Characterization of Adsorbents for Sample Preparation Processes

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Introduction

- Overview of Adsorbents Program at Supelco
  - thermodynamic studies
  - kinetic studies

- Future of Adsorbents Program at Supelco

Introduction

Supelco's commitment to adsorbents technology has been on-going for more than 2 decades. The research and development effort has been broad in scope, and has ranged from purification process development to research focusing on the thermodynamic and kinetic properties of adsorbents. Understanding the performance characteristics of adsorbents has been our primary goal.

One of the primary projects focused on the thermodynamic properties of two key groups of carbons, the graphitized carbon blacks (GCBs) and the carbon molecular sieves (CMSs).

Other adsorbents (i.e., porous polymers, zeolites, silica gels, etc.) were also investigated, however with the limits of detection stepping progressively lower over the last 2 decades, the use of thermal desorption becoming increasingly necessary, the use of thermally stable adsorbents (i.e., the GCBs and the CMSs) became necessary as well. The emphasis on the data presented in the following series of slides will be for this desorption technique.

The following slide illustrates a table which provides a physical description of the carbons currently prepared at Supelco, as well as some other commercially available adsorbents.

The GCBs and the CMSs have been found to function well in thermal desorption applications, and the reasons for these performance characteristics will be addressed.

PHYSICAL CHARACTERISTICS OF SUPELCO CARBON/OTHER ADSORBENTS

Adsorbent	BET surface area (m2/g)	density (g/mL)	porosity micro-pores (cc/g)	meso- (cc/g)	macro- (cc/g)	pore diameter (Å)
graphitized carbons						
Carbopack X	240	0.41	^	0.62	^	100
Carbopack Z	220	0.18	^	1.73	^	255
Carbopack B	100	0.35	^	^	^	N/A
Carbopack Y	24	0.42	^	^	^	N/A
Carbopack C	10	0.68	^	^	^	N/A
Carbopack F	5	0.64	^	^	^	N/A
carbon sieves						
Carboxen-563	510	0.53	0.24	0.15	0.24	7-10
Carboxen–564	400	0.60	0.24	0.13	0.14	6-9
Carboxen-569	485	0.58	0.20	0.14	0.10	5-8
Carboxen-1000	1200	0.48	0.44	0.16	0.25	10-12
Carboxen-1001	500	0.61	0.22	0.13	0.11	5-8
Carboxen-1002	1100	0.43	0.36	0.28	0.30	10-12
Carboxen-1003	1000	0.46	0.38	0.26	0.28	5-8
Carboxen-1006	715	-----	0.29	0.26	0.23	7-10
Carboxen-1010*	675	0.60	0.35	^	^	6-8
Carboxen-1011	1100	0.48	0.41	0.19	0.24	10-12
Carboxen-1012	1500	0.50	^	0.66	^	19-21
Carboxen-1016	75	0.52	^	0.34	^	^
Carbosieve S-III	820	0.61	0.35	0.04	^	4-11
Carbosieve S-II	1059	-----	0.45	0.01	^	6-15
Carbosieve G	1160	-----	0.49	0.02	^	6–15
NASA 20/45 (Carboxen-1017)	61	0.55	^	0.33	^	^
Supelcarb	1150	0.46	0.47	0.26	0.28	5-8
Tenax-TA	24	0.18	^	0.007	0.046	N/A
Tenax-Gr	22	0.19	^	0.005	0.060	N/A
Activated charcoal	1000	0.44	0.43	0.44	^	4–20
XAD-2	375	0.32	0.10	0.63	0.10	10–20
Mol sieve 5Å	520	0.60	0.21	0.09	^	4–6
Mol Sieve 13X	585	0.55	0.23	0.08	^	4-10

* microporous, monoporous carbon sieve with pores = 7.0 +/- 1.0 Å
^ pores do not exist in this region
N/A not applicable

Description of Terms

carbon black : a pure, granular (i.e., pentagonal shape) carbon, typically prepared above 1200ºC, which possesses graphite-like properties; these graphitic properties can be further categorized as turbostratic (0.365Å layer distance) or graphitic (0.335Å layer distance); typically non-porous; predominant sp^2 hybrid orbitals

graphitized carbon black : a carbon black further treated at >2500°C

carbon molecular sieve : an amorphous, spherical carbon possessing pores which can range from microporous to macroporous; typically prepared from porous polymers; also termed polymer carbons; predominant sp^3 hybrid orbitals

pores : any cavity present on a solid surface which has a depth:width ratio of ~10:1

pore size: macropore : > 500Å
mesopore : 20 - 500Å
macropore : < 20Å

Description of terms (continued)

porosimetry : the analytical tool used to measure pores

adsorption : the enrichment of one or more components in an interficial layer, when an adsorbate comes in contact with an adsorbent surface

adsorption isotherm : relation, at constant temperature, between the amount adsorbed and the equilibrium pressure of the gas

desorption : denotes the converse of adsorption, in which the amount adsorbed decreases

DFT plot : density functional theory relating/plotting the relative pressure established by the amount of gas adsorbed and the pore diameter of the adsorbent filled at the pressure obtained

Thermodynamic Properties

The use of gas-solid chromatography (GSC) and inverse-gas chromatography (IGC) has been used as the analytical tool to characterize the thermodynamic properties of the adsorbents.

Classification of the adsorbents and adsorbates (analytes) followed historical IGC efforts, as follows:

Classification of Adsorbents and Adsorbates

Adsorbate molecules	Adsorbents: Type I	Type II	Type III
Group A Spherically symmetrical shells σ bonds	Nonspecific interactions/dispersion forces		
Group B Electron density concentrated on bonds/links π bonds	Nonspecific interactions	Nonspecific and specific interactions	
Group C (+) charge on peripheral links	Nonspecific interactions	Nonspecific and specific interactions	
Group D Concentrated electron densities (+) charge on adjacent links	Nonspecific interactions	Nonspecific and specific interactions	

Further Classification of Adsorbents and Adsorbates (Kiselev)

Adsorbent	Surface	Classification (Kiselev)
GCB	graphitic carbon	Type I
CMS	amorphous carbon	weak Type III
activated siliica gel	oxides of silica	Type II
activated charcoal	oxides of amorphous carbon	Type III
porous polymers	amorphous “plastics”	weak to strong Type III

Adsorbate

Group A: n-alkanes
Group B: aromatic hydrocarbons, chlorinated hydrocarbons, ketones
Group C: organometallics
Group D: organic acids, organic bases, aliphatic alcohols

The primary equations utilized for the IGC studies were:

Specific Retention Volume

$$V^t_g = j\, F_c \frac{(t_r - t_a)}{W_a}$$

where: j = pressure correction factor
: F_c = flow rate
: t_r = adsorbate absolute retention time
: t_a = system dead volume
: W_a = adsorbent bed weight
: V^t_g = specific retention volume

Adsorption Coefficient

$$K_a = \frac{V^t_g}{A°_s\, R\, T_k}$$

where: $A°_s$ = surface area of adsorbent
: R = universal gas constant
: T_k = temperature

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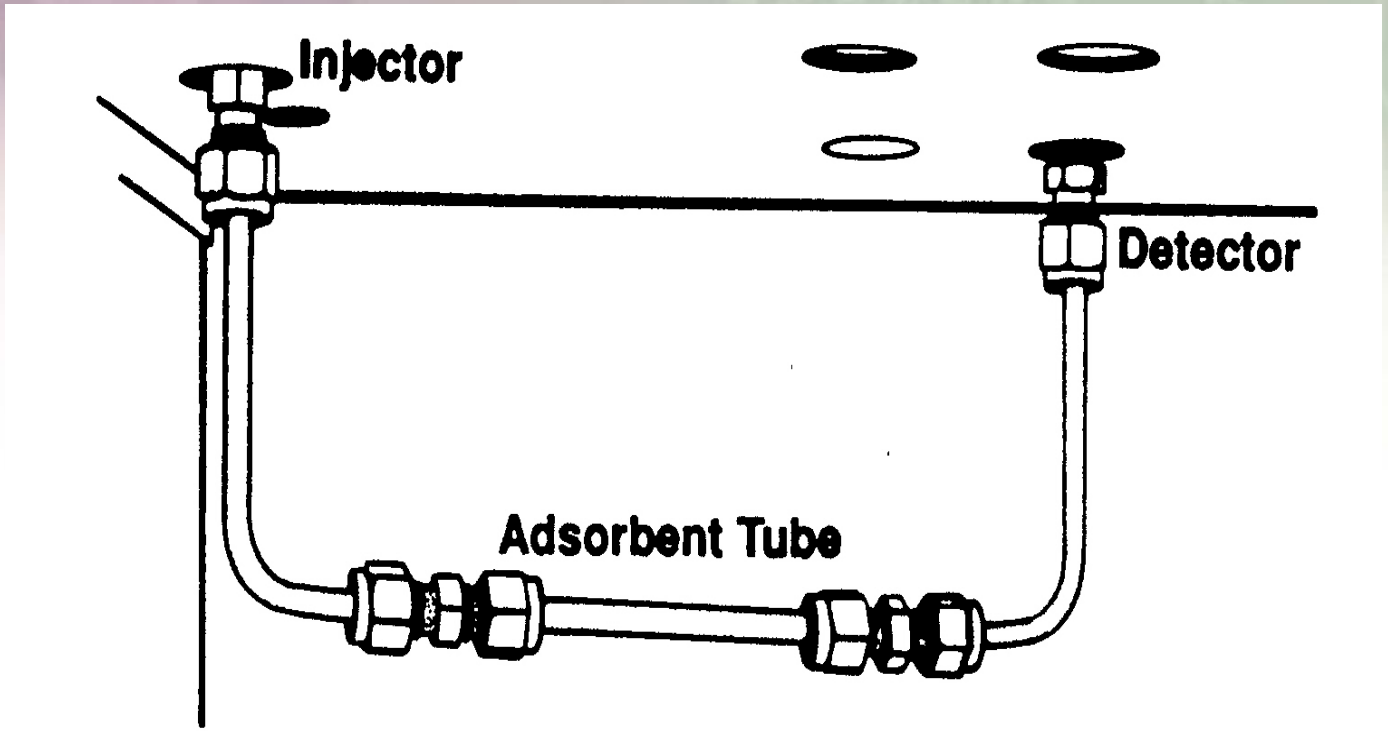
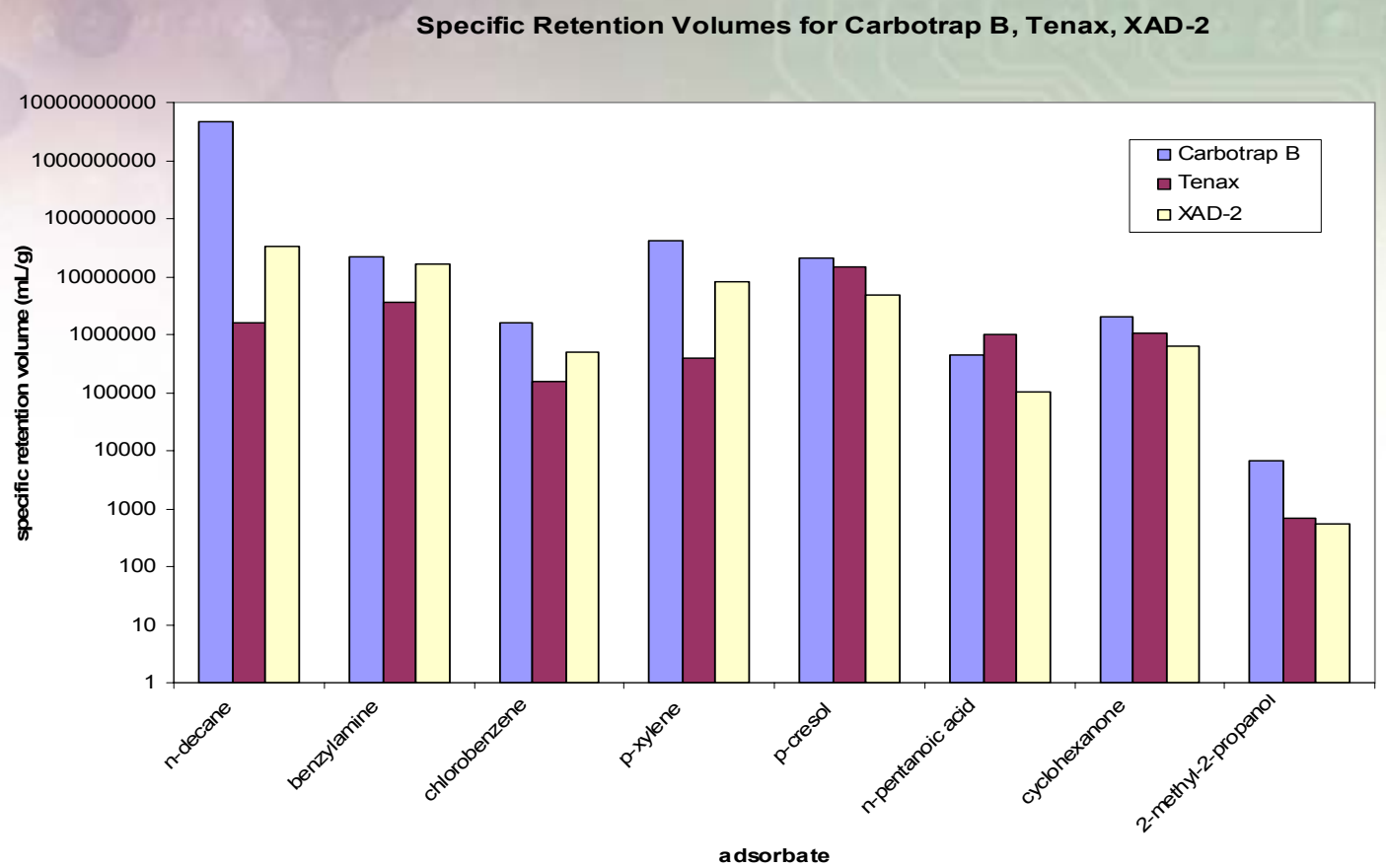
The IGC system used for these thermodynamic studies is illustrated below.



Comparative Study Data for Carbotrap B, Tenax and XAD-2



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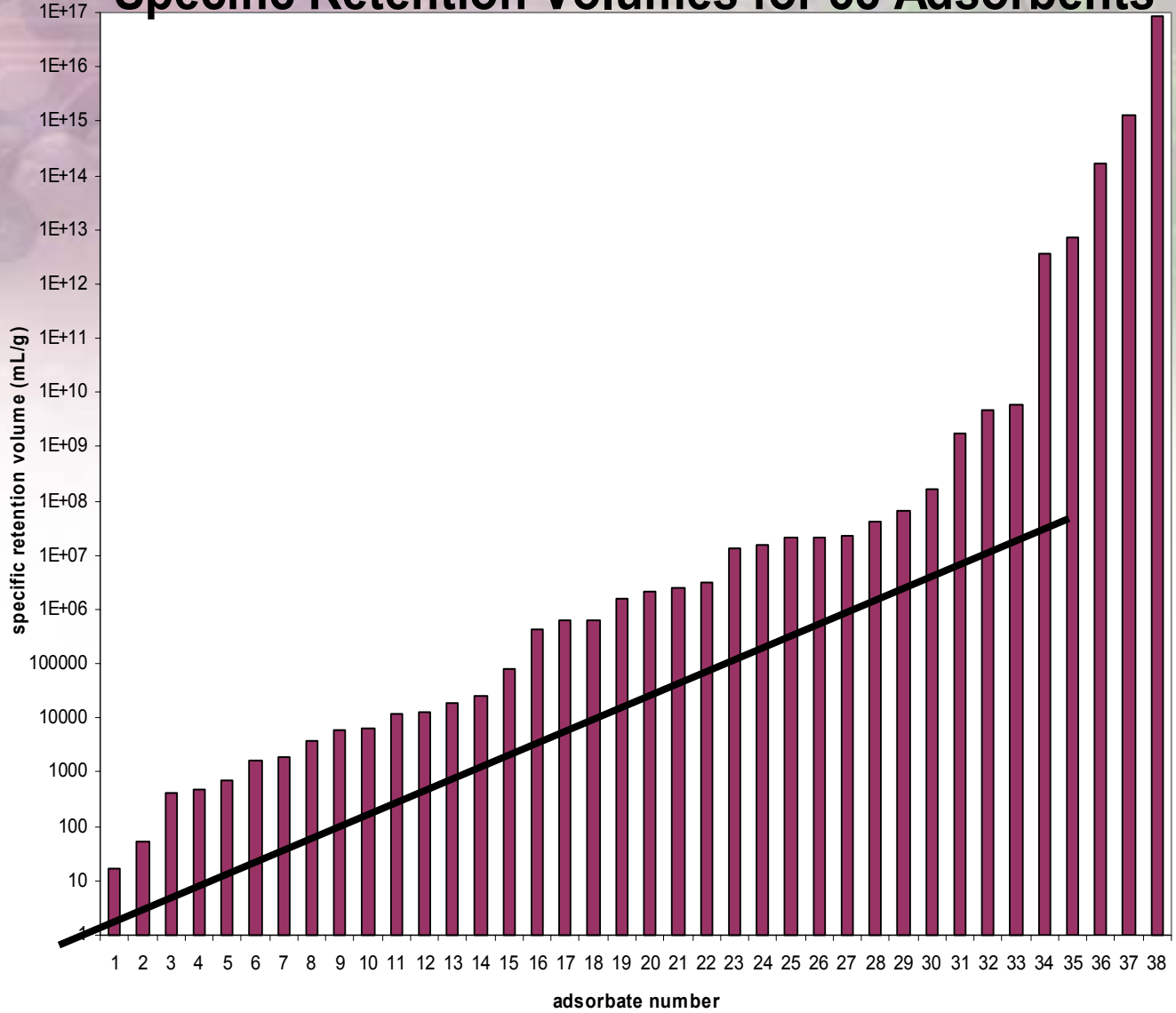
Further studies involving Carbotrap B indicated that Type I adsorption behavior was present. The following list of compounds could be ranked by breakthrough volume or molecular size, molecular weight or molecular polarizability.

ethane
n-propane
n-butane
ethanol
acetic acid
propionic acid
1,2-dichlorethane
2-butanone
n-pentane
2-methyl-2-propanol
benzene
1,1,2-trichloroethylene
n-butanol
1,1,2-trichloroethane
n-hexane
n-pentanoic acid
phenol
toluene
chlorobenzene
cyclohexanone
n-butylamine
4-heptanone
dichlorobenzene
n-octane
ethylbenzene
p-cresol
benzylamine
p-xylene
acetophenone
isopropylbenzene
n-propylbenzene
n-decane
n-butylbenzene
biphenyl
n-hexylbenzene
n-dodecane
n-octylbenzene
n-tetradecane

Specific Retention Volumes for 38 Adsorbents



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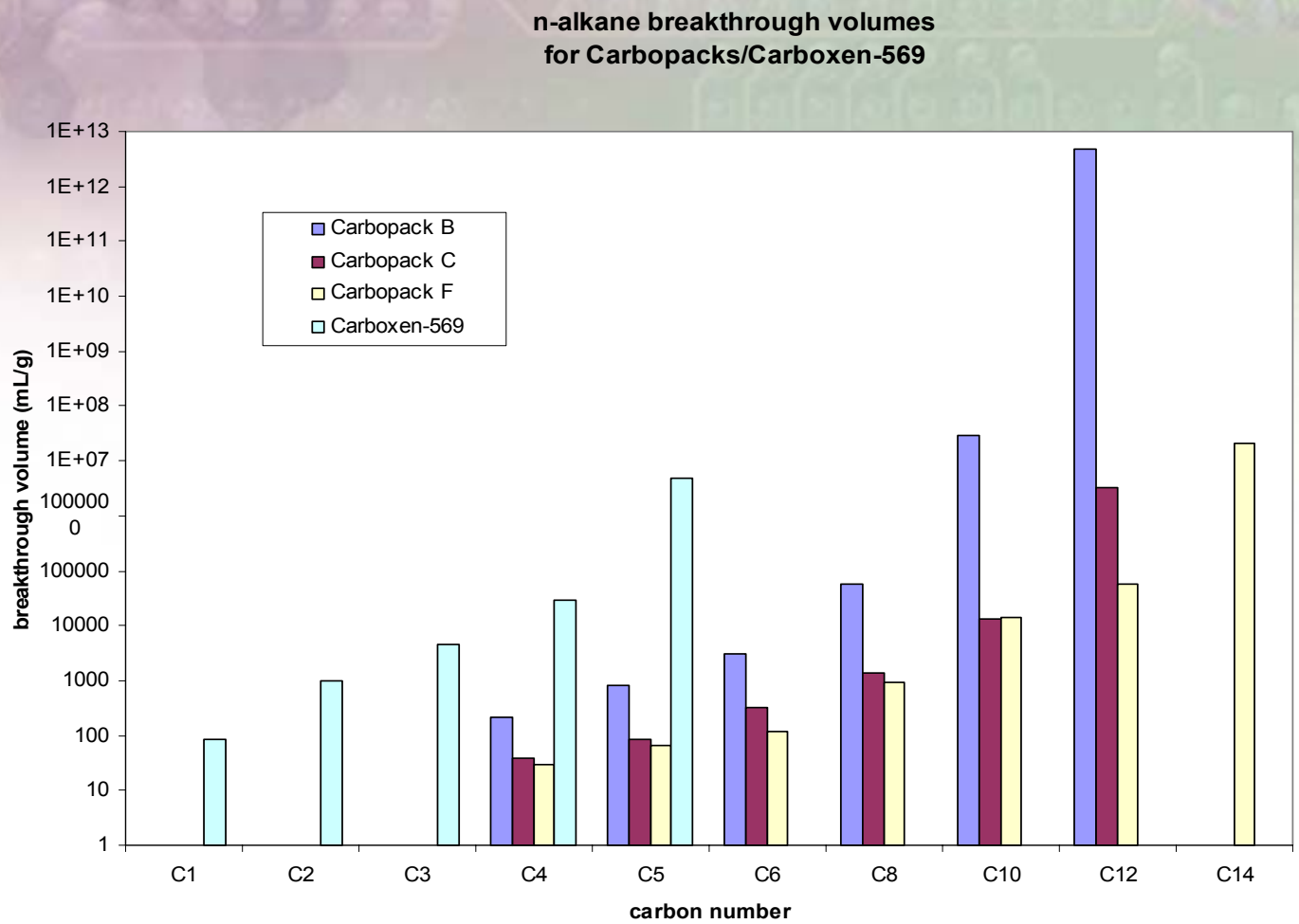
Further Studies Included Additional Adsorbents



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Additional thermodynamic studies focused on adsorption isotherm data generated via chromatographic systems.

The equations for the adsorption isotherm study are:

X-axis (pressure axis)

$$p = \frac{(m)(x)(R)(T)}{(S)(f)} \quad (h)$$

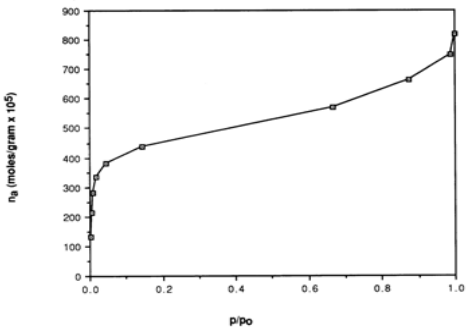
Y-axis (uptake axis)

$$q = \frac{(m)(10^5)}{W}$$

where : m = moles of adsorbate injected
: x = chart speed
: R = universal gas constant
: T = temperature
: S = adsorbate peak area
: f = corrected flow rate
: h = adsorbate peak height
: q = moles of sample adsorbed
: W = adsorbent bed weight

The dynamic, chromatographic data were utilized to rank the adsorbents according to their adsorption strengths, and thermal and solvent desorption studies were performed to study and prepare several families of adsorbent tubes.

Dichloromethane Isotherm for Macro/Meso/Microporous Carbon Molecular Sieve



Adsorbent	breakthrough volume (liters)	Surface area (m2/g) CH2Cl2	Surface area (m2/g) N2	Surface usage (%)
Carbosieve S-III	66.2	697	820	**85**
Carboxen-569	43.2	466	485	**96**
Activated charcoal	39.2	526	1070	49
Carbosieve S-II	31.5	506	1060	48
Carboxen-564	31.5	380	400	**95**
Purasieve	5.05	364	950	38
Carboxen-563	1.56	291	510	**57**
Spherocarb	1.05	291	880	33

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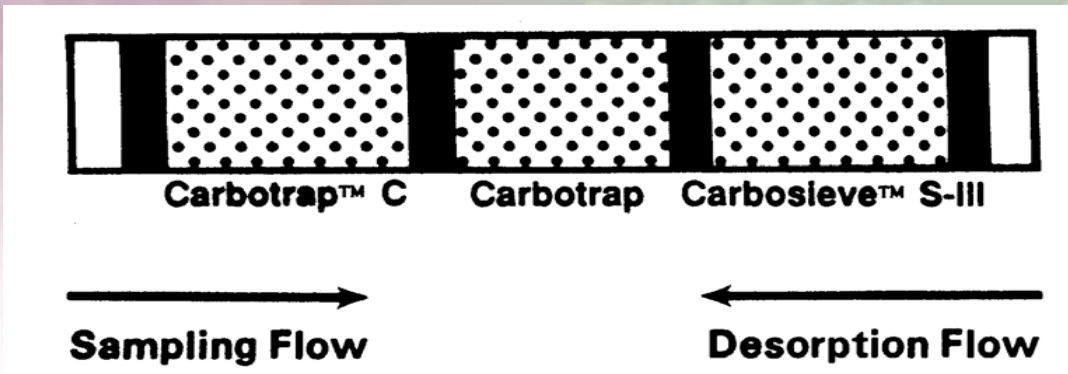
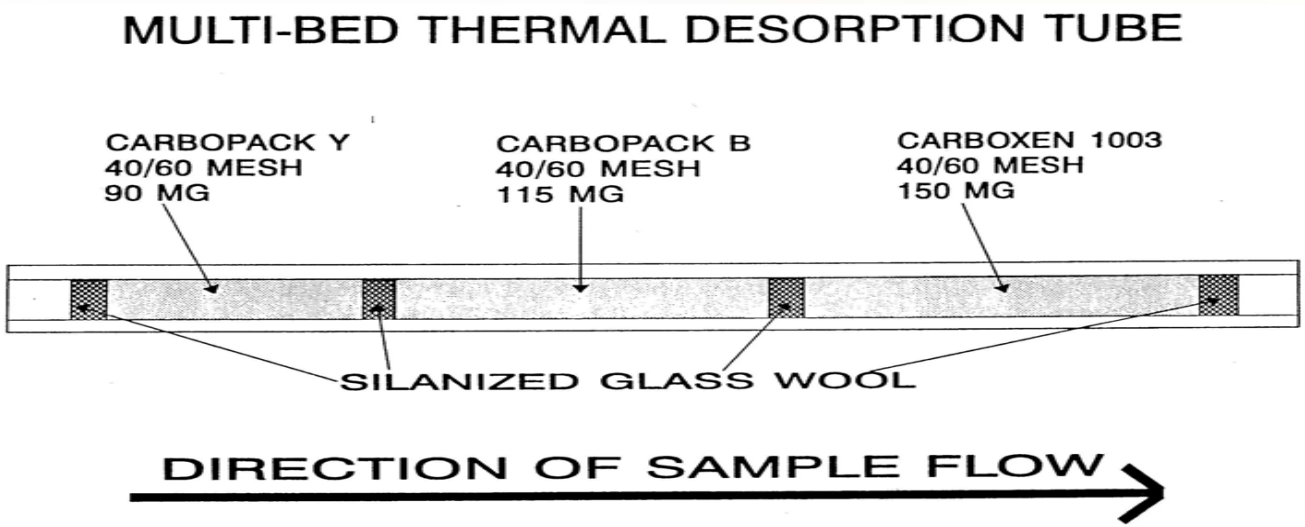
Illustrated below are the two multi-bed tubes prepared for thermal desorption applications. For example, the multi-bed tube (Carbotrap 300) was prepared for EPA methods TO-1 and TO-3, and the Carbotrap 301 tube was prepared for the NIOSH indoor air screening method.



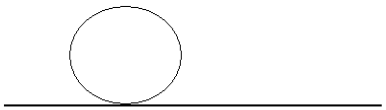


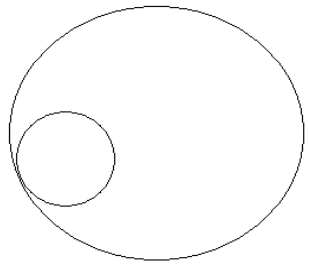
Further studies were used to begin to understand the relationship between surface area, pore structure , and breakthrough volume. Adsorption on the surfaces of non-porous particles, dictated by two dimensional adsorption, and porous particles dictated by 3 dimensional adsorption, can be described by the spreading pressure (inversely proportional to the surface area), as well as the contact angle, as follows:

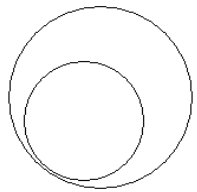
$$\Pi = \frac{RT}{SM} \int_0^{p/po} [q/(p/po)]\, d(p/po)$$

and

$$\cos\theta = -1 - \frac{\Pi}{v_1} + \frac{(2v_1v_2)}{v_1}$$



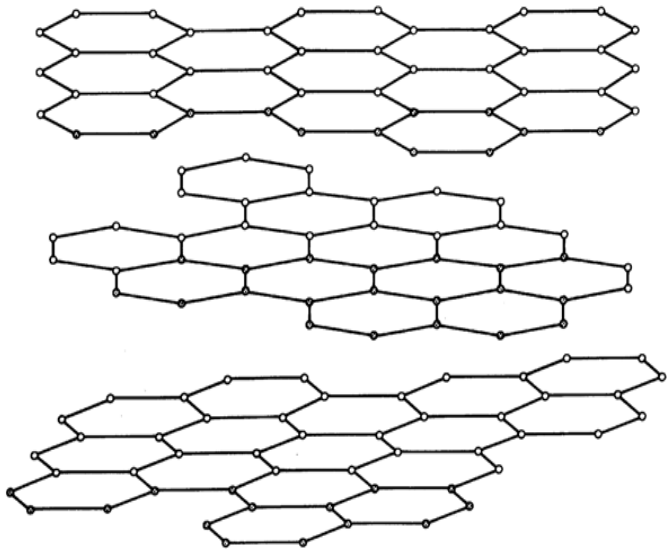




Illustrations of the Carbon Surfaces

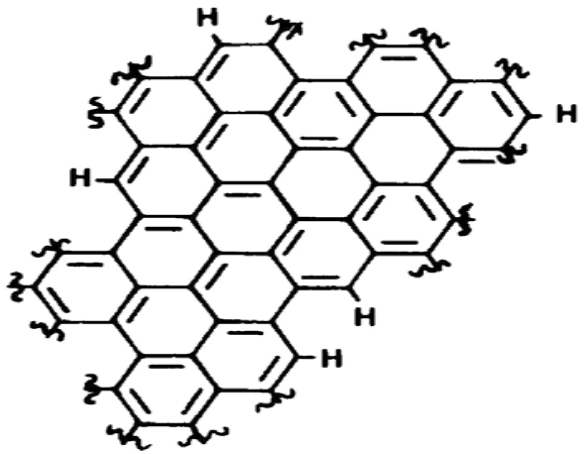
Non-porous graphitized carbon black

predominantly sp^2



Porous carbon molecular sieve

predominantly sp^3



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Kinetic Studies

Gas-solid chromatography (GSC) and inverse-gas chromatography (IGC) have also been used as the analytical tools to characterize the kinetic properties of the adsorbents.

These kinetic studies focused on the use of the fundamental band broadening equation employed for packed chromatographic columns. The HETP (height equivalent to theoretical plates) equation allowed for the understanding of the following:

1. particle size versus tube diameter considerations,
2. particle pore diffusivity,
3. pore diameter contributions to mass transfer,
4. particle shape effects on mass transfer and convection.

The following equation(s) assist in describing the kinetic properties of the packed adsorbent beds:

$$HETP = A + \frac{B}{\bar{u}} + (C_s + C_m)\,\bar{u}$$

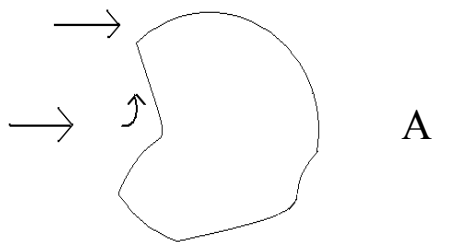
$$HETP = 2\cdot\lambda\cdot d_p + \frac{2\gamma\cdot D_m}{\bar{u}} + \frac{2\cdot k\cdot d_f^{\,2}\cdot \bar{u}}{3\cdot D_s (1 + k)^2} + \frac{w\cdot d_p^{\,2}\cdot \bar{u}}{D_m}$$

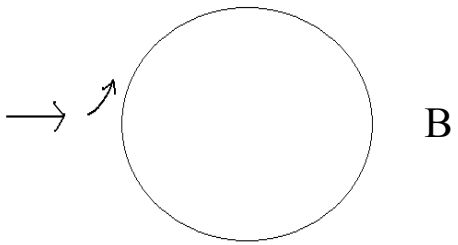
where: A term represents the contribution from eddy diffusion
: B term represents the contribution from longitudinal diffusion
: C term represents the contributions from mass transfer in the mobile phase and stationary phase

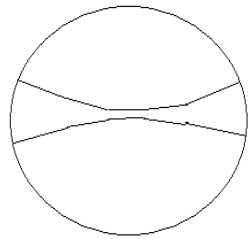
: $\bar{u}$ = average mobile phase velocity
: λ = packing/particle shape factor (i.e., spherical versus granular)
: d_p = particle diameter
: γ = obstruction or tortuosity factor (pore velocity contribution)
: D_m = adsorbate diffusion in the mobile phase
: k = capacity factor
: D_s = diffusion coefficient in the stationary phase
: w = packing factor function (corrects for radial diffusion)

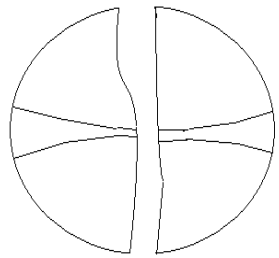
Some of the data obtained from the kinetics studies are presented below.

Graphical Representation of : A. convection (eddy diffusion in granular packed beds)
B. reduced eddy diffusion in spherical packed beds
C. throughput pores in spherical particles
D. disruption of pores in milled/crushed particles









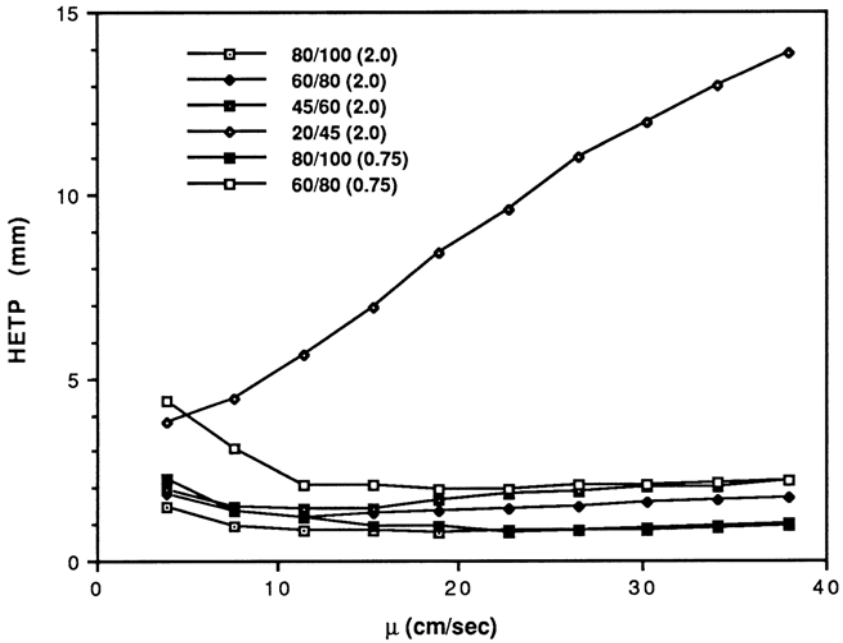
Results From the Kinetic Studies for Carboxen-1000

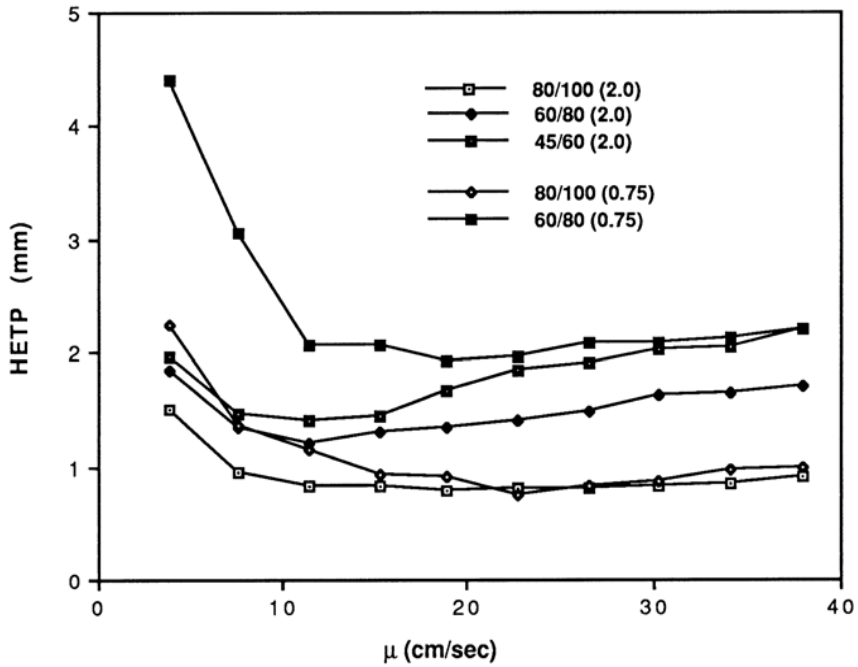
PARAMETERS FOR CARBON MOLECULAR SIEVE (CARBOXEN-1000) COLUMN KINETICS STUDY

Description	*Parameter*					
Column Length (m)	2.0	2.0	2.0	2.0	2.0	2.0
dc (mm)	2.0	2.0	2.0	2.0	0.75	0.75
dp (mesh)	80/100	60/80	45/60	20/45	80/100	60/80
dp/dc	0.08	0.11	0.15	0.30	0.22	0.28
HETP (mm) {co_2}	0.80	1.21	1.41	3.80	0.76	1.93
HETP (mm) {C_2H_6}	0.80	1.23	1.42	4.04	0.72	1.77
k' {co_2}	22.6	11.6	11.0	6.0	20.2	10.7
k' {C_2H_6}	23.7	15.2	13.2	5.9	21.1	11.7
n {co_2}	2500	1658	1418	526	2635	1036
n {C_2H_6}	2500	1626	1408	495	2778	1130
μ (cm/sec) {co_2}	18.9	11.4	11.4	3.79	22.7	18.9
μ (cm/sec) {C_2H_6}	18.9	18.9	15.2	3.79	18.9	18.9
C (sec x10^{-4}) {co_2}	5.34	16.5	32.5	295	5.90	18.9
C (sec x10^{-4}) {C_2H_6}	7.80	16.0	23.5	270	4.80	15.5
K (cm^2 x10^{-7}) {co_2}	1.42	3.12	3.72	25.1	1.53	4.84
K (cm^2 x10^{-7}) {C_2H_6}	1.46	3.38	3.28	29.3	1.36	4.36

Graphical presentations of the data obtained illustrate the following:

1. A dp/dc range of 0.10 - 0.25 is effective,
2. Mass transfer for porous solids is optimum if mesopores and/or macropores are present,
3. Substitution in the C-term for micropore diffusivity indicates that the velocity differences between the macropores and interparticle spaces is insignificant, and





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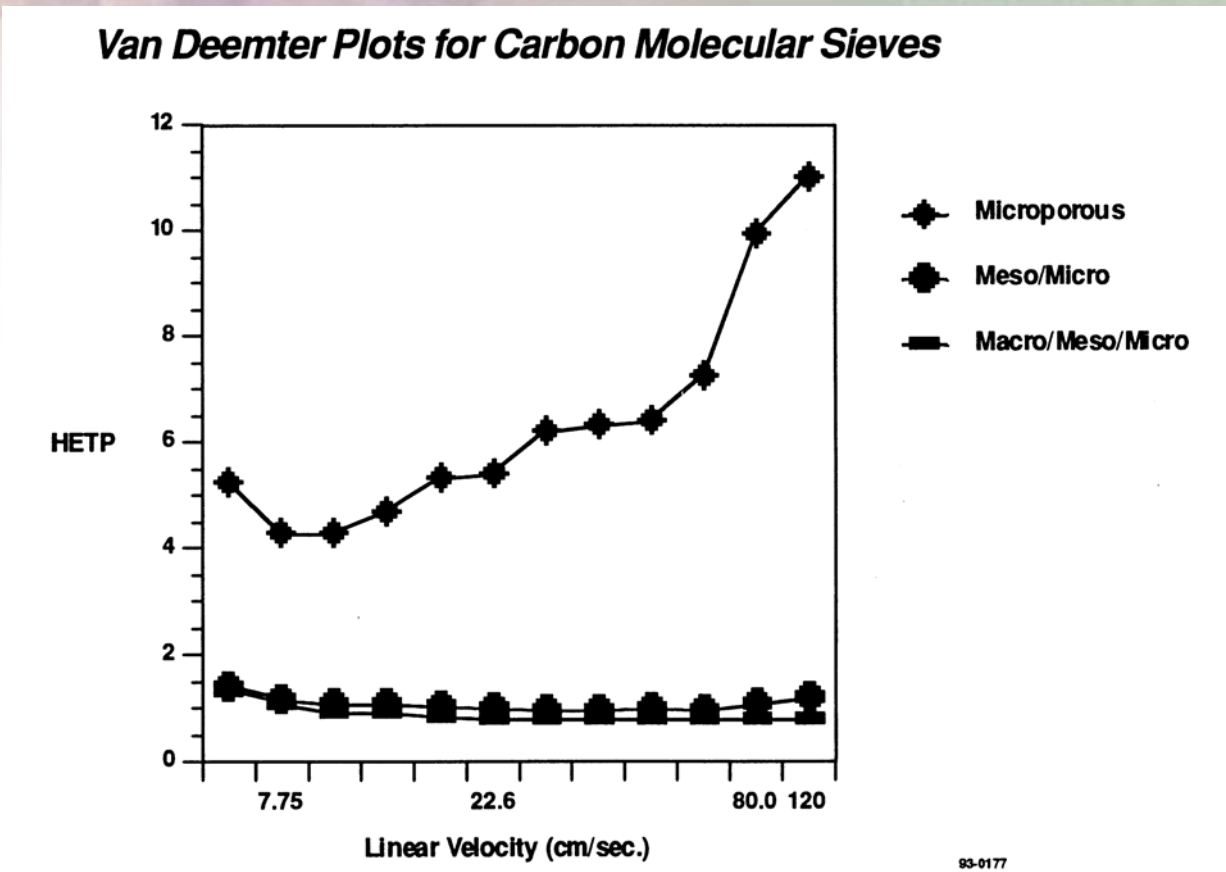
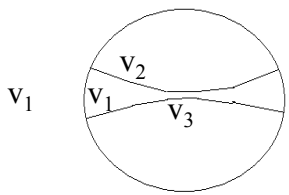
4. **The gas velocity differences between macropores and micropores is 100-1000X. This significant difference is noted in the following graph and table (shown earlier).**





v_1 = interparticle velocity
= macropore velocity
v_2 = mesopore velocity
~ 0.1 v_1
v_3 = micropore velocity
~ 0.01-0.001 v_1

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The ranking of the adsorbents is better understood with the addition of the kinetic studies.

Adsorbent	breakthrough volume (liters)	Surface area (m2/g) CH2Cl2	Surface area (m2/g) N2	Surface usage (%)
Carbosieve S-III	66.2	697	820	**85**
Carboxen-569	43.2	466	485	**96**
Activated charcoal	39.2	526	1070	49
Carbosieve S-II	31.5	506	1060	48
Carboxen-564	31.5	380	400	**95**
Purasieve	5.05	364	950	38
Carboxen-563	1.56	291	510	**57**
Spherocarb	1.05	291	880	33

Based on the thermodynamic, kinetic and porosimetry studies, the following table of suggestions has been prepared.

Adsorbent	Adsorption Strength	Comments
GCB		
Carbopack X	1	bridge between GCBs and CMSs
Carbopack Z	2	effective substitute for Tenax
Carbopack B	3	effective mid-range adsorbent (C5-C20)
Carbopack Y	4	effective, weaker mid-range adsorbent
Carbopack C	5	effective for high molecular weight adsorbates
Carbopack F	6	effective for high molecular weight adsorbates
CMS		
Carbosieve S-III	1	strong adsorbent
Carboxen-1003	2	kinetics similar to 1000; more hydrophobic
Carboxen-569	3a	closed micropores; hydrophobic
Carboxen-1000	3b	most kinetically efficient

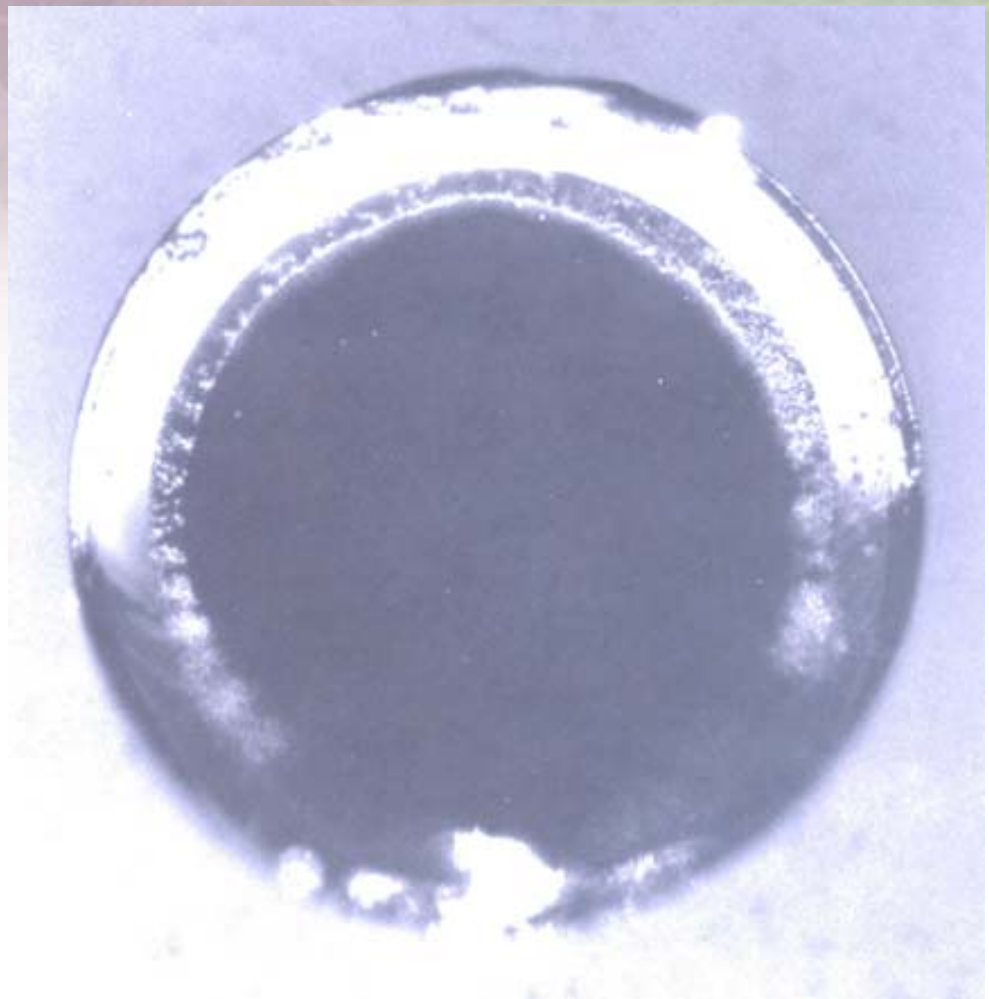
Additional Adsorbents Programs at Supelco

Synthesis of porous polymers and polymer carbons in the 1-10 micron size range. These powders have found applications in a wide variety of coatings such as SPME, PLOT columns, denuder-type surface applications, etc.

Illustrated below are:

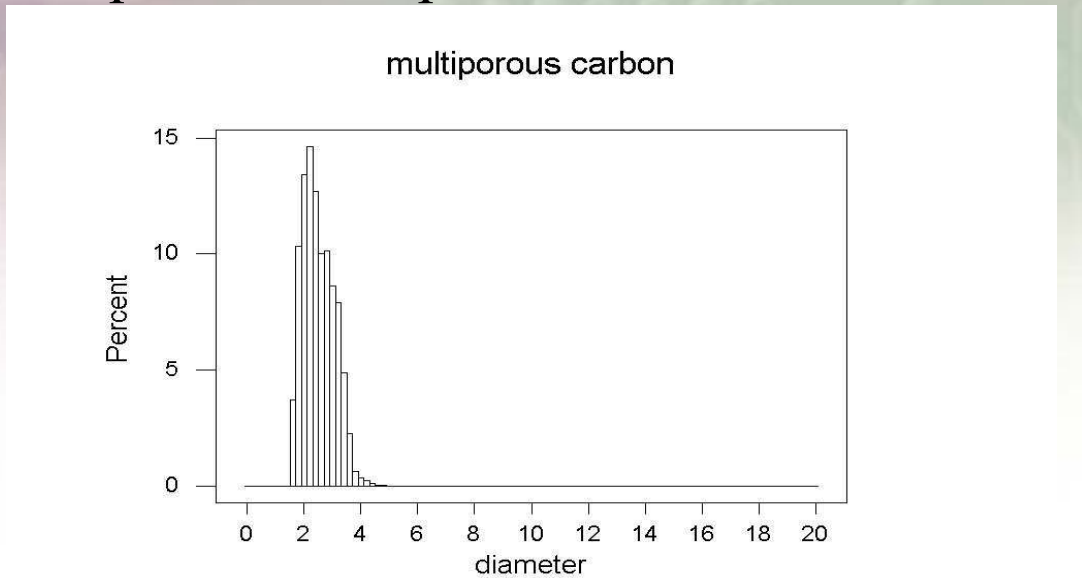
a photograph of a Carboxen-1006 PLOT column, and a particle size distribution graphs of Carboxen-1006 and Carboxen-1010.

Photo of Carboxen-1006 PLOT Column
(30 micron film thickness / 0.53mm ID Column)



Graph 1. Multiporous carbon

Carboxen-1006



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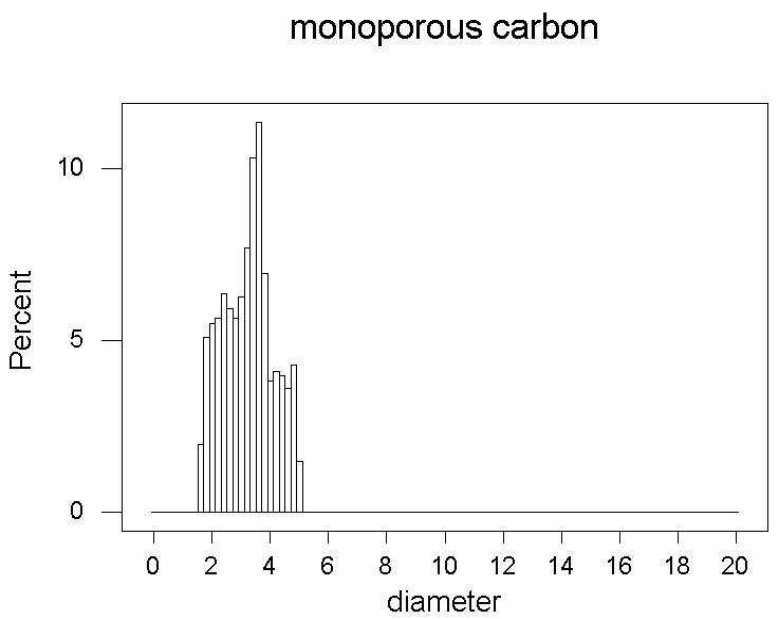
Graph 2. Monoporous carbon

Carboxen-1010



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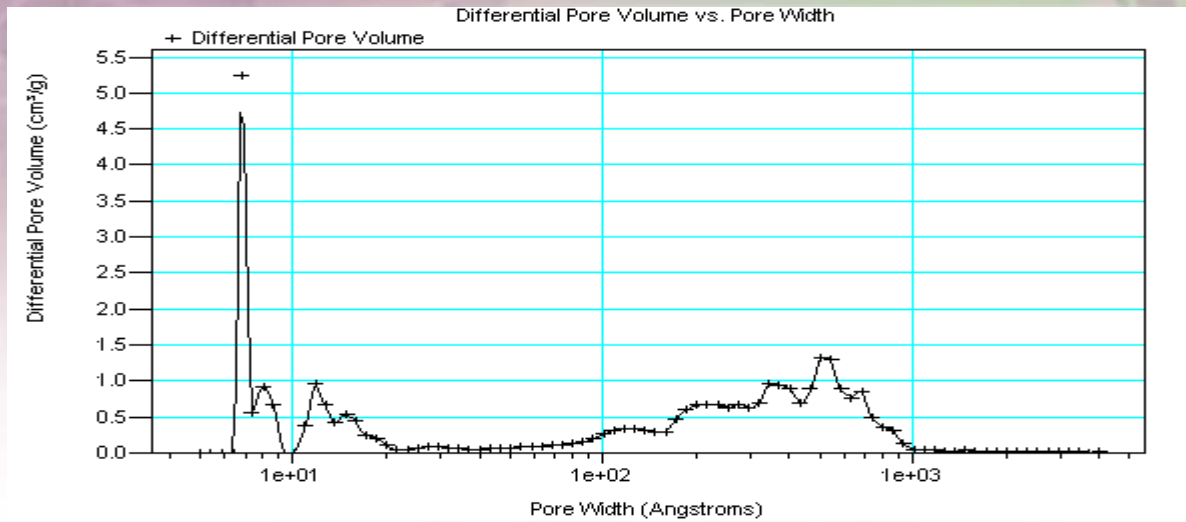
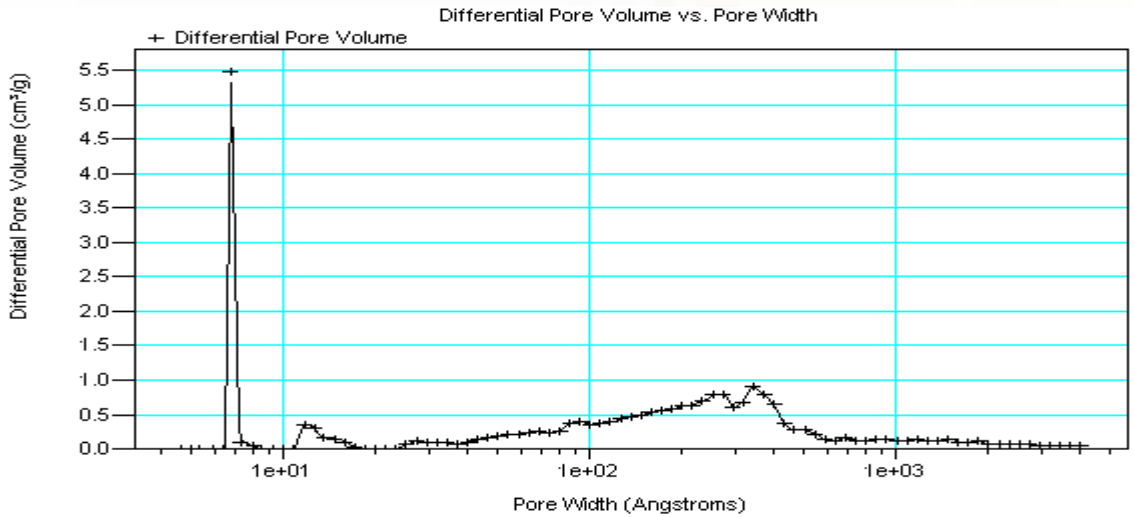
Understanding of the pore structures porous solids is augmented with DFT plots.

Carboxen-1000
DFT plot



Carboxen-1006
DFT plot



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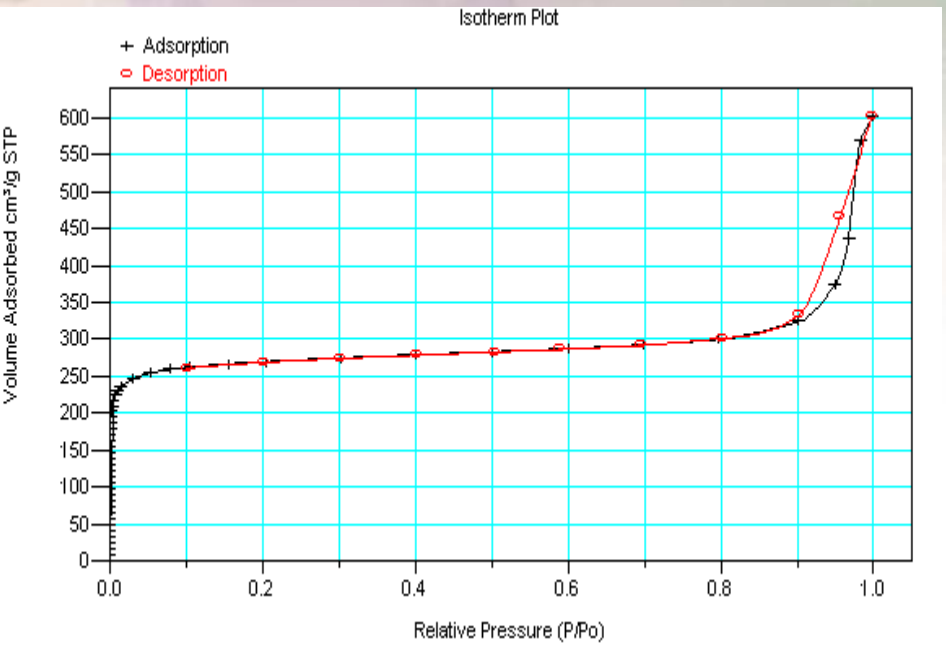
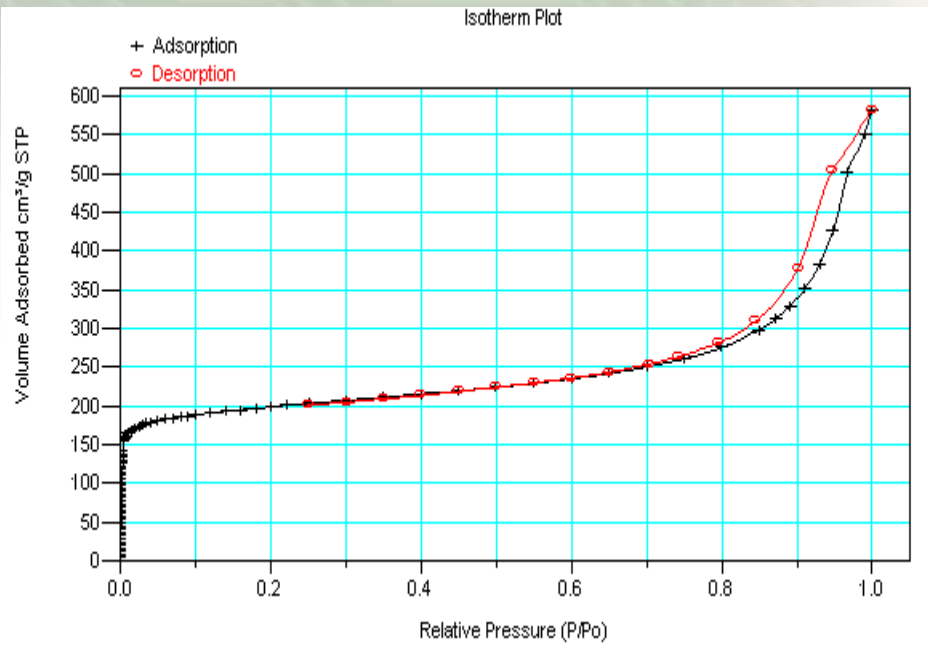
The nitrogen isotherm plots of the Carboxen-1000 and the Carboxen-1006 (l to r) illustrate subtle differences in the micropore volumes, macropore volumes, and hysterisis loops. Two different polymers were used to prepare these two multiporous carbons.





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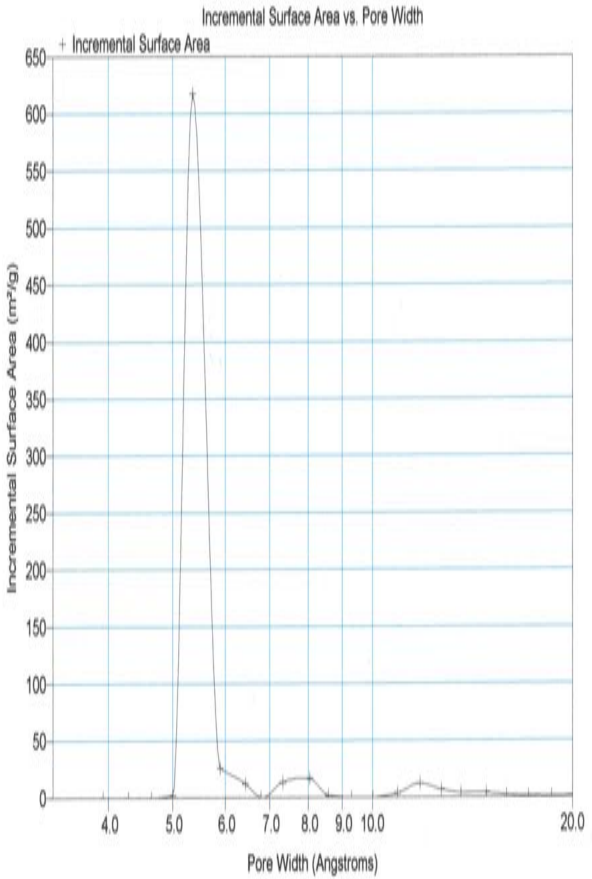
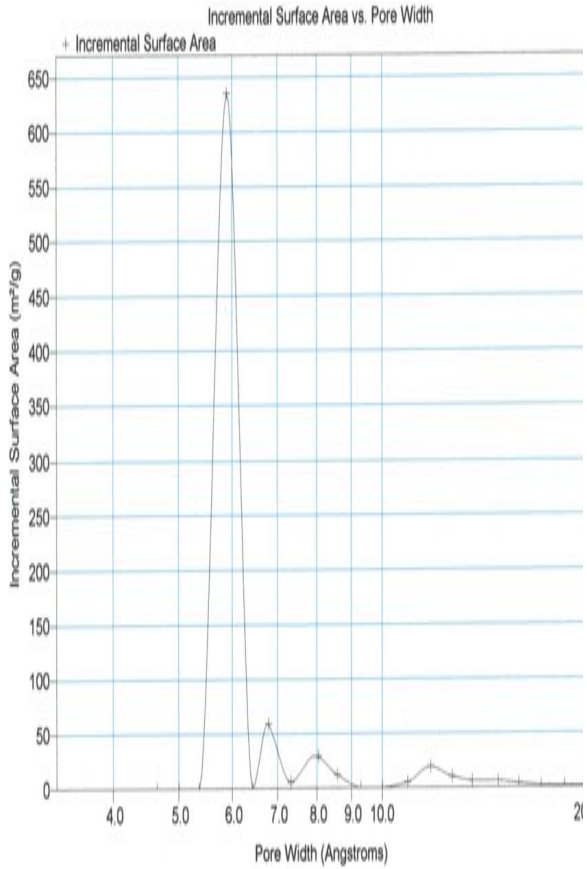
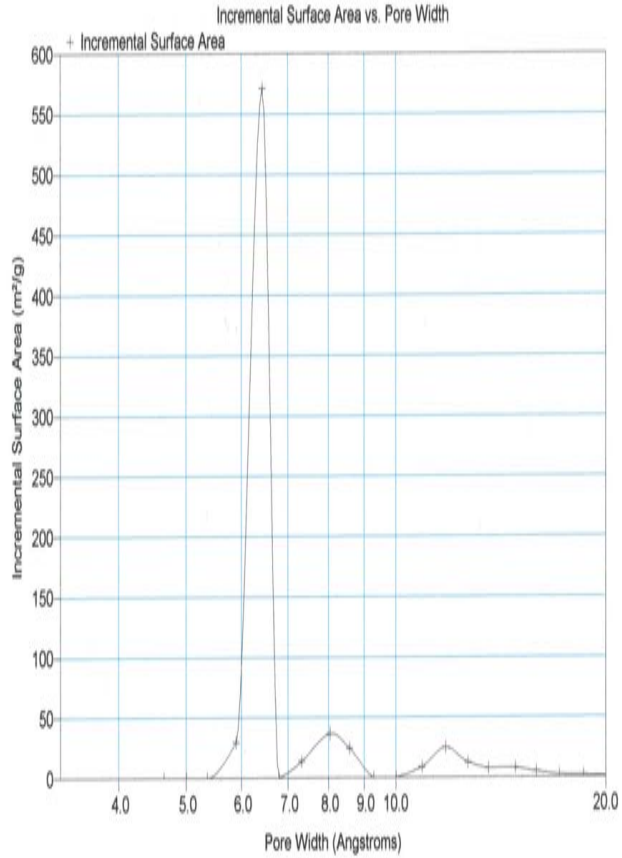
Two research projects focused on microporous carbons for applications where slow mass transfer and strong adsorption processes are required. Illustrated are DFT plots for 3 tailored carbon sieves.







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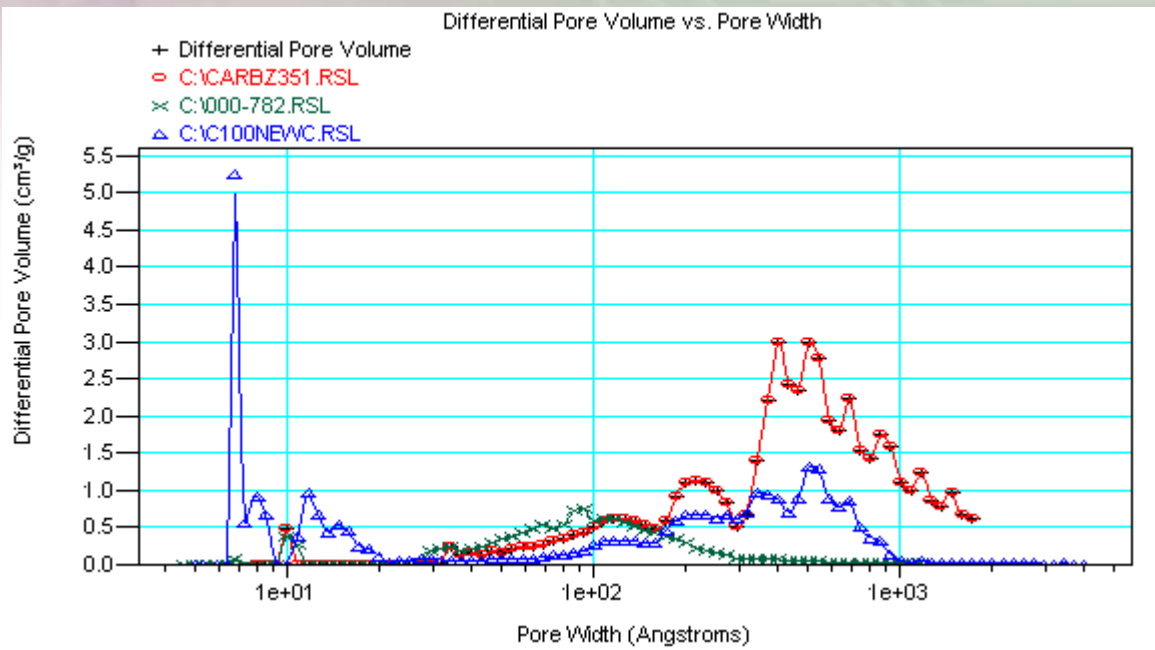
DFT plots are helpful in ordering multi-bed tubes

Red = Carbopack Z (first bed)

Green = Carbopack X (second bed)

Blue = Carboxen-1000 (third bed)



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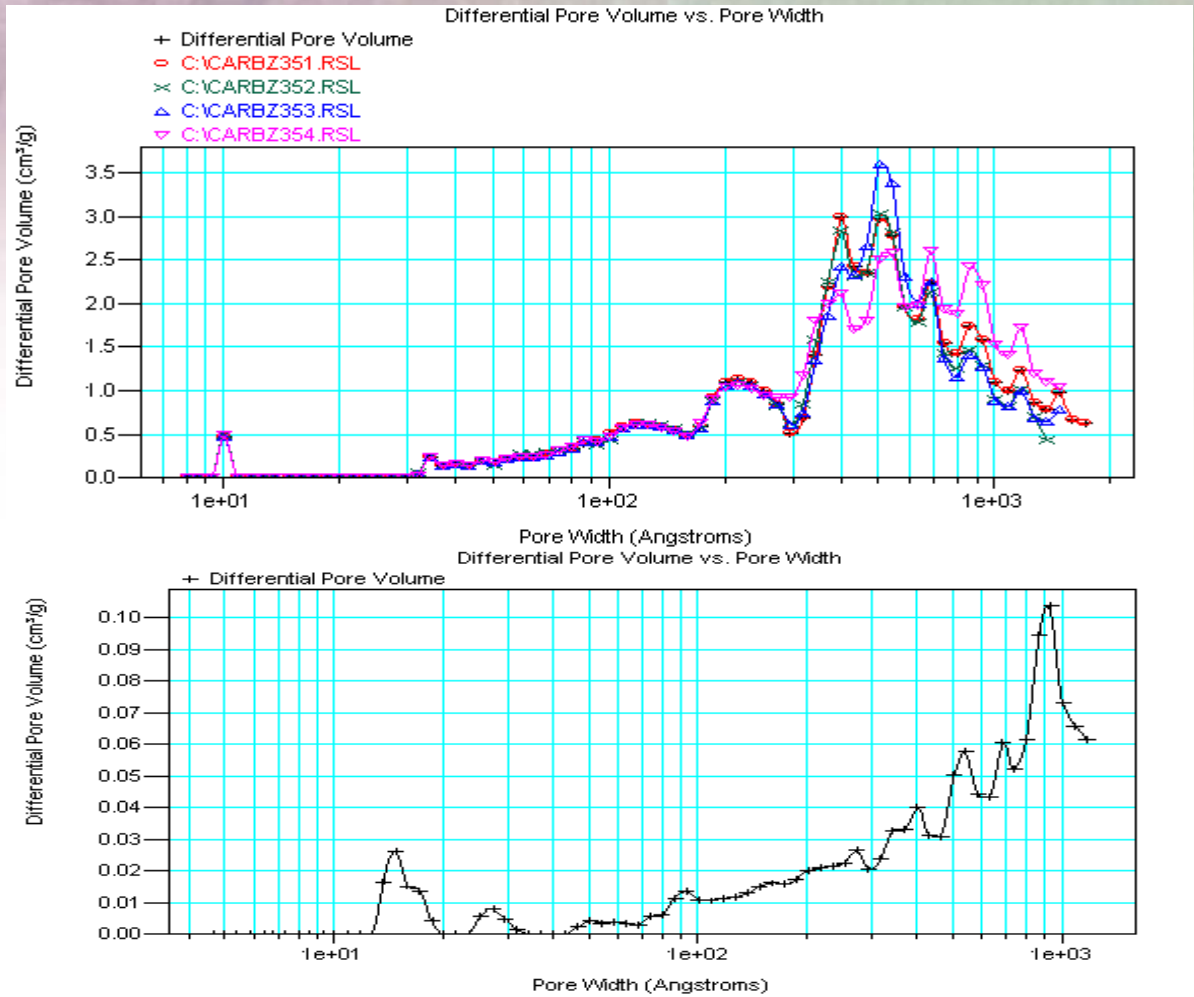
A new GCB, entitled Carbopack Z, has been investigated by the Japan EPA, and found to be an effective, improved substitute for Tenax. Illustrated below are DFT plots of Carbopack Z (4 batches) and Tenax.



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Future of Adsorbents Program

1. Continue to prepare new adsorbents as required for customer applications.
2. Continue to relate the thermodynamic, kinetic and physical properties of the adsorbents for selecting the proper adsorbents for thermal desorption applications.
3. Continue to expand the adsorbents product line to meet the customers needs.