Characterization of Polymer Carbon Molecular Sieves and Graphitized Carbon Blacks for Use in Sample Preparation Applications

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Abstract

Spherical carbon molecular sieves have been synthesized from polymer precursors. These carbon molecular sieves possess similar pore structures obtained during the polymerization process by converting the polymer to an ion-exchange resin prior to the carbonization step. Both pyrolytic and graphitization temperatures have been employed to meet the requirements of the specific applications. The high purity characteristics of the carbons enable these carbons to function effectively for the applied processes.

Granular, graphitized carbon blacks have been prepared at graphitization temperatures. The graphite lattice structure and/or pore structure results from the starting carbon and temperature employed. The high purity of these carbons enables them to function effectively for the applied processes (Kiselev, 1969).

Abstract (contd.)

A nitrogen porosimeter has been used to study the surface areas, pore size distributions and total pore volumes of the carbons (Webb, 1997). Carbon pore diameter plots have been generated using DFT software. Carbon adsorbent capacities and reversible adsorption characteristics have been determined using the respective sample preparation processes.

Introduction

Carbon powders packed in various cartridges and tubes at Supelco have been utilized effectively for several decades as sample preparation tools. These tools are specifically used for concentrating/adsorbing analytes in gas phase, liquid phase and solid phase sample environments. Typically, the analytes must be desorbed from the carbon packed beds to facilitate introduction into an analytical instrument for analyte identification and quantification. Preparation of the carbon powders may be specific for each application, with several key characteristics necessary for every application.

These key characteristics are: adsorption strength, desorption efficiency, particle diameter/tube diameter ratio, and particle shape (Betz, 1991). The adsorption strength and desorption efficiency are functions of surface area, pore size(s) and shape(s), pore volume and surface chemistry.

Introduction (contd.)

The particle size and shape affect the total working surface of the packed beds and the pressure drops of the system(s).

Some of the high-purity CMSs and GCBs discussed below include: a 2-3 µm CMS bonded to various surfaces in Figures 1, 2, and 3, and a GCB combined with 2 CMSs for use in breath sampling applications in Figures 3-7.

Experimental

- The CMSs are spherical, and possess pore structures similar to their respective polymeric precursors. Table 1 describes some of the physical characteristics of several CMSs.
- Table 2 describes some of the physical characteristics of the GCBs.

Experimental (contd.)

Table 1. Physical Characteristics of Several Supelco Carbon Molecular Sieves

Adsorbent	Surf. Area (m^2/g)	Packing Density (g/mL)	Total Pore Volume Micro -Pores (cc/g)	-Meso -Pores (cc/g)	-Macro -Pores (cc/g)	Micropore Diameter (Å)
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	–	0.35	NA	NA	6 - 8
Carboxen-1011	1100	0.48	0.41	0.19	0.24	10 - 12
Carboxen-1012	1500	0.50	NA	0.66	NA	19 - 21
Carboxen-1018	675	0.60	0.35	NA	NA	6 - 8
Carboxen-1021	600	0.62	0.30	NA	NA	5 - 7

Experimental (contd.)

Table 1. Physical Characteristics of Several Supelco Carbon Molecular Sieves (contd.)

Adsorbent	Surf. Area (m^2/g)	Packing Density (g/mL)	Total Pore Volume Micro -Pores (cc/g)	Total Pore Volume -Meso -Pores (cc/g)	Total Pore Volume -Macro -Pores (cc/g)	Micropore Diameter (Å)
Carbosieve S-III	820	0.61	0.35	0.04	NA	4 - 11
Carbosieve S-II	1059	0.45	0.01	NA	NA	6 - 15
Carbosieve G	1160	0.49	0.02	NA	NA	6 - 15
Supelcarb	1150	0.46	0.47	0.26	0.28	5 - 8
NASA 20/45 gcms	61	0.55	NA	0.33	NA	NA
Carboxen-1016	75	0.40	NA	0.34	NA	NA

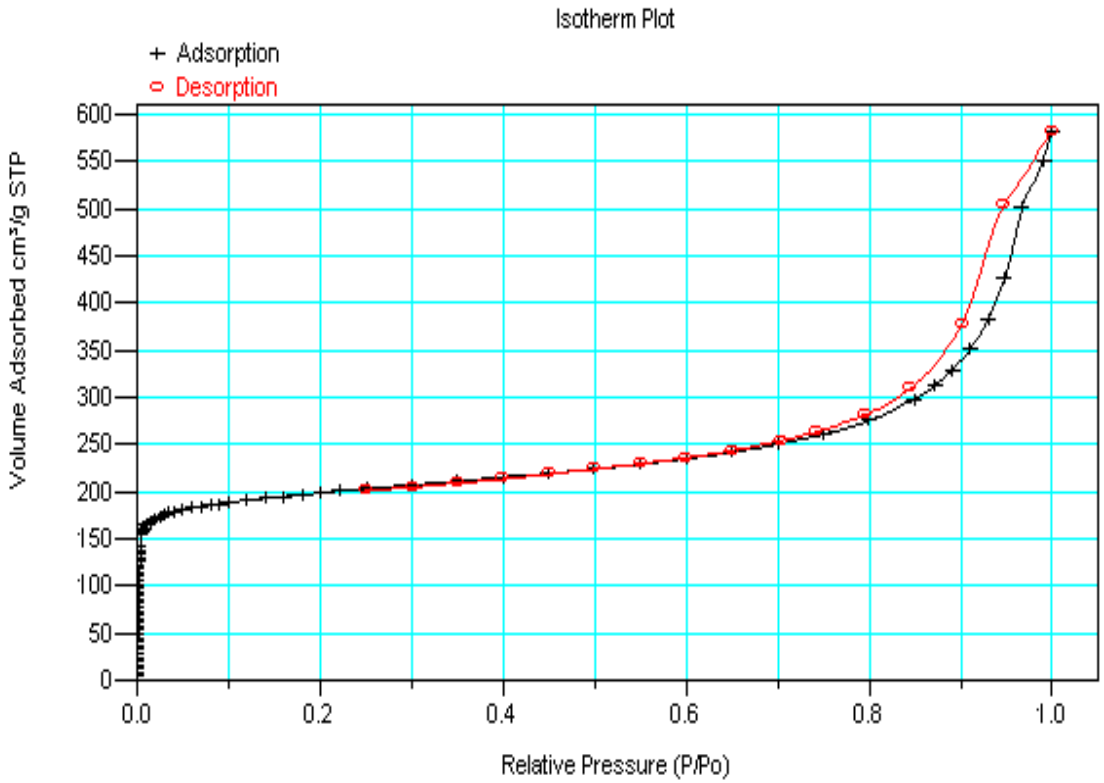
Experimental (contd.)

Table 2. Physical Characteristics of Supelco Graphitized Carbon Blacks

Adsorbent	BET surface area (m^2/g)	Packing Density (g/mL)	Total Pore Volume Mesopores (cc/g)	Mesopore Diameter (Å)	Graphite Crystallinity (%)
Carbopack X	240	0.41	0.62	100	2.0%
Carbopack Z	220	0.18	1.73	255	2.0%
Carbopack B	100	0.35	NA	NA	20%
Carbopack Y	24	0.42	NA	NA	75%
Carbopack C	10	0.68	NA	NA	90%
Carbopack F	5	0.64	NA	NA	95%

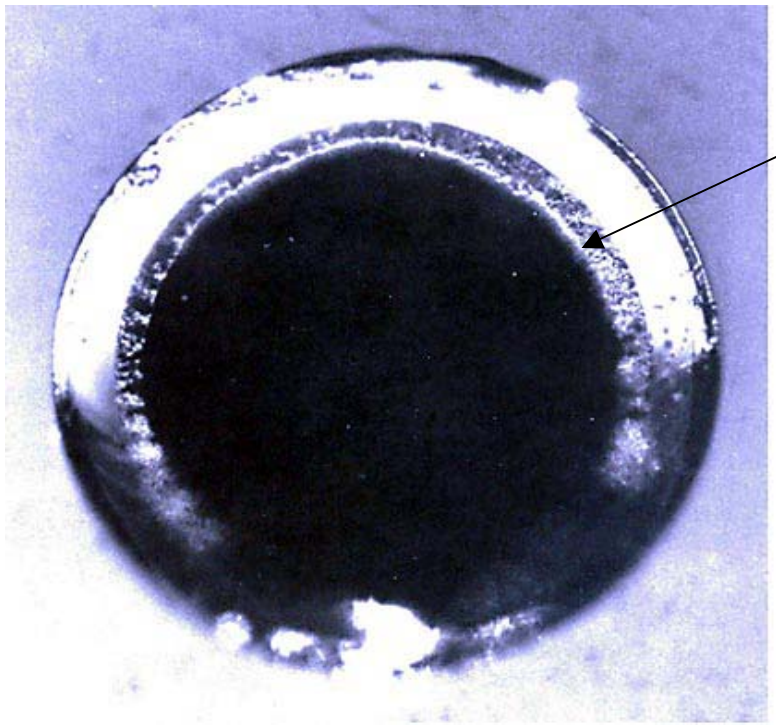
Experimental (contd.)

Figure 1. Nitrogen isotherm plot of a multi-porous carbon molecular sieve (i.e., 2-3 micron Carboxen-1006) used in high-efficiency sample preparation and chromatographic separation applications.



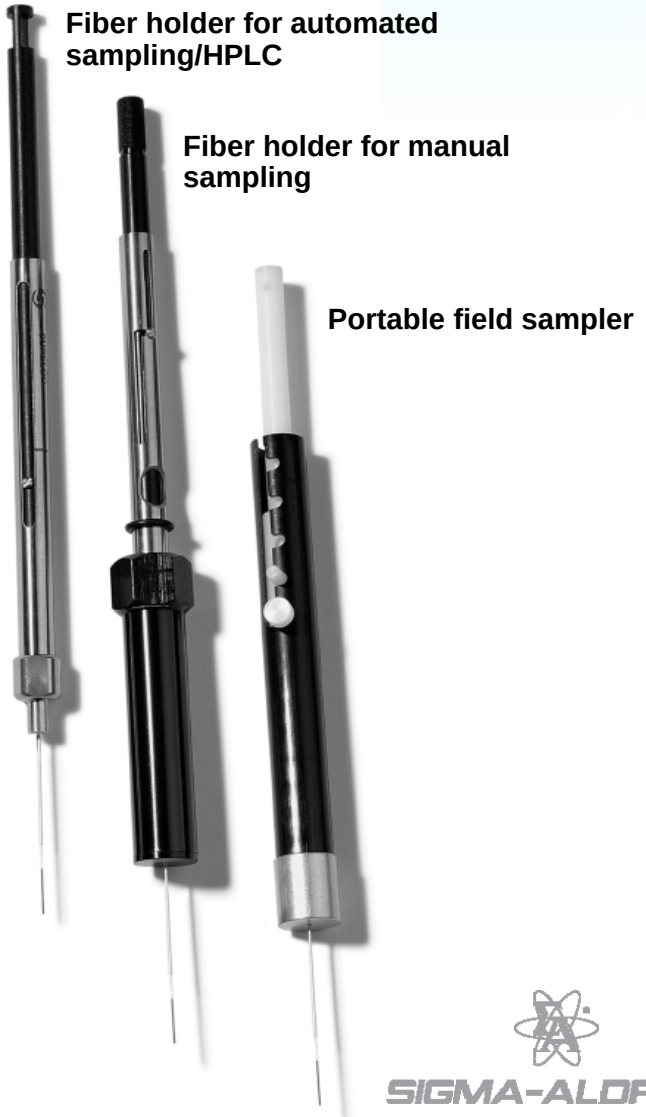
Experimental (contd.)

Figure 2. A light microscope photo of 2-3 µm CMSs bonded to the inside walls of a glass, capillary PLOT (porous layer open tubular) column.



Experimental (contd.)

Figure 3. A photo of an SPME (solid phase microextraction) fiber and device. The glass fiber has a multi-layer of 2-3 µm CMS bonded to its external surface for sample extraction from air and water matrices.

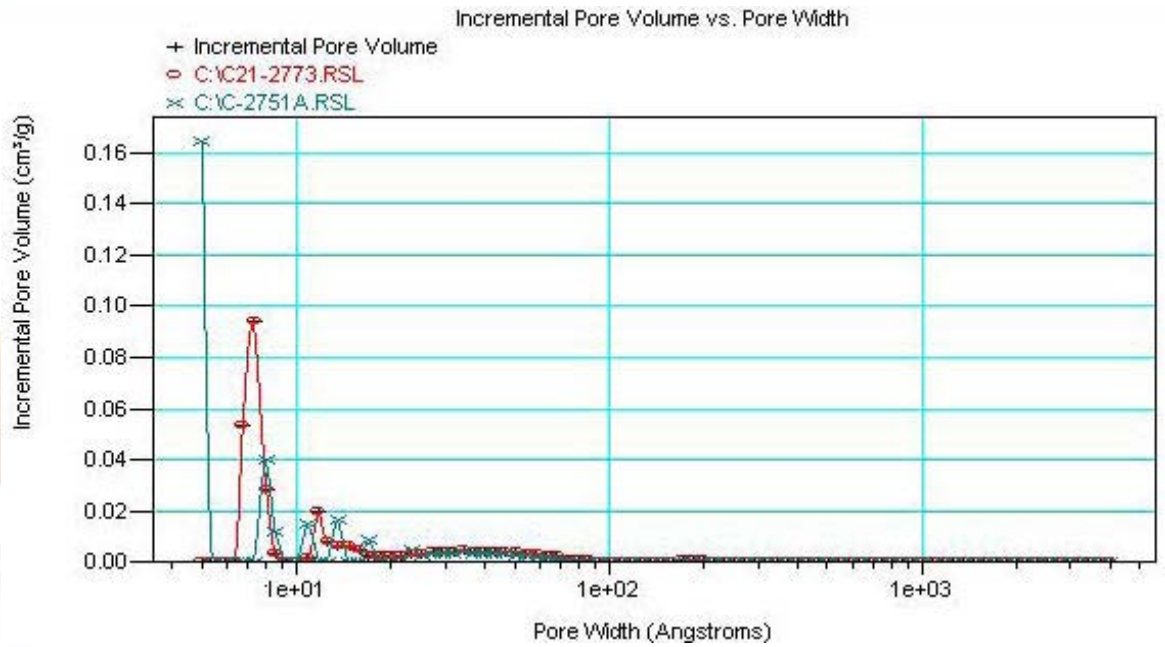


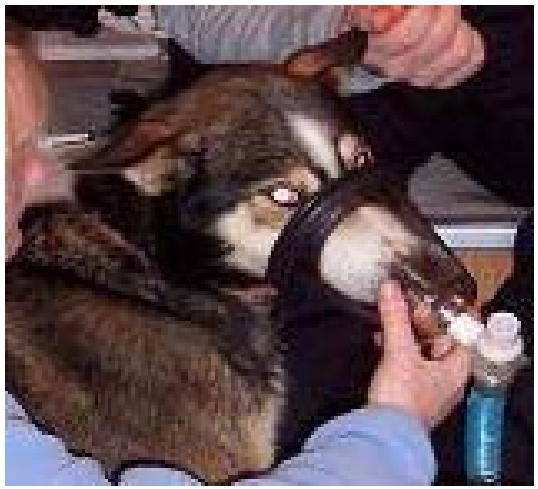
Experimental (contd.)

Figure 4. DFT plot overlays of 2 CMSs used in a 3-bed breath sampling tube for monitoring oxidative stress in Alaskan sled dogs (Hinchcliff, 1997) (photo courtesy of Dr. Michael Davis, Oklahoma State University).

red = Carboxen-1018

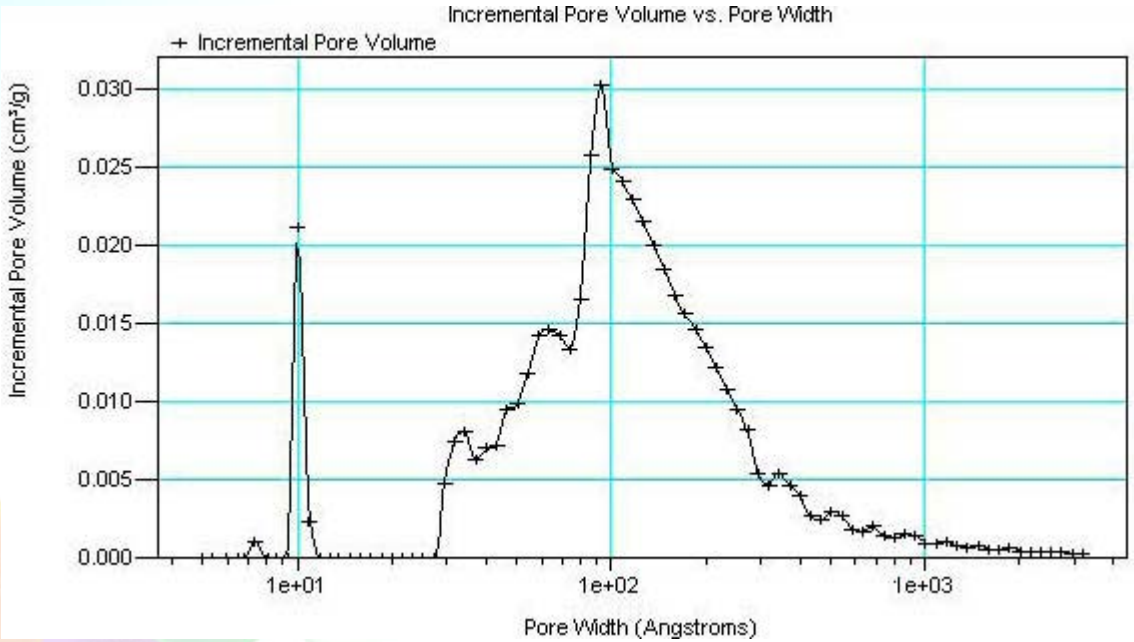
green = Carboxen-1021

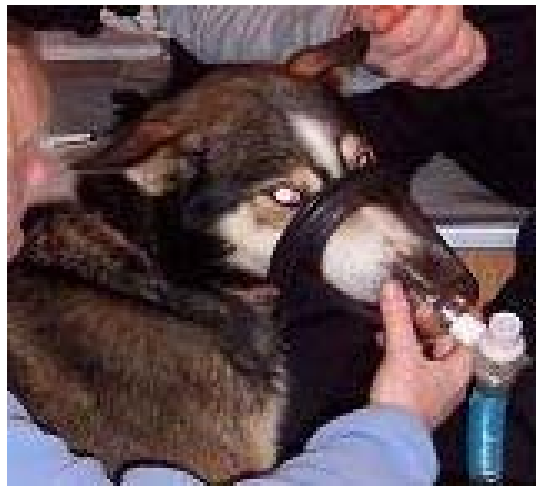




Experimental (contd.)

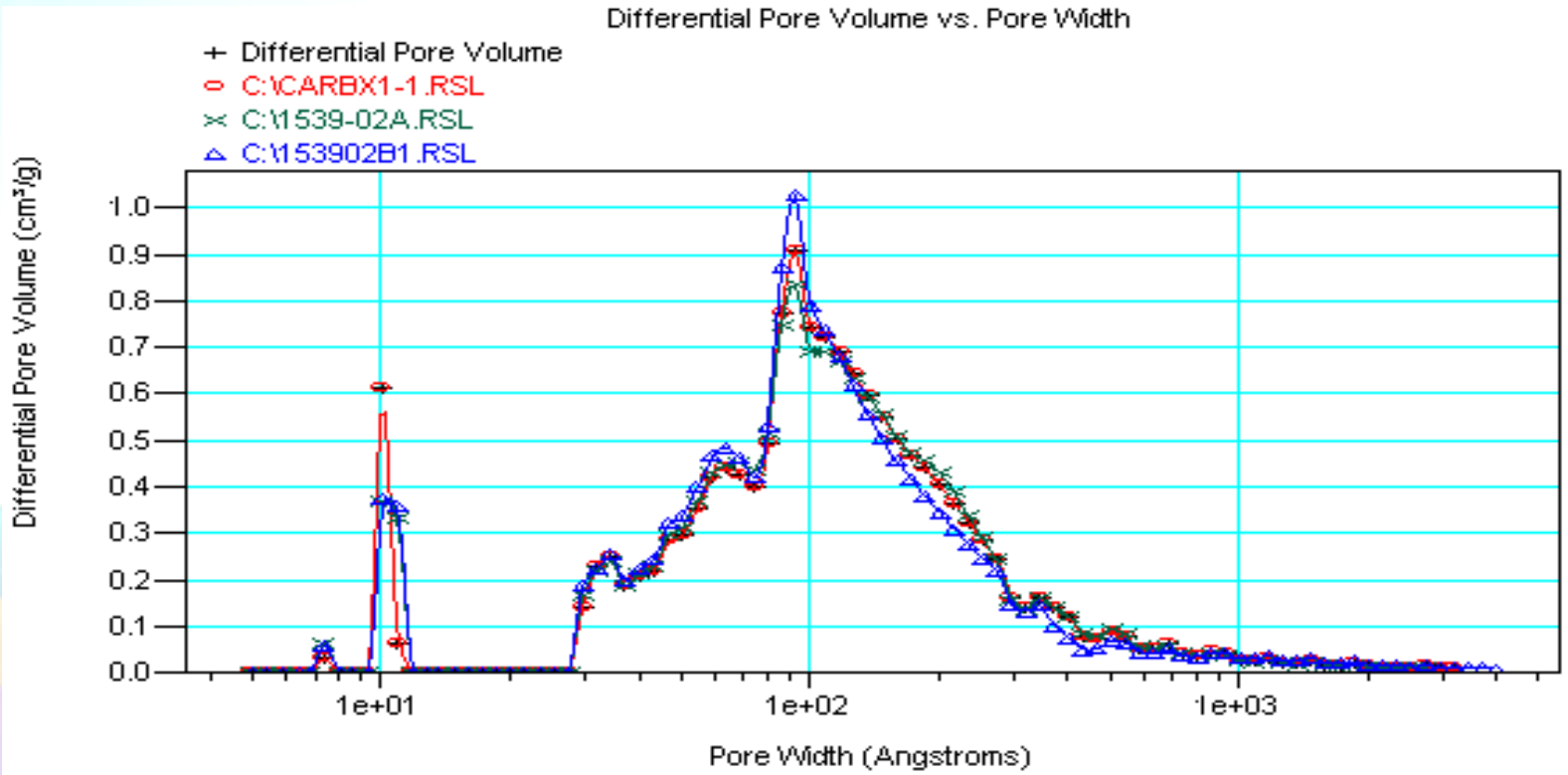
Figure 5. DFT plot of the 100Å GCB (i.e., Carbopack X) used as the filtering carbon in the 3-bed breath sampling tube.





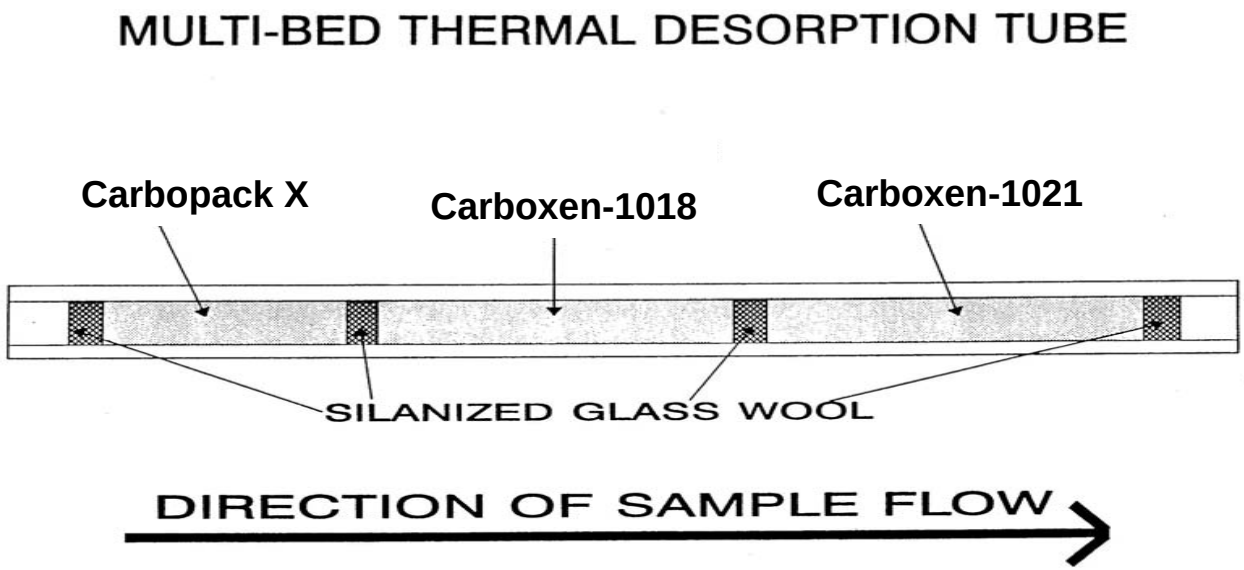
Experimental (contd.)

Figure 6. DFT overlay plots; Carbopack X process repeatability data.



Experimental (contd.)

Figure 7. A schematic of the 3-bed breath sampling tube.



Experimental (contd.)

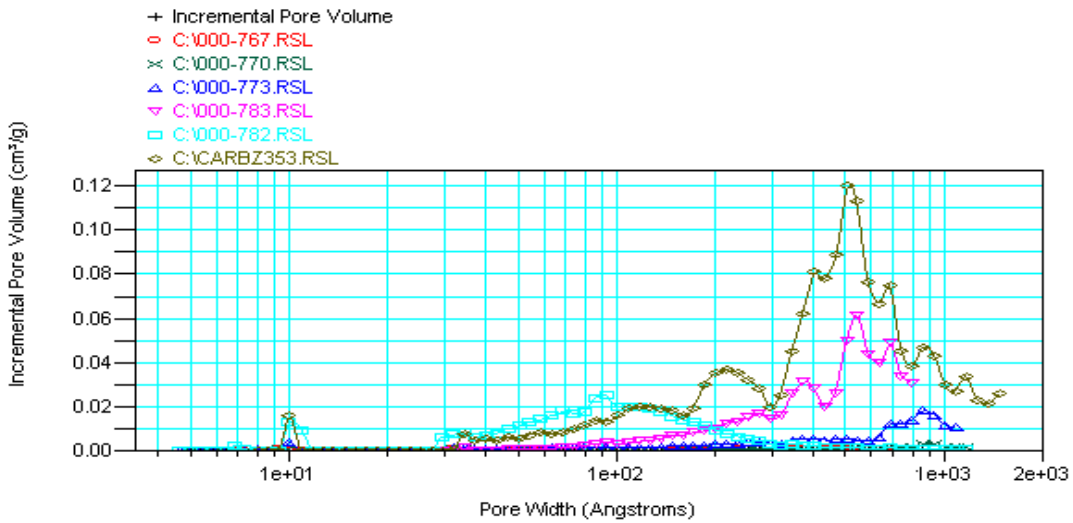
Why Carbon Sampling Tubes for breath sampling applications?

1. The multi-bed tubes permit long-term storage of samples under extremely adverse, primitive conditions.
2. No need for active cooperation by subjects.
3. Samples can be transported to the analysis site with no detectable loss of sample integrity.
4. Subsequent analyses can detect compounds present in the original breath sample at ppb concentrations after only 2 minutes of sample collection.
5. The carbons are hydrophobic (i.e., function effectively for the adsorption of the key analytes in 100% humid atmospheres).

Experimental (contd.)

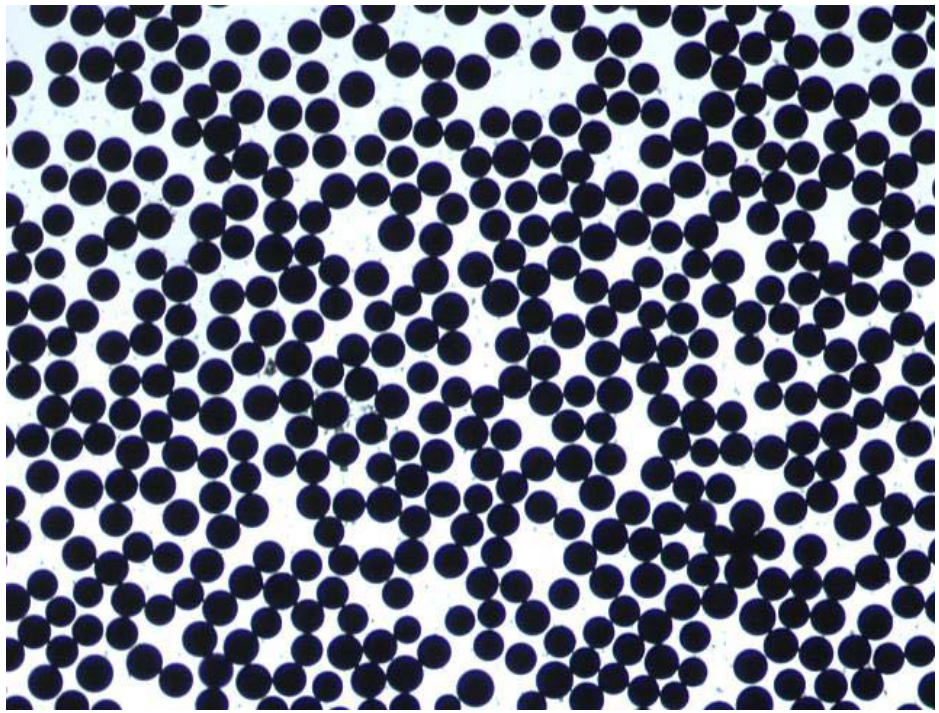
Figure 8. DFT Plots of the 6 GCBs are presented below. Note the incorporation of porosity for Carbopacks X and Z.

- **F = 5 m^2/g**
- **C = 10 m^2/g**
- **Y = 24 m^2/g**
- **B = 100 m^2/g**
- **Z = 220 m^2/g**
- **X = 240 m^2/g**



Experimental (contd.)

Figure 9. Light microscope photo of 50 +/- 5 µm CMS beads used for SPE (solid phase extraction) liquid applications.



Experimental (contd.)

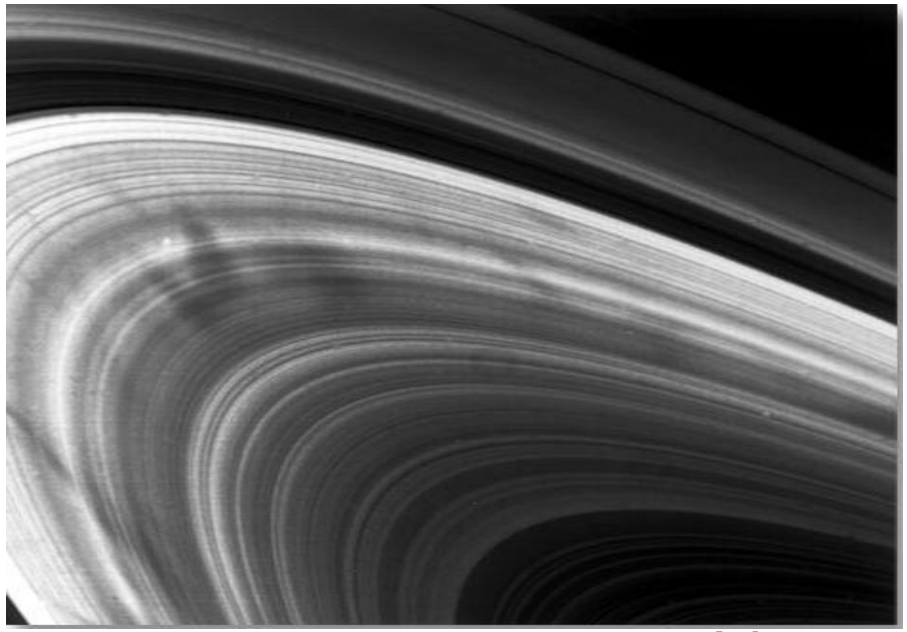
- Two high-purity carbons prepared at Supelco are currently onboard the Cassini-Huygens NASA mission to Saturn. One carbon has been used to analyze the gases in the Titan moon's atmosphere (successful experiments completed), and the second carbon is analyzing the atmosphere surrounding the Cassini satellite which is in orbit around Saturn.

Experimental (contd.)

Figures 10 and 11. Two Supelco carbons onboard the Cassini-Huygens mission.

Carboxen-1017
(GC-MS on Huygens probe on Titan)

Carboxen-1004
(CMS on Cassini Spacecraft/orbiter)



Conclusion

- High-purity carbon molecular sieves and graphitized carbon blacks have been synthesized for use in sample preparation and gas chromatographic applications. These carbons have been tailored to meet specific application requirements. The wide range of physical and surface chemistry properties, and reproducibility of scale, enable the construction of a wide range of effective, analytical process tools.

References

1. Kiselev, A.V. and Yashin, Y.A. (1969), *Gas Adsorption Chromatography*, Plenum Press, New York.
2. Webb, P.A. and Orr, C. (1997), *Analytical Methods in Fine Particle Technology*, Micromeritics, Norcross, GA.
3. Betz, W.R. and Lambiase, S.J. (1991), Dynamic gas-solid chromatographic techniques for characterizing carbon molecular sieves, *J. of Chromatography*, 556, 433-440.
4. Hinchcliff K.W., Reinhart G.A., Burr J.R., Schreider C.J. and Swenson R.A., Metabolizable energy intake and sustained energy expenditure of Alaskan sled dogs during heavy exertion in the cold. *Am J Vet Res* 58: 1457-1462, 1997.