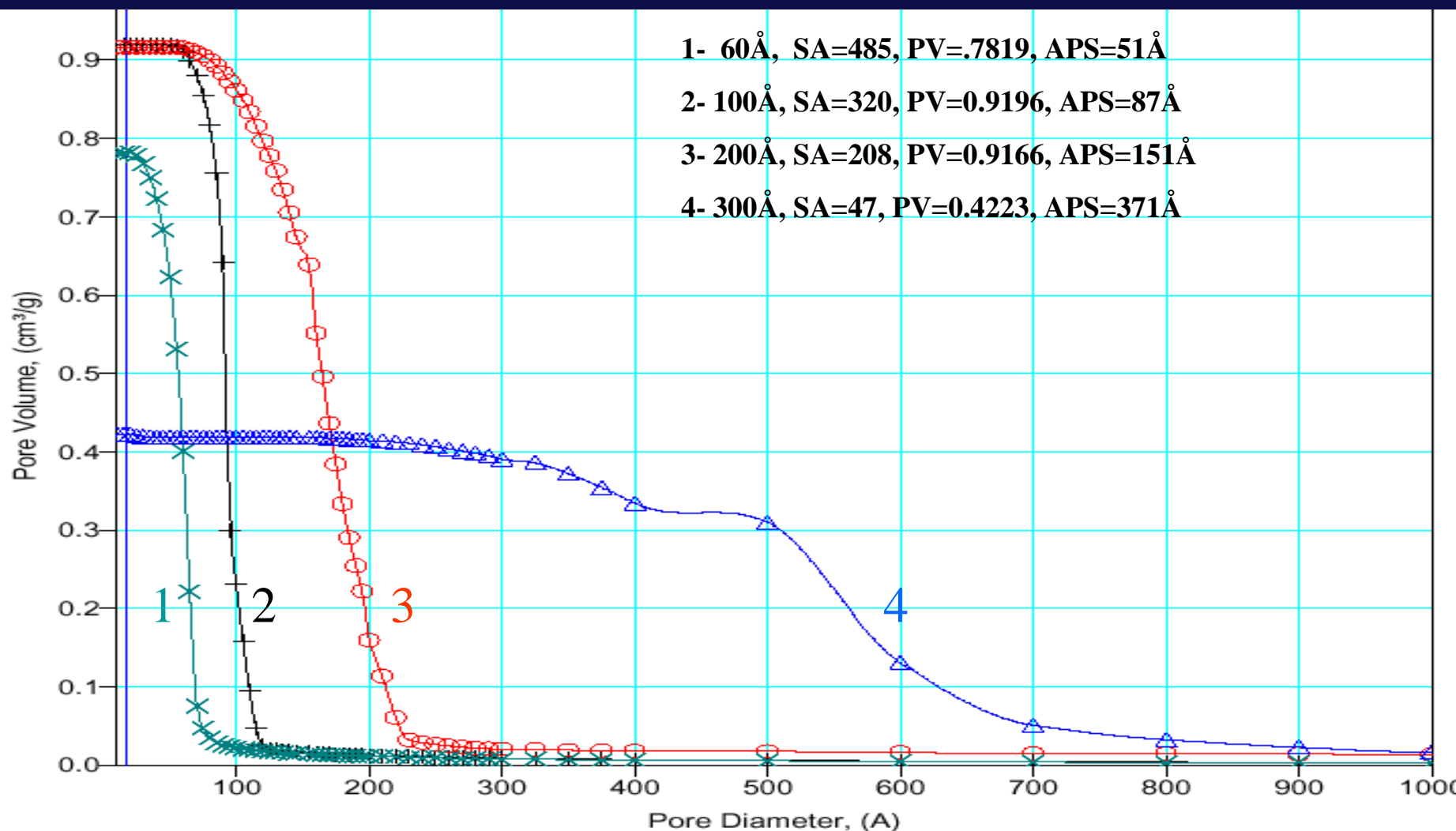- The material having the smallest pore size will have the quickest inflection.

BET Surface Overlay Plot

1- 60Å, SA=485, PV=.7819, APS=51Å

2- 100Å, SA=320, PV=0.9196, APS=87Å

3- 200Å, SA=208, PV=0.9166, APS=151Å

4- 300Å, SA=47, PV=0.4223, APS=371Å

BET Surface Area Interpretation

- BET theory named for Brunaeur, Emmett, and Teller incorporates the assumption of multimolecular layered adsorption within a pore.

- Assumes that the forces active to produce condensation of the gas are also responsible for the binding energy in multimolecular adsorption.

- The material having the lowest available surface area will come to equilibrium the fastest and will have the greatest slope.

- Theory assumes cylindrical pores, but the shape of pores can influence the adsorption rates. BET values are calculated during the adsorption cycle.
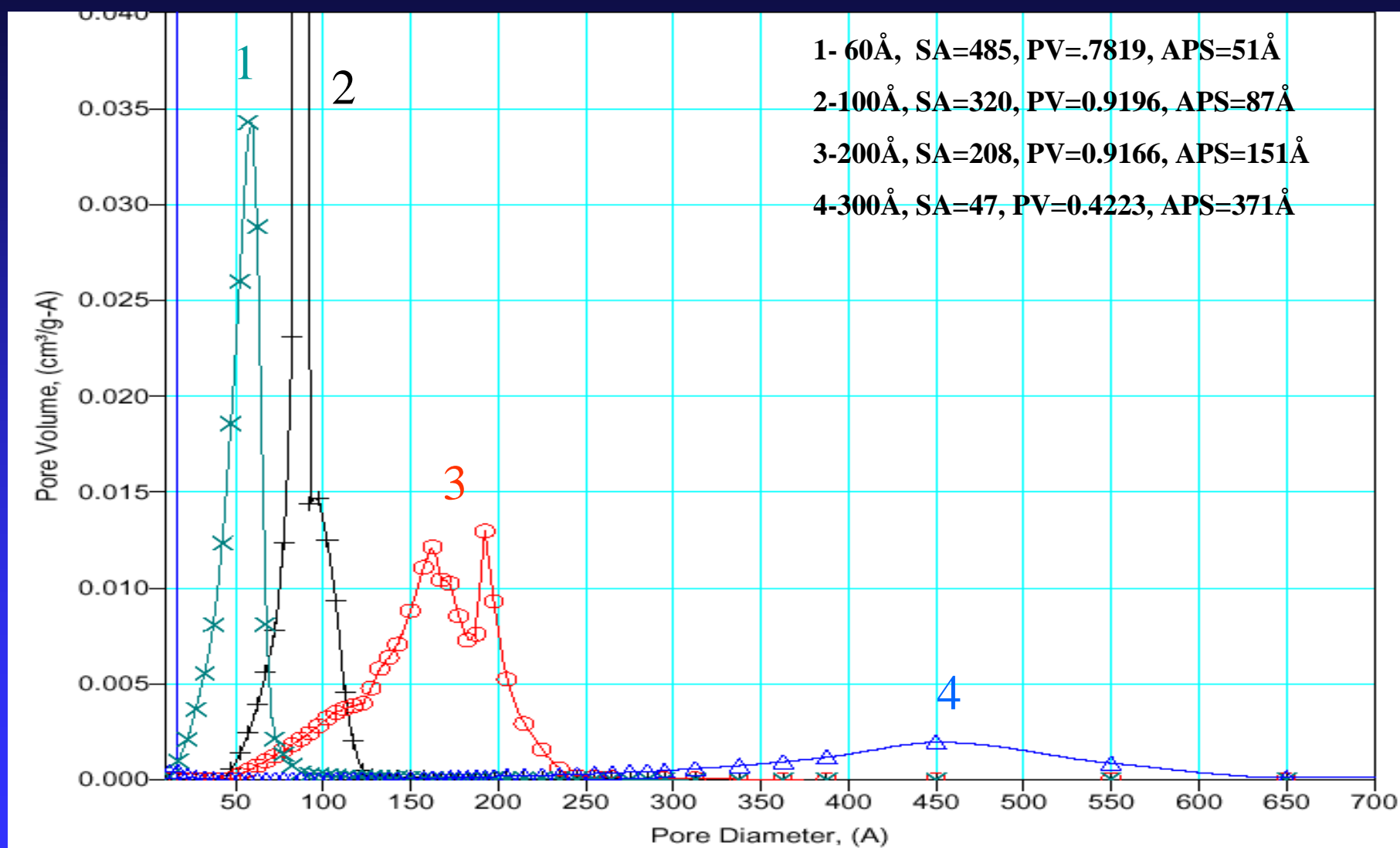
BJH Desorption Cumulative Pore Volume

1- 60Å, SA=485, PV=.7819, APS=51Å

2- 100Å, SA=320, PV=0.9196, APS=87Å

3- 200Å, SA=208, PV=0.9166, APS=151Å
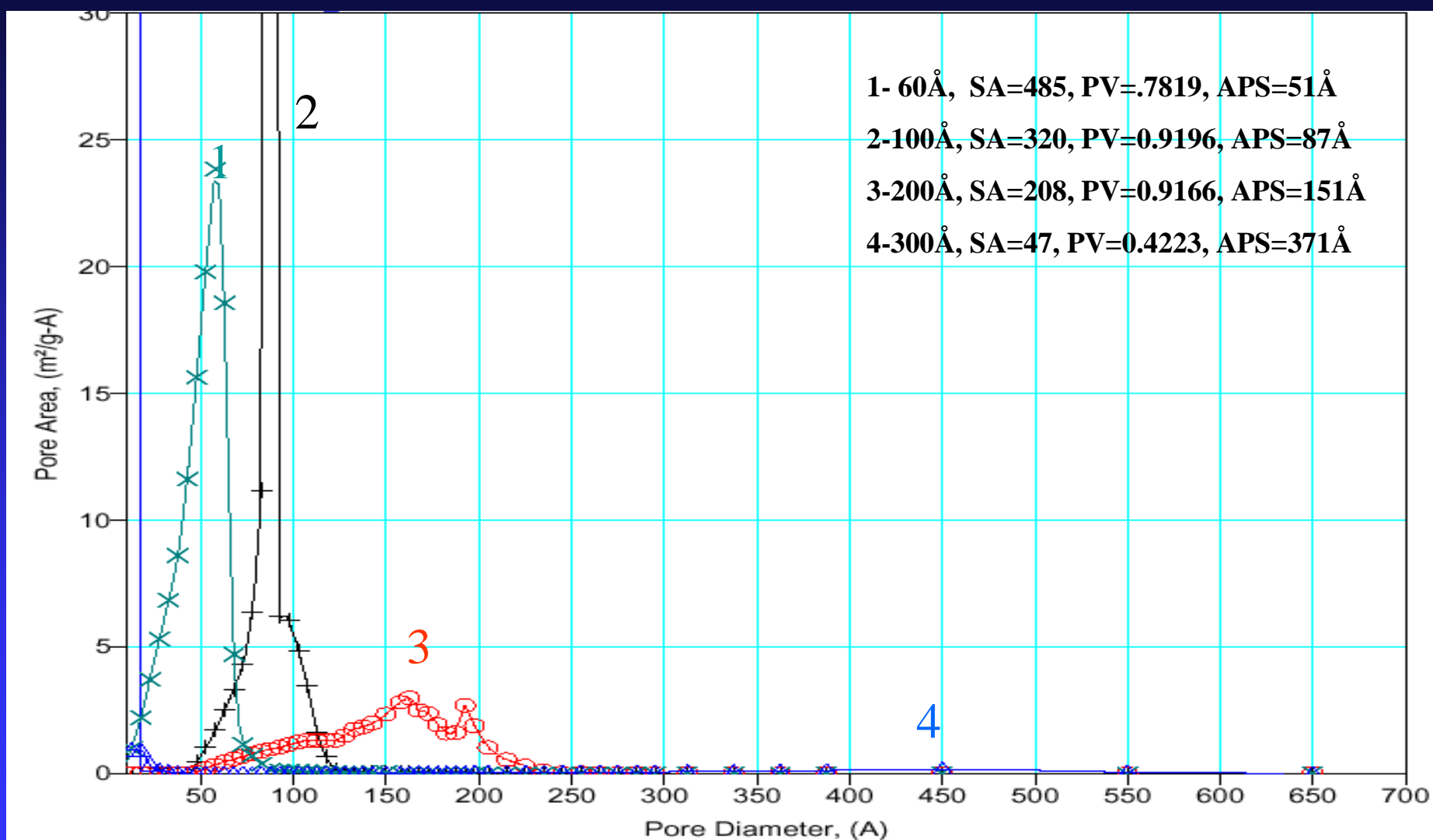
4- 300Å, SA=47, PV=0.4223, APS=371Å

Cumulative Pore Volume Analysis

- Named for calculations by Barret, Joyner, and Halenda
- Test reveals the amount of gas adsorbed/desorbed across the range of pores.
- During adsorption the smaller pores fill more quickly (right to left)
- During desorption the larger pores empty first (left to right).
- A sharper slope (toward +/- infinity) reveals a tighter pore distribution.
- When no gas is being adsorbed or desorbed the slope reaches zero for that region.

BJH Desorption dV/dD Pore Volume

1- 60Å, SA=485, PV=.7819, APS=51Å
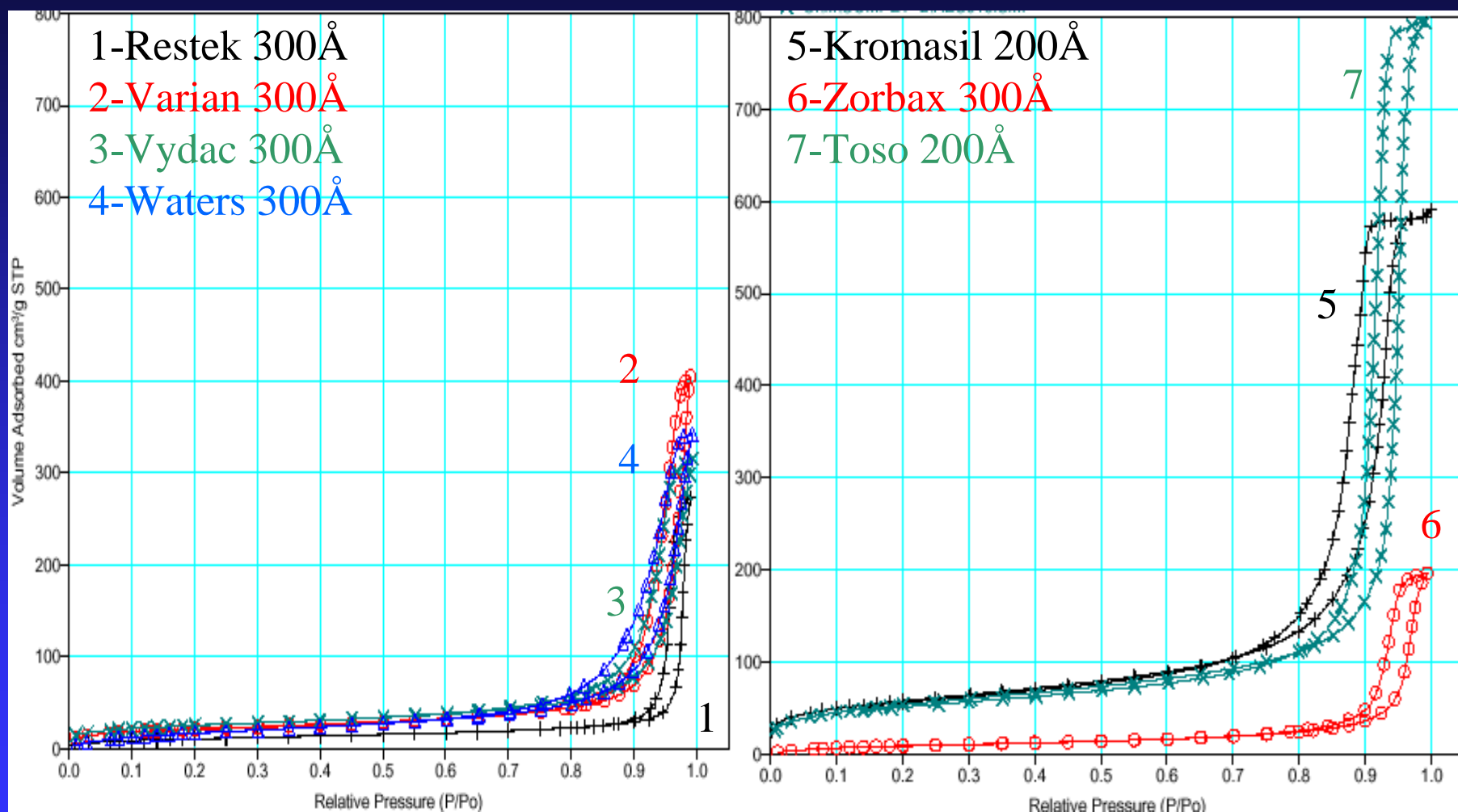
2-100Å, SA=320, PV=0.9196, APS=87Å

3-200Å, SA=208, PV=0.9166, APS=151Å

4-300Å, SA=47, PV=0.4223, APS=371Å

BJH Desorption dA/dD Pore Area

1- 60Å, SA=485, PV=.7819, APS=51Å

2-100Å, SA=320, PV=0.9196, APS=87Å

3-200Å, SA=208, PV=0.9166, APS=151Å

4-300Å, SA=47, PV=0.4223, APS=371Å

BJH dV/dD and dA/dD Interpretation

- Reports are generated during both the absorption and desorption data cycles.

- dV/dD reveals the porosity volume distribution in terms of cubic centimeters over the pore range. The dA/dD reveals the adsorption/desorption surface area contribution to the total surface area by individual pore sizes.

- A monoporous material would appear as a single straight line. The greater the number of a certain pore size, the greater the contribution to the total volume and total surface area.

- These factors are very important to insure that the analytes can enter and be separated within the pores of that size range.

- Area and volume profiles that overlay for a particular pore size range are good indicators of depth uniformity for the range (assuming a cylindrical pore.)
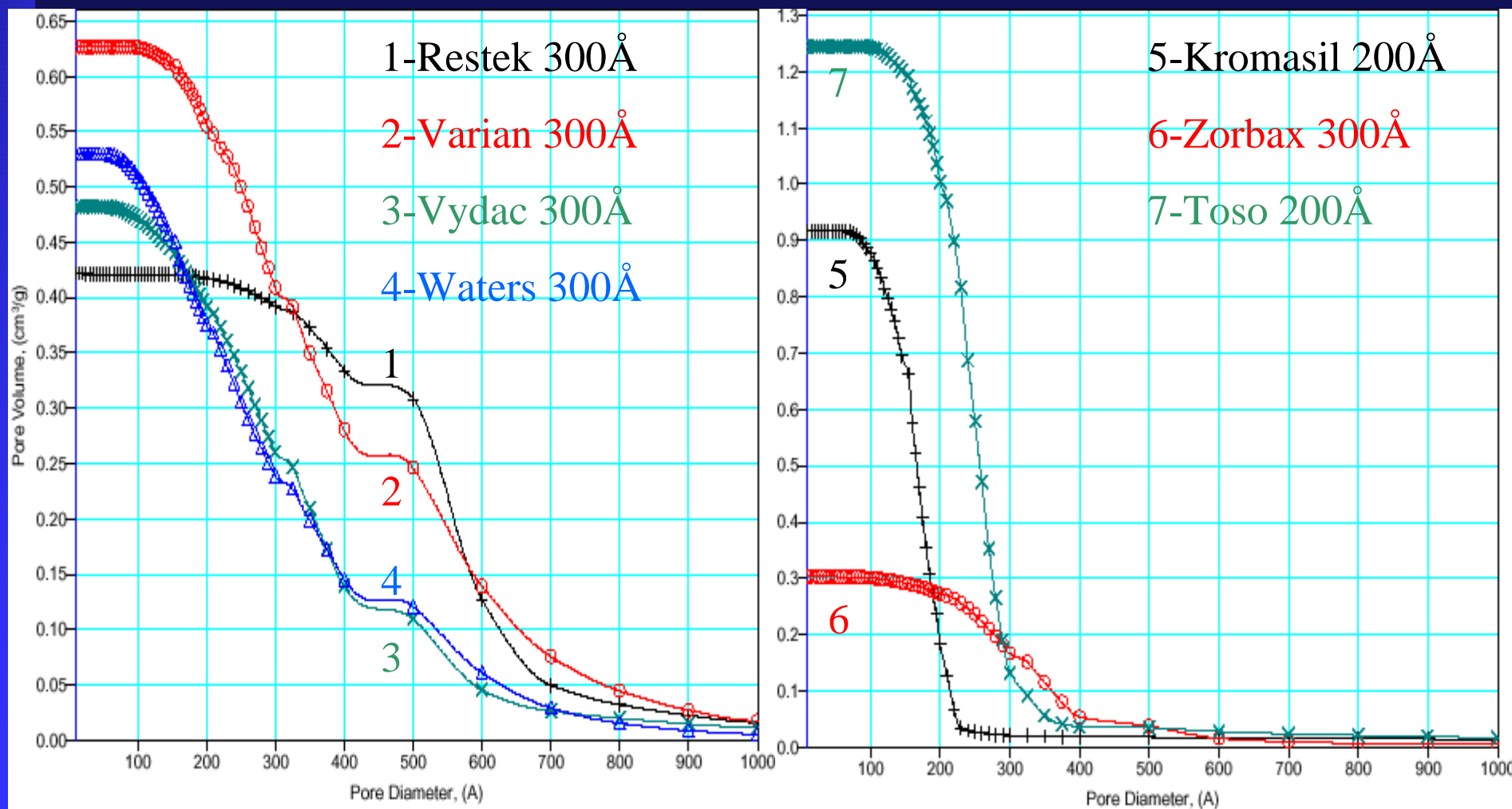
Properties of Analyzed Wide Pore Silica

- Some materials do not possess a high pore volume in the needed pore size ranges to create a highly retentive material for large molecules.

- Materials with high pore volumes in the 250Å-350Å range or larger should provide the greatest access for large molecular analytes with linear masses > 3000 daltons.

- A silica must have surface area within pore ranges accessible by the analyte to create stronger retentions and hopefully better selectivity.

- Silicas with narrow pore size distributions accessible by the analytes, may give further advantages in separations through subtle discrimination of hydrodynamic size differences between closely related analytes.
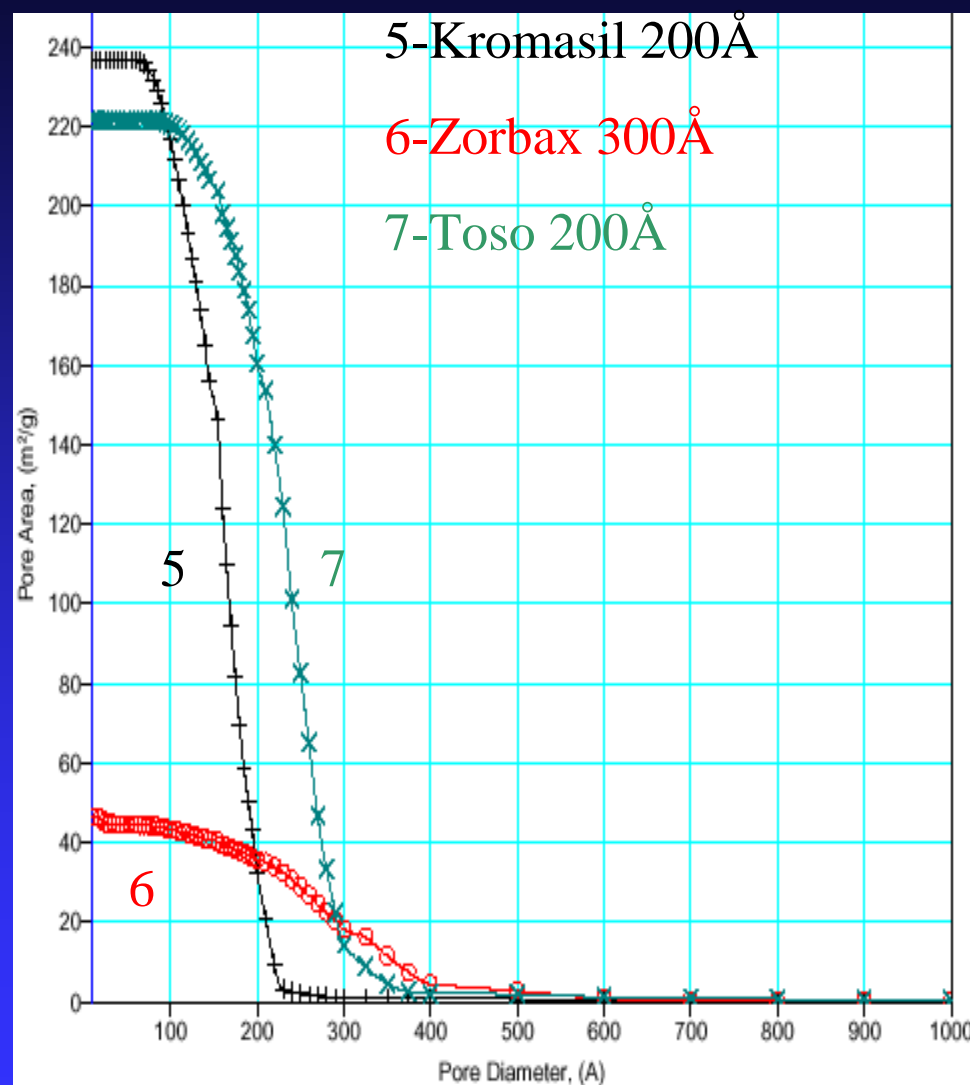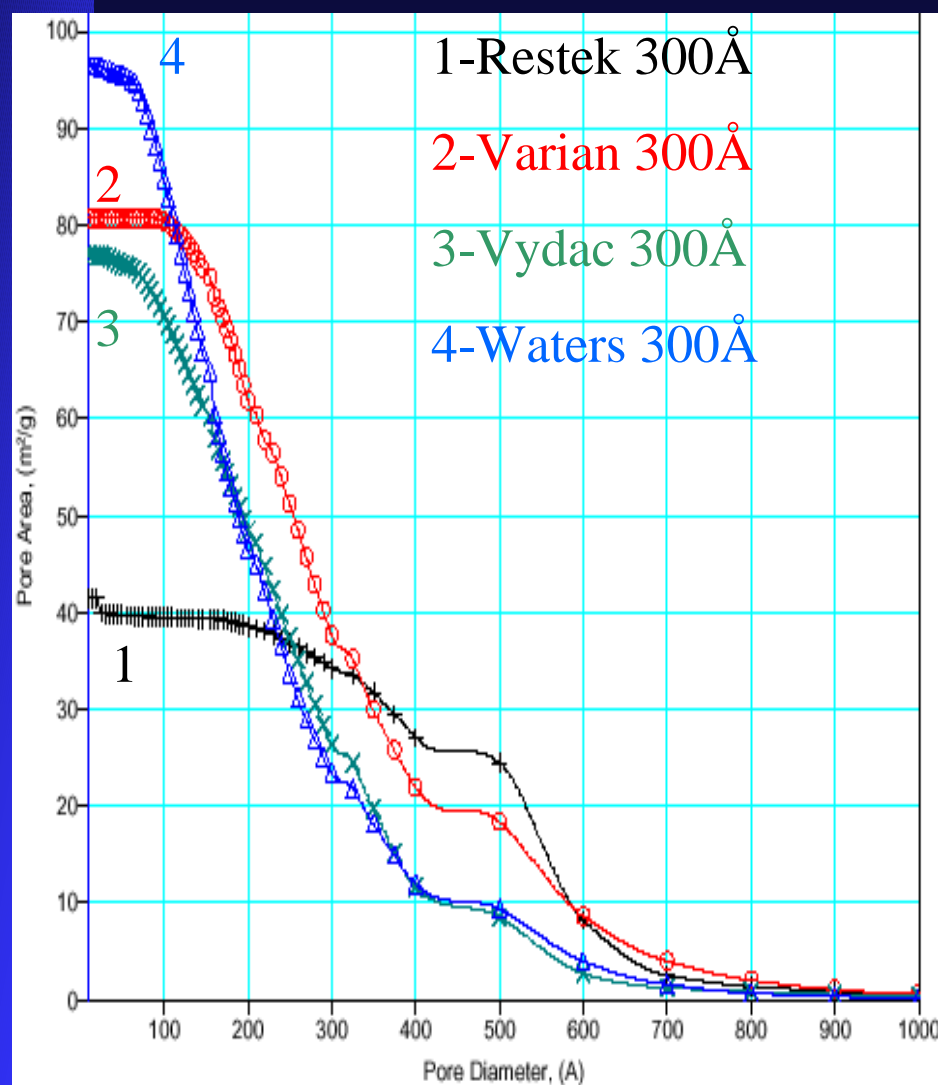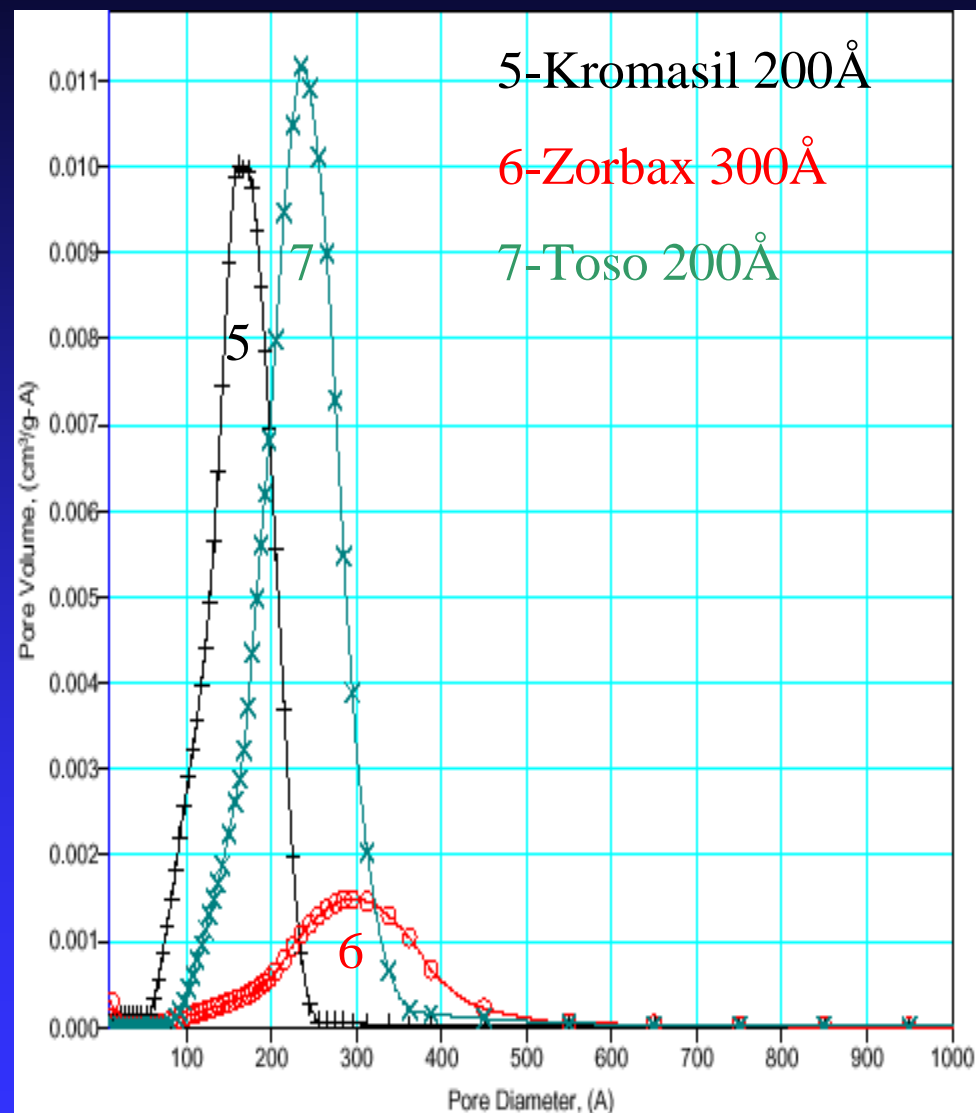
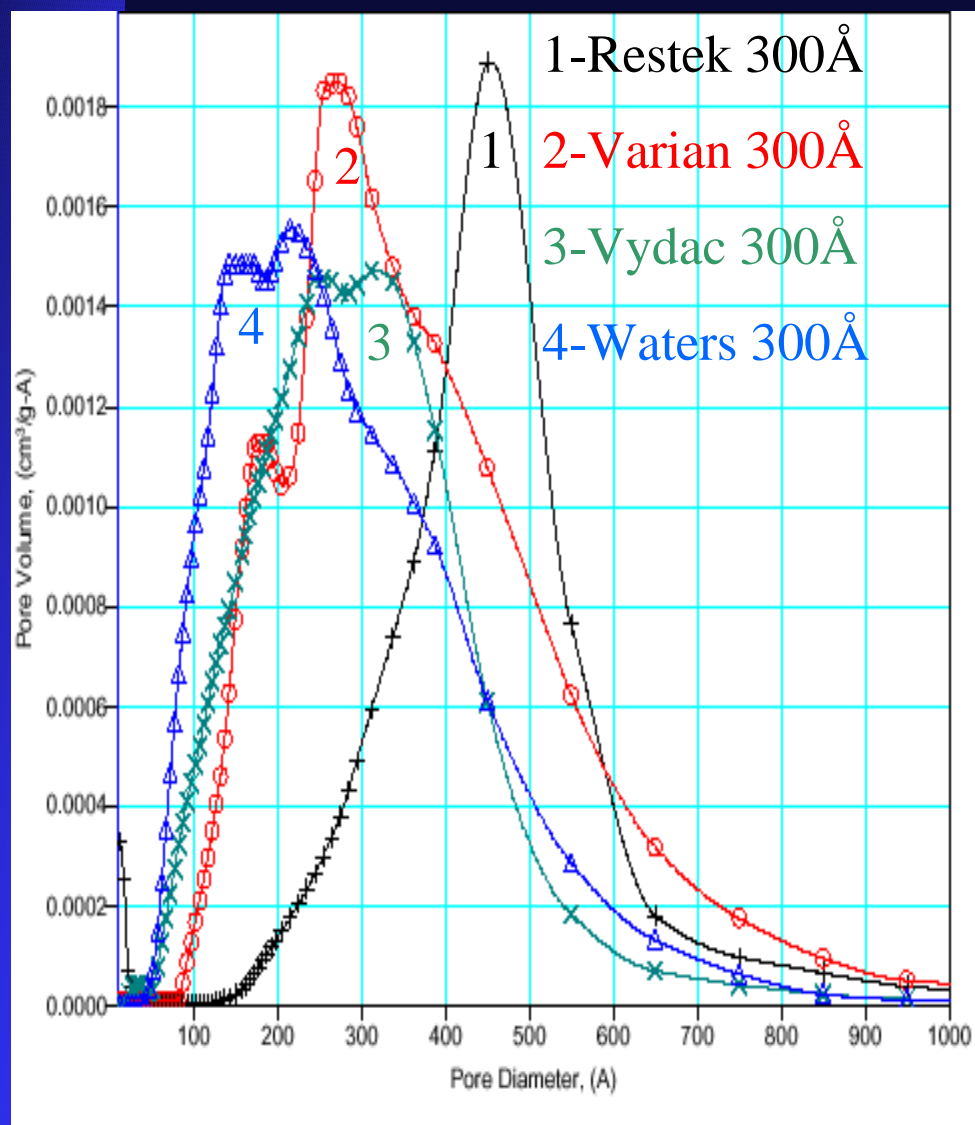# Isotherms of 300Å and 200Å Materials

1-Restek 300Å
2-Varian 300Å
3-Vydac 300Å
4-Waters 300Å

5-Kromasil 200Å
6-Zorbax 300Å
7-Toso 200Å

BJH Desorption Cumulative Pore Volumes

1-Restek 300Å

2-Varian 300Å

3-Vydac 300Å

4-Waters 300Å

5-Kromasil 200Å

6-Zorbax 300Å

7-Toso 200Å

BJH Desorption Cumulative Pore Area

1-Restek 300Å

2-Varian 300Å

3-Vydac 300Å

4-Waters 300Å

5-Kromasil 200Å

6-Zorbax 300Å

7-Toso 200Å

BJH Desorption dV/dD Pore Volume

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2-Varian 300Å
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BJH Desorption dA/dD Pore Area

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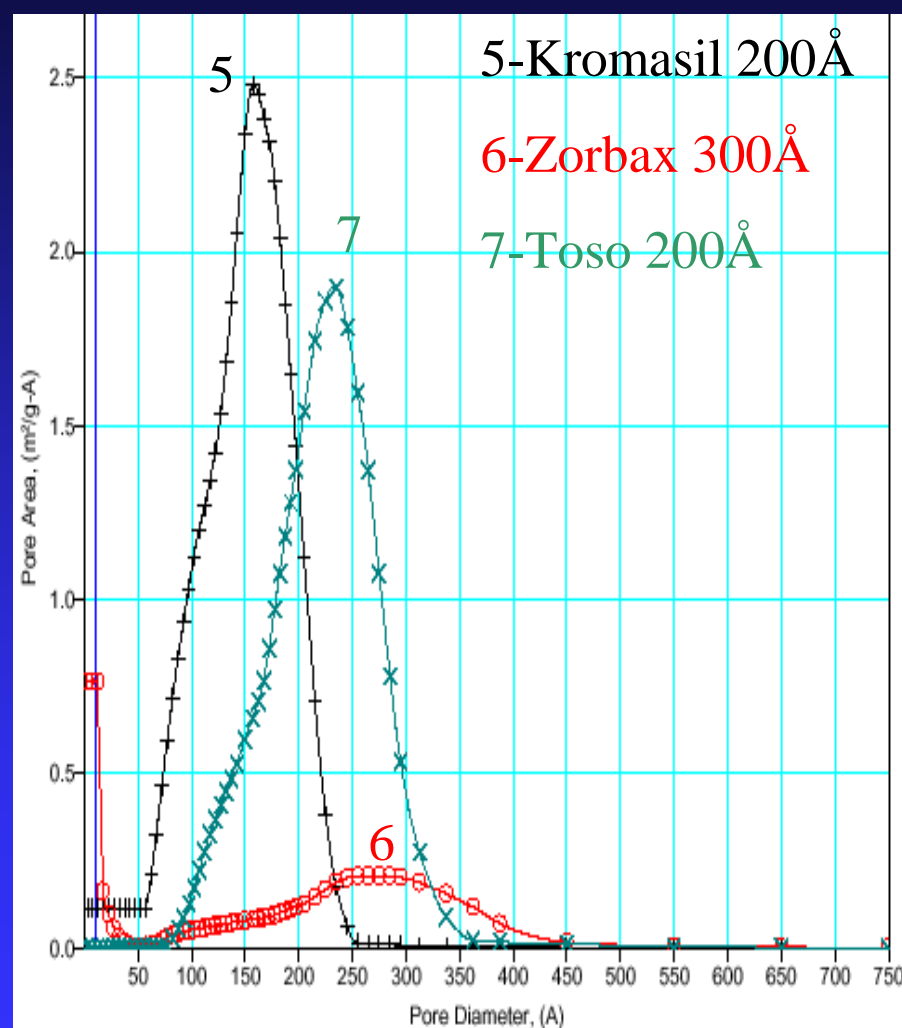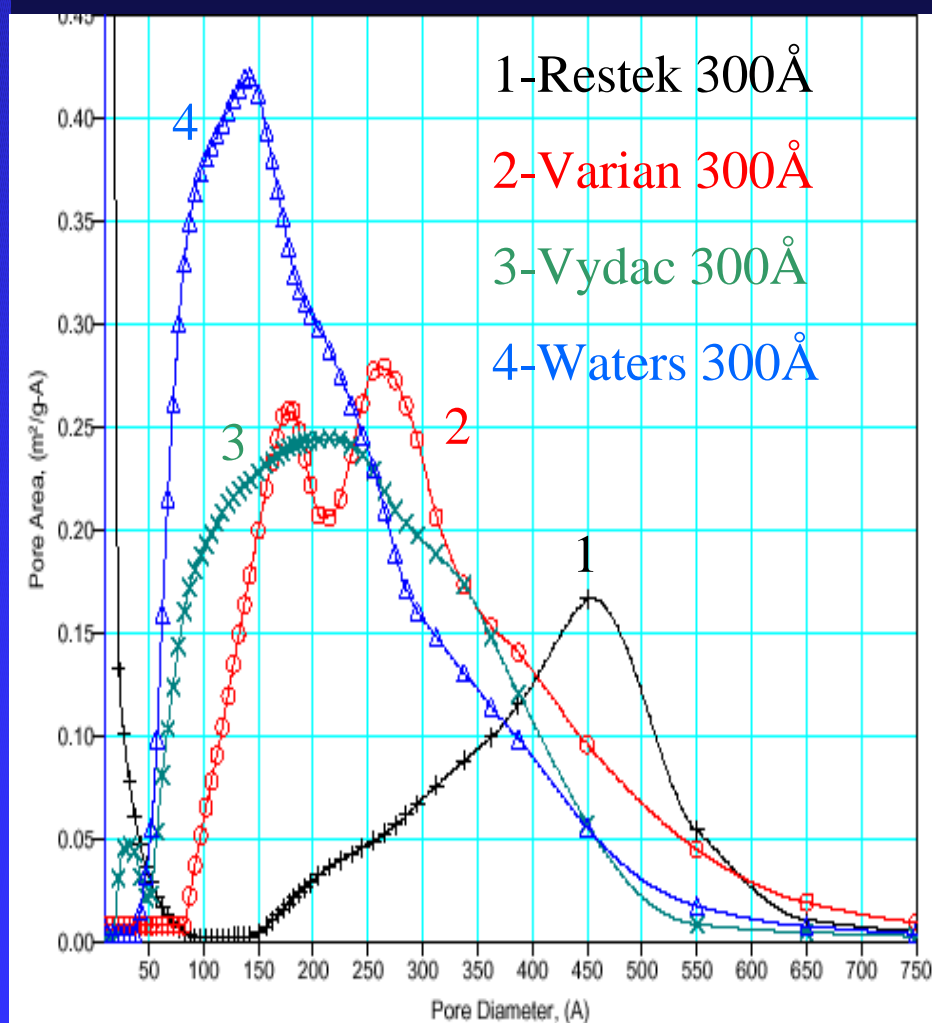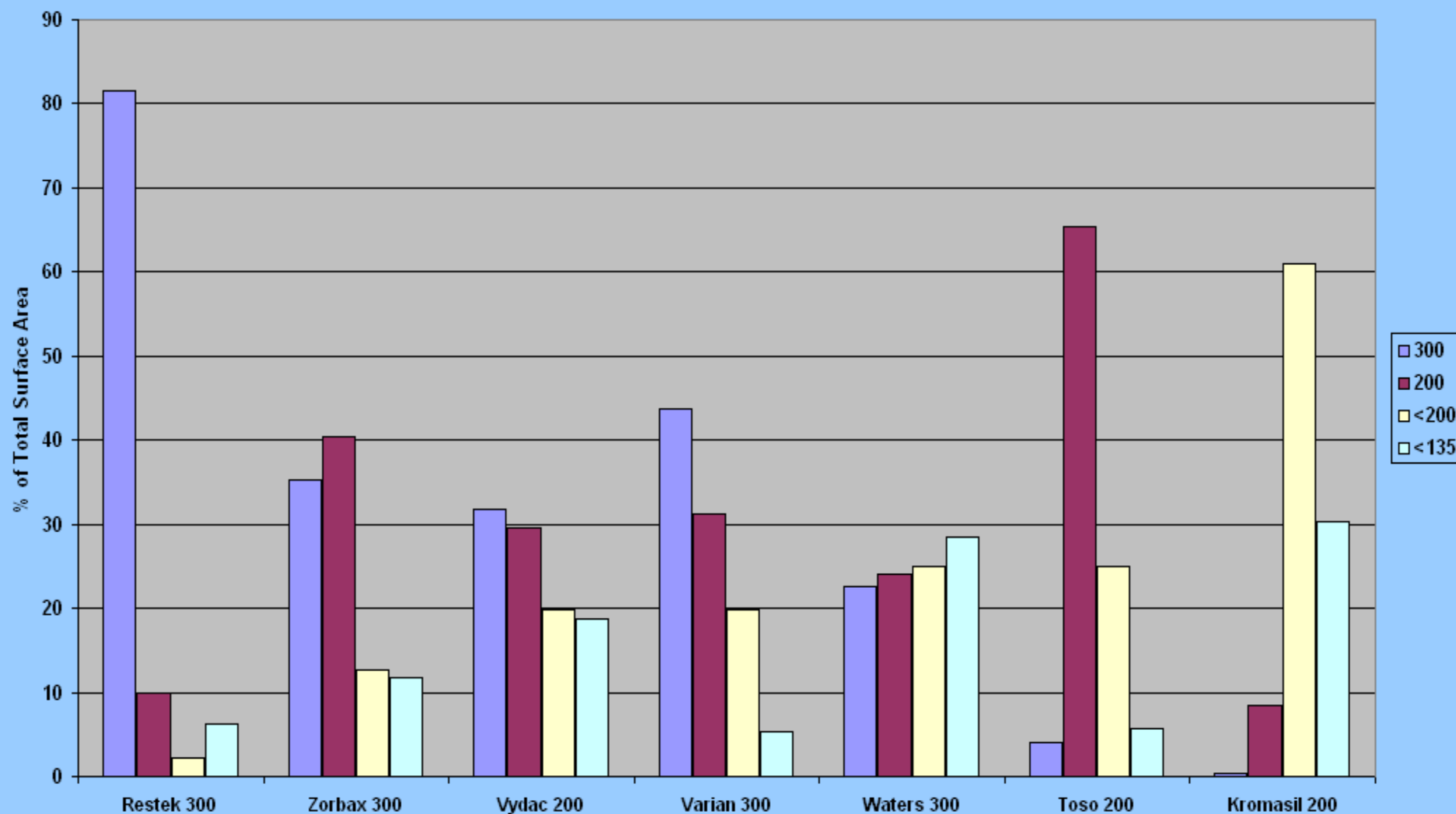
Surface Area Distribution for Pore Size Range (Angstroms)
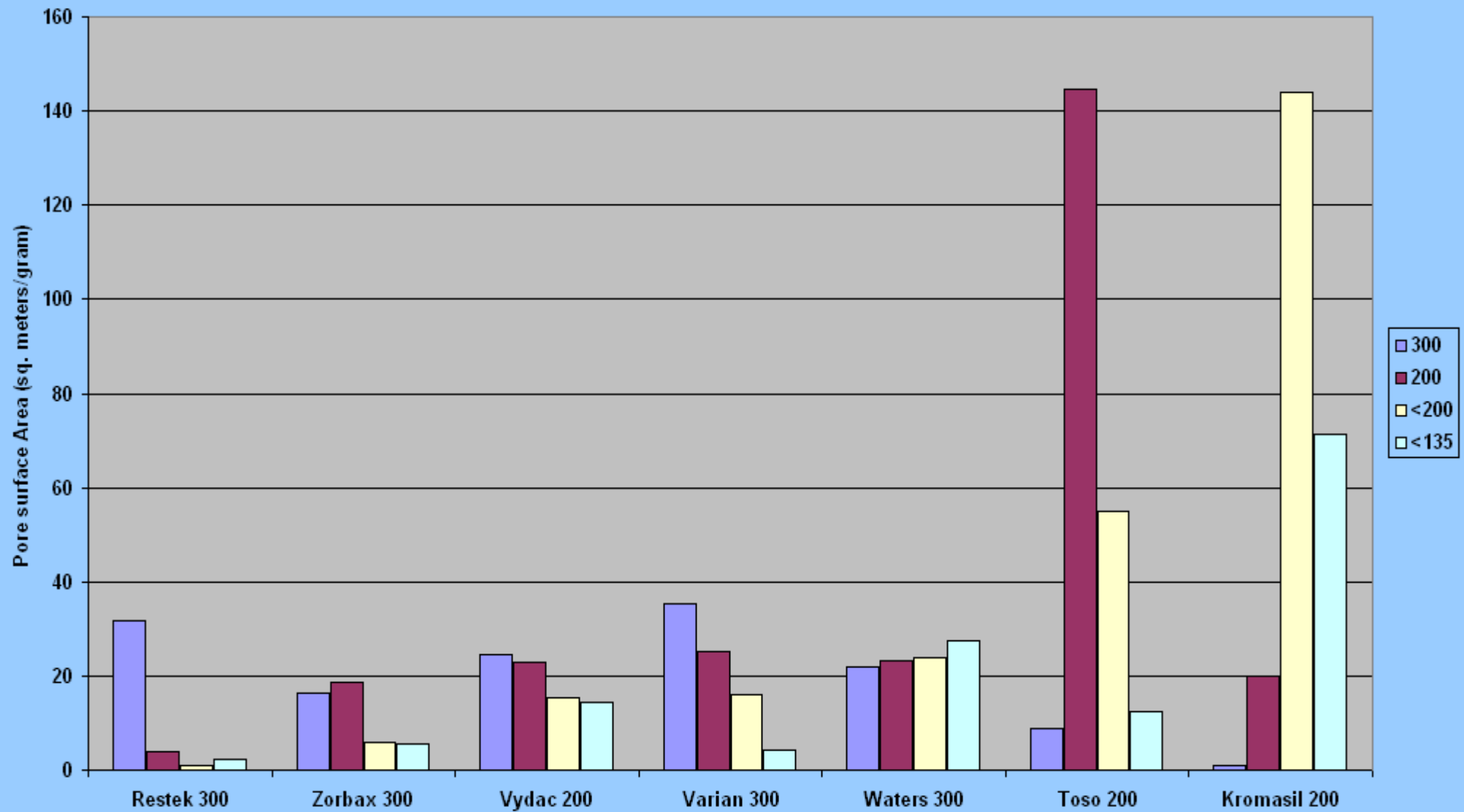
% of Total Available Surface Area by Pore Size Range (Angstroms)

Surface Area vs Pore Size Range (meters²/gram)

	300 Å	200 Å	Total Surface
Varian 300	35.2	25.2	80
Restek 300	31.9	3.9	39
Vydac 200	24.5	22.8	77
Waters 300	21.8	23.2	96
Zorbax 300	16.4	18.8	47
Toso 200	9.0	144.7	221
Kromasil 200	0.9	20.0	236

Unaccounted pore areas are in regions less than 200 Å

Conclusions

- Wide Pore Silica can vary widely in available surface area and pore distribution.

- The more narrow the desorption profile, the greater the available surface area near the pore mean.

- The more narrow the desorption profile, the more theoretical discrimination in size between molecules of similar molecular masses.

- Less than 30% of the available surface area may be available to molecules requiring a 300Å or larger pore size.

- Know the pore size distribution of your material.