Characterization of Polymer Carbon Sieves, Graphitized Polymer Carbons and Graphitized Carbon Blacks for Sample Preparation Applications

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T410103

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Abstract

The use of carbons in sample preparation techniques such as solid phase extraction (SPE) and air sampling has been ongoing for several decades. Recent advancements in sample preparation techniques have led to the use of carbons in micro-SPE (i.e., pipette tips packed with particles), solid phase microextraction (SPME) techniques and carbon coatings for both gas and liquid sample preparation techniques. Improvements in carbon purities, particle size distribution, pore structure and surface chemistries have led to the ability to analyze trace levels of the respective analytes.

The preparation of spherical, high-purity 2 micron carbon molecular sieves (CMS) with a large microporous regime allowed for the preparation of coated surfaces for environmental applications. The applications focused on a range of analytes from light gases to the semi-volatiles. These CMS carbons have been bonded to glass, metal and plastic substrates using patented, proprietary adhesives (1).

Abstract (contd.)

The preparations of spherical, high-purity 2 micron graphitized polymer carbons (GPC) have led to development of coated surfaces for liquid phase applications focused on semi-volatile and nonvolatile compounds. These GPC carbons have been bonded to glass, metal and plastic substrates using patented, proprietary adhesives.

The preparation of 175nm graphitized carbon blacks (GCB) has also led to the development of coated substrates for sample preparation of semi-volatile compounds.

Nitrogen porosimetry, helium pycnometry, titration and inverse gas chromatography (IGC) techniques were used to study the carbons. Additional adsorbent capacities and reversible adsorption characteristics have been determined using the respective sample preparation processes.

Introduction

A 2 micron CMS specialty carbon has been prepared for coating surfaces intended for gas phase and liquid phase sample preparation applications. The analyses of trace levels of environmental, industrial, warfare chemicals and explosive contaminants are now realized due to improvements in the carbon purities, particle size distribution, pore structures and surface chemistries. Preparation of a microporous only CMS with a surface of approximately 700 m^2/gram (2) has been effective for the concentration and desorption of airborne, volatile compounds such as Methyl Chloride. The presence of 5Å pores augments the condensation of the Methyl Chloride molecules in the deep micropores of the carbon.

The purity of these specialty carbons and carbon surfaces also allows for the effective adsorption and subsequent desorption of polar compounds such as Ethyl Acetate, Nitromethane, and Propionaldehyde. The technique of Inverse Gas Chromatography (IGC) was utilized for the initial capacity testing of the carbons (3).

Introduction (contd.)

The preparation of a 2 micron spherical, high-purity specialty graphitized polymer carbon (GPC) has led to development of coated substrates for environmental applications (both gas-phase and aqueous samples).

The preparations of a high-purity, specialty 175nm graphitized carbon black (GCB) with microporosity and mesoporosity has led to coatings of substrates with these carbons for the adsorption and subsequent desorption of semi-volatile compounds.

The use of these 2 micron and sub-micron particles and adhesives have led to a series of coated surfaces for use in environmental, biological and defense applications.

Experimental Method

The preparation of the microporous CMS entailed the processing of a spherical polymer bead using a suspension polymerization process. This polymer was prepared to possess a microporous only regime. Following polymerization, an ion-exchange resin (IER) was prepared by addition reaction of the ion-exchange group to the unsaturated ring structure of the aromatic polymer. The IER was subsequently pyrolyzed to obtain the CMS.

The preparation of the GPC carbon entailed the preparation of a spherical polymer with large macropores tapered to mesopores in a range of 50 to 500 Å. Following polymerization an ion-exchange resin was prepared, then pyrolyzed and subsequently graphitized.

Experimental Method (contd.)

The preparation of the 175 nm GCB entailed graphitization of a carbon black precursor at >2500 °C.

A nitrogen porosimeter was used to study the surface areas, pore size distributions and total pore volumes of the carbons. A helium pycnometer was used to determine the helium density of the carbons. A modified HP-6890 gas chromatograph was used to determine the capacities/ breakthrough volumes of specific analytes with the respective carbons. Film thicknesses of the coatings were measured using a light microscope with a graduated ocular.

Results and Discussion

Table 1. Textural Data for a CMS, GPC and GCB Carbon

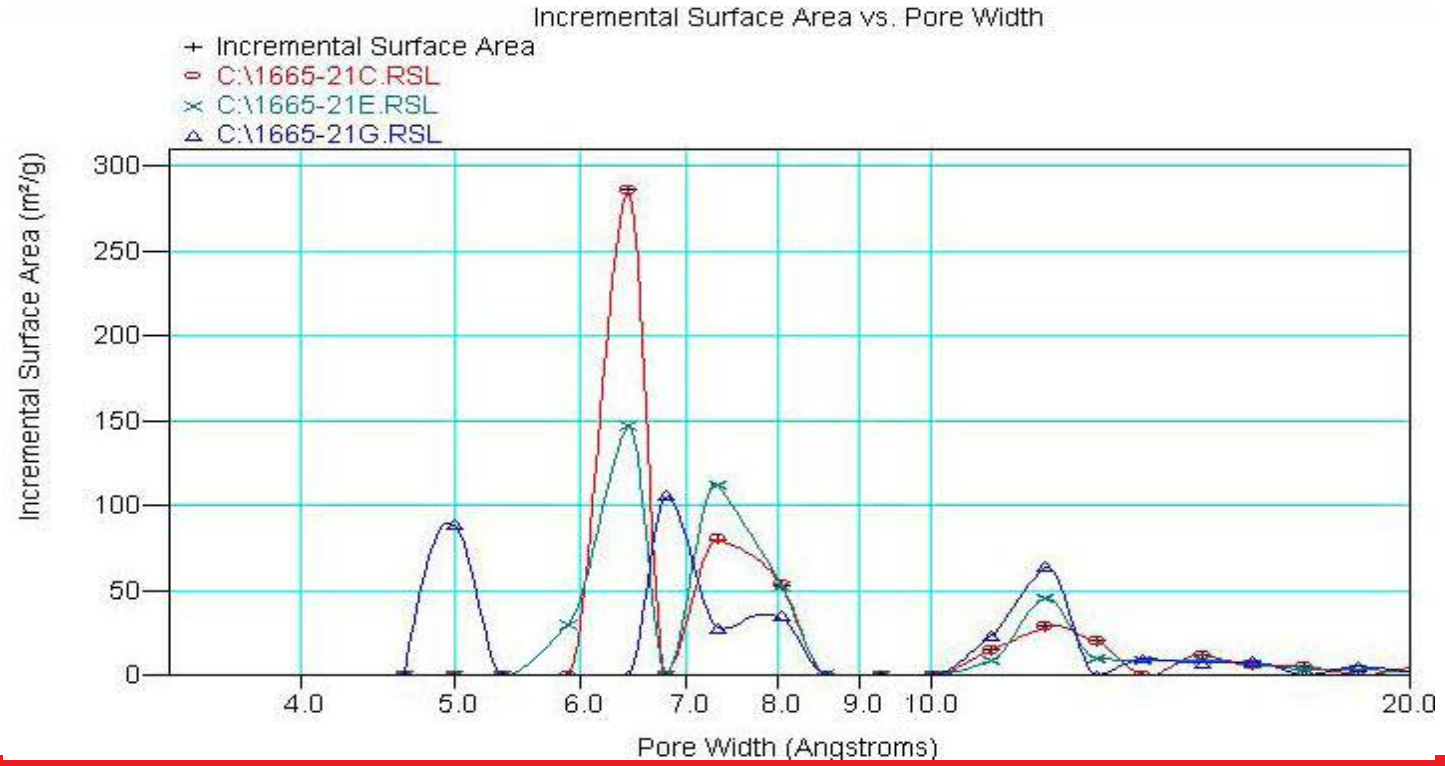
The textural data for 3 of the carbons are presented in Table 1.

	BET	BET	BET	
Carbon Description	**surface area (m^2/g)**	**total pore volume (cc/g)**	**average pore diameter (angstroms)**	**particle size (µm)**
CMS	418	0.221	11	2.0
GPC	126	0.542	173	2.0
GCB	202	0.458	90.4	0.3

Results and Discussion (contd.)

Figure 1. Density Functional Theory (DFT) Plot of 2.0 Micron CMS Carbons

The DFT plot for 3 CMS carbons are presented below in Figure 1. Carbon 21G was used for the IGC testing.



Results and Discussion (contd.)

Table 2. Specific Retention Volume Data for 10 Airborne, Volatile Compounds

The CMS carbon was tested using IGC. The goal of the project was to prepare a carbon with a maximum breakthrough volume during air sampling (sample concentration step). The results indicate that a breakthrough volume value of 47L for the highly volatile Chloromethane molecule was effective (see Table 2 below).

Compound	Specific Retention Volume (CMS) (mL)
Ethanol	325000
Hexane	616036
Toluene	16511000
1,3-Butadiene	20516
Carbon Disulfide	46960
Benzyl Chloride	3224000000
Vinyl Acetate	1105000
2-Butanone (MEK)	3711409
Vinyl Chloride	317852
Chloromethane	47384

Results and Discussion (contd.)

Light microscope photographs of the CMS bonded to wire mesh substrates are presented in Figures 2 and 3.

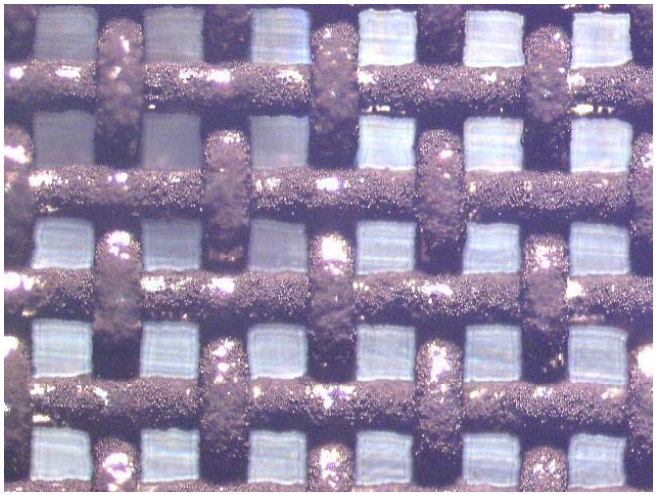


Figure 2. Light Microscope photograph of CMS bonded to a mesh screen (40X)

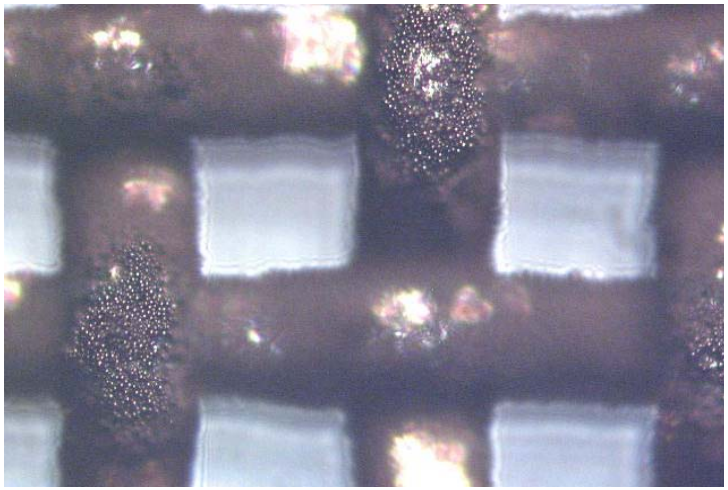


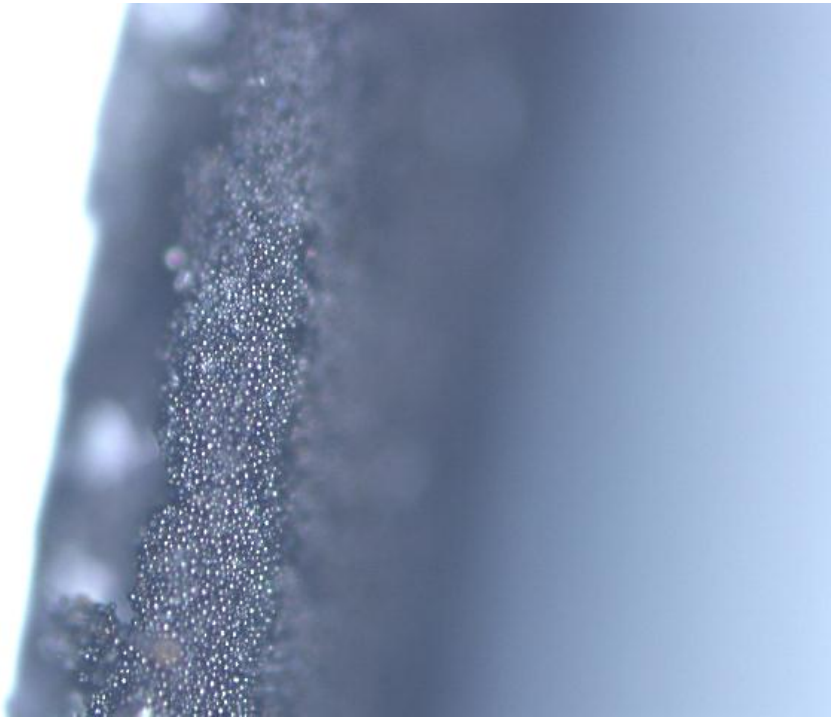
Figure 3. Light Microscope photograph of CMS bonded to a mesh screen (100X)

Results and Discussion (contd.)

Figure 4a. Light Microscope photograph of the CMS coated on a dissolvable substrate; template has been removed and the resultant/flexible mass (CMS and adhesive) rolled into final configuration

Results and Discussion (contd.)

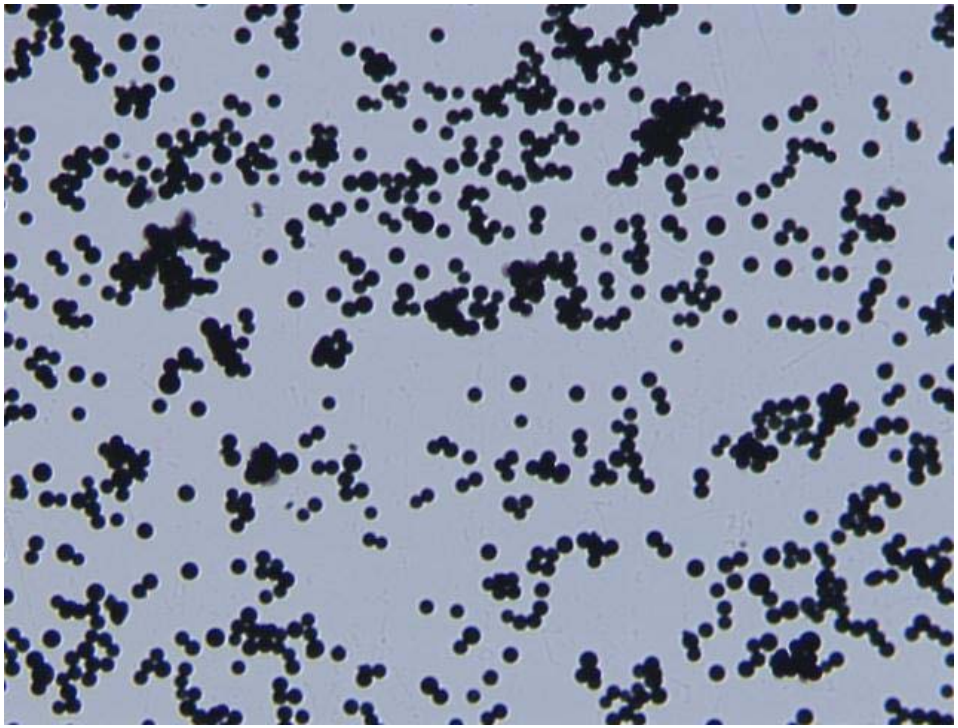
Figure 4b. Light Microscope photograph of the CMS/adhesive bonded on a dissolvable template; side view after template removal



Results and Discussion (contd.)

Figure 5. Light Microscope photograph of 2 µm GPC Carbon

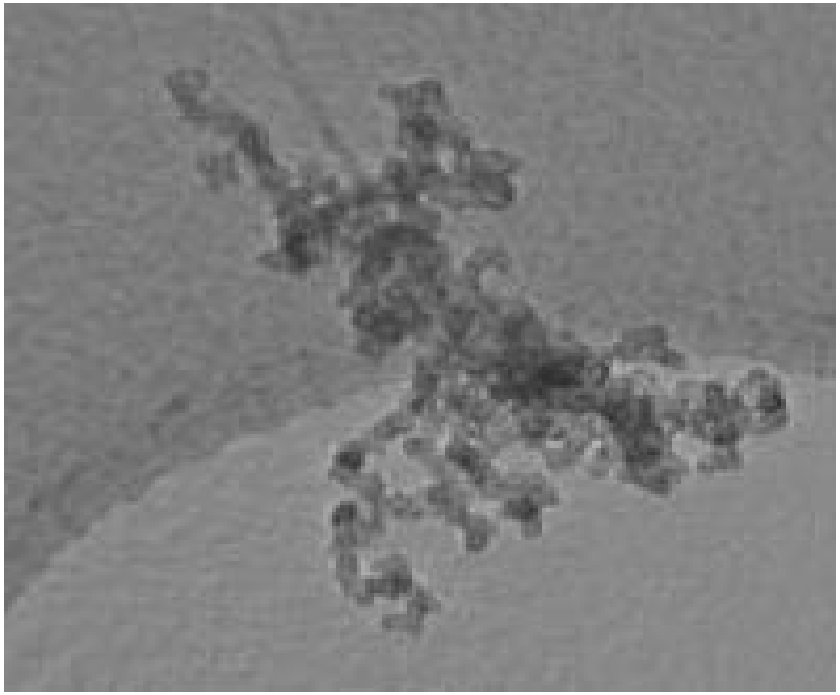
The 2 µm GPC carbon was also used to coat the wire mesh substrates.



Results and Discussion (contd.)

Figure 6. TEM photo of 300 nm GCB

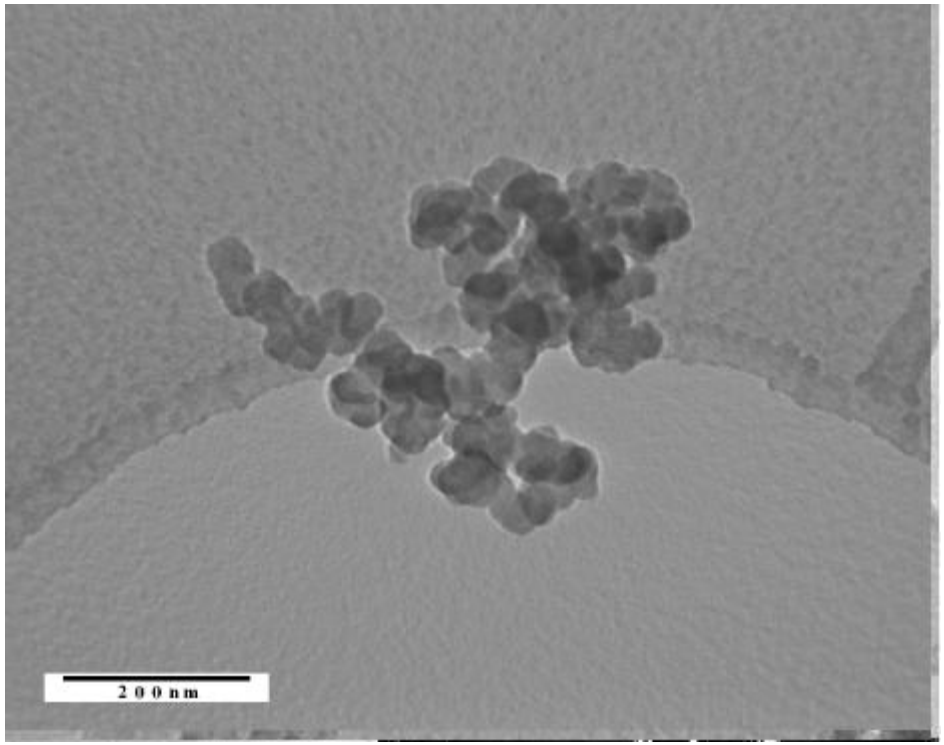
The 300 nm GCB was also used for coating substrates using an adhesive. Figures 6 and 7 Illustrate 2 TEM photos of the GCB.



Notes:
High level of aggregation
Conductance ~10^2-10^4 siemens/m

Results and Discussion (contd.)

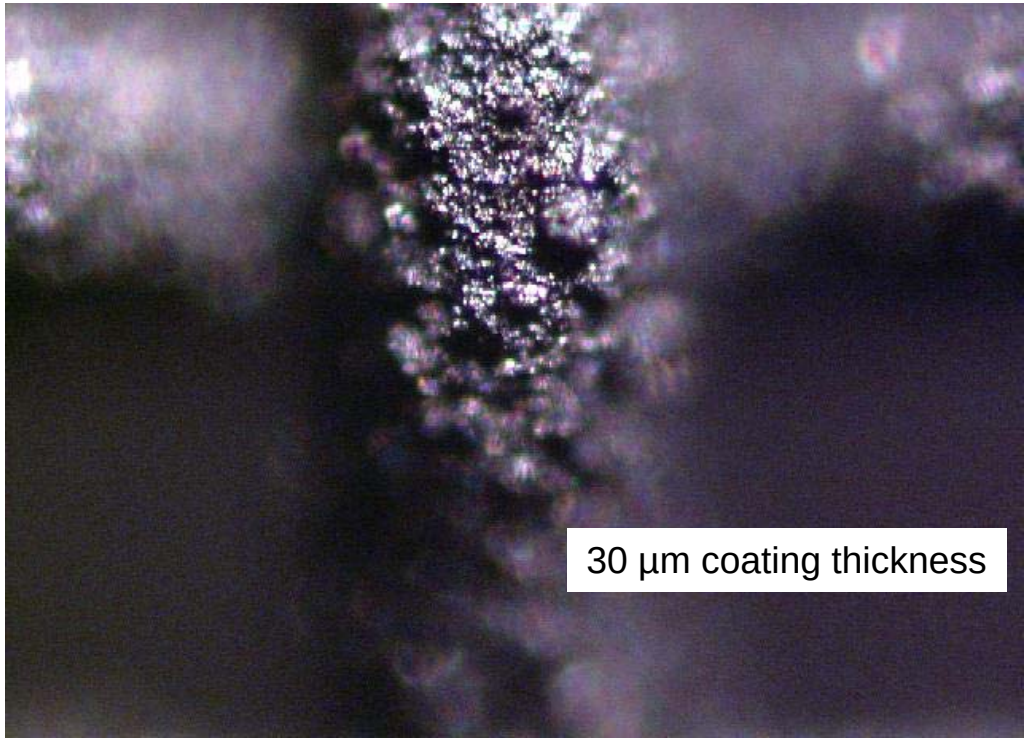
Figure 7. TEM photo 2 of 300 nm GCB



Results and Discussion (contd.)

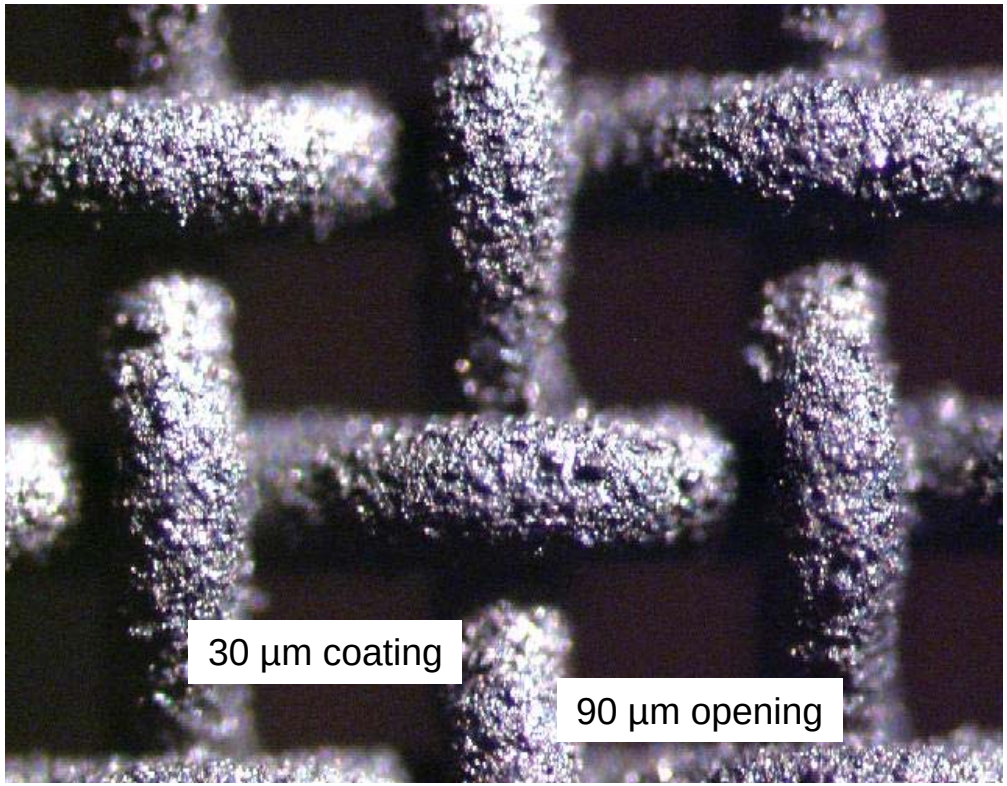
Figure 8. Light microscope photo (100X) of 30 µm coating of the GCB on a wire mesh substrate

The GCB was also bonded/coated onto a wire mesh substrate using an adhesive for sample preparation applications.



Results and Discussion (contd.)

Figure 9. Light Microscope photo (40X) of 30 µm bonding/coating of the GCB on a wire mesh substrate



Conclusion

The textural and performance characteristics of several new spherical 2 micron carbons and a graphitized nanocarbon black have been determined. Optimization of the carbons for the specified applications was based on the changes observed with the physical characterization methods employed. The data obtained indicate that the carbons performed effectively for the respective applications.

References

1. Betz, W. and Desorcie, J., Nucleophilic Bodies Bonded to siloxane and Use There of for Separations from Sample Matrices, US Patents US05599445, US05607580, US05609756, US05620603, US05630937.
2. Webb, P.A. and Orr, C., Analytical Methods in Fine Particle Technology, Micromeritics, Norcross, GA, 1997.
3. Kiselev, A.V. and Yashin, Y.A. (1969), Gas Adsorption Chromatography, Plenum Press, New York.