SCIENCE & TECHNOLOGY INNOVATIONS

High Purity Carbon Adsorbents for Sample Preparation and Chromatographic Applications

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Introduction

The first high purity Supelco® carbon adsorbents were made for gas chromatographic packed columns. Then, specialty carbons were developed for thermal desorption tubes followed by the introduction of carbons in solid phase extraction (SPE) cartridges. In later developments, Supelco® carbons were used to make porous layer open tubular (PLOT) columns as well as solid phase microextraction SPME fibers. Current Supelco carbon technologies include nanocarbons for electronic applications.

Merck, under the Supelco® brand, has a total of 75 carbon intermediates that are utilized combined or stand-alone in different analytical devices. These carbons are highly customizable, high capacity, synthetic, and reusable which differentiates them from activated charcoal. These carbons are categorized below.

- Carboxen® and Carbosieve® are amorphous carbon molecular sieves suitable for permanent gas analyses and small molecule analysis at high pressures (16,000-20,000 psi), volatile organic compound analysis using air sampling tubes, and for extracting small molecules from aqueous samples for SPE analyses.
- Carbopack™ and Nanocarbons are graphitized carbon blacks. These carbons are effective for separating volatile, semi-volatile, and non-volatile compounds for gas chromatographic analyses, and for extraction of semi-volatile and non-volatile compounds from aqueous samples for SPE applications. Carbopacks typically can only withstand 400 psi, but are effective adsorbents for separation of semi-volatiles and non-volatiles in air sampling applications.
- Graphsphere™ are graphitized polymer carbons, and represent an additional benefit over the graphitized carbon blacks due to their spherical particle shape in packed bed systems. Graphsphere™ is also non-friable; it can withstand superior pressures (16,000-20,000 psi) when used in packed bed systems in gas and liquid applications. The uniformly defined graphite surface provides unique selectivity for both chromatography and sample preparation.

All four families of carbons are processed at the Supelco® site in Bellefonte, USA where all carbon containing devices are manufactured. For those research groups that are investigating new applications, these carbons are also available in family kits containing either carbon molecular sieves, graphitized carbon blacks or graphitized polymer carbons.

Carbon Properties

Particle Size Distribution

The particle size range of all the carbons is 200 nm to 850 µm; therefore, the particle size distribution can be tailored to a specific application.

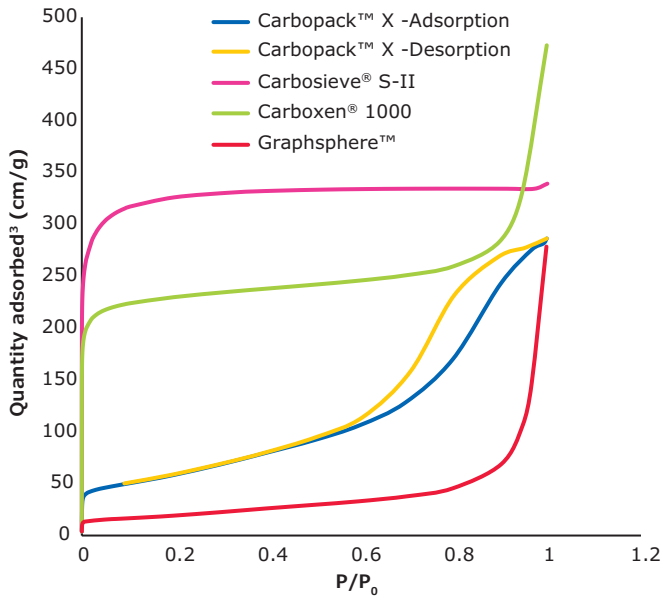
Pore Size Distribution

The pore structure of all our carbon adsorbents can be modified to possess ultramicropores (pore diameter less than 7 Å) to macroporous with pore diameters larger than 500 Å. The plots in **Figure 1** show the N_2 adsorption isotherms at 77 K for different adsorbents. Type I isotherms as seen with Carbosieve® S-II are characteristic of microporous materials, while mesoporous materials such as Carbopack™ X show a hysteresis loop characteristic of a mesoporous material.

Non-porous materials, such as Graphsphere™, show very low adsorption values.

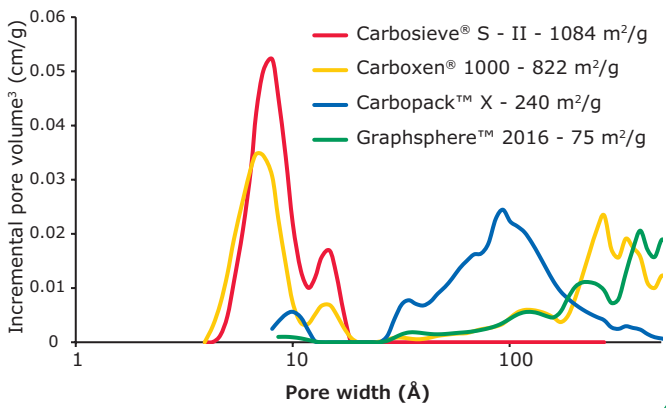
Multiporous carbons are also available; these carbons contain different pores with various sizes. An overlay

Figure 1. N_2 Adsorption isotherms for Supelco® carbons



of representative examples of four families of carbons which have different pore size distributions is shown in **Figure 2**. On the y-axis of this figure, the specific volume of nitrogen gas fitted at a pore size interval is plotted against the pore size/width in the x-axis. Micropores are defined as pores below 20 Å, mesopores are those pores between 20-500 Å, and pores larger than 500 Å are considered macroporous. **Figure 2** shows the pore size distributions of various carbons containing either micro, meso and/or macro pores. Carbosieve® S-II is a microporous only carbon with an apex at 8 Å, while Carboxen® 1000 is a multiporous carbon that contains both micro and macropores. Carbopack™ X is a mesoporous only carbon while Graphsphere™ has pores mostly in the macropore region. Microporous carbons such as the Carbosieves and Carboxens have larger surface areas and provide larger capacities compared to macroporous carbons like Carbopack™ and Graphsphere™.

Figure 2. Pore size distributions (PSD) and surface areas (m^2/g) for representative Supelco® carbons



Example Applications of Supelco® Carbons

Gas Chromatography

Supelco® microporous carbons can be used in packed columns for the separation of permanent gases such as N_2 and O_2. Carbosieve® S-II and Carboxen® 1000 effectively separate air in stainless steel packed columns with 6 ft x 1/8 in dimensions (see **Figure 3**). Lateral diffusion of gas molecules is significant in packed columns, and because of this phenomenon, the diameter of the column can affect the separation efficiency and is balanced by optimizing the particle size.

The use of 180-250 µm particles in a 4.8 m x 3.18 mm packed column has the same retention time as a 30 m x 0.53 mm ID PLOT column with 2 µm particles adhered to the side walls [i.e., porous layer open tubular (PLOT)] (see **Figure 4**), although the peak width will be wider. In **Figure 4**, the red chromatogram represents the signal from a thermal conductivity detector and the black chromatogram represents the signal from a methanizer/flame ionization detector (FID).

Figure 3. Separation of air using chromatographic columns packed with Carbosieve® S-II and Carboxen® 1000

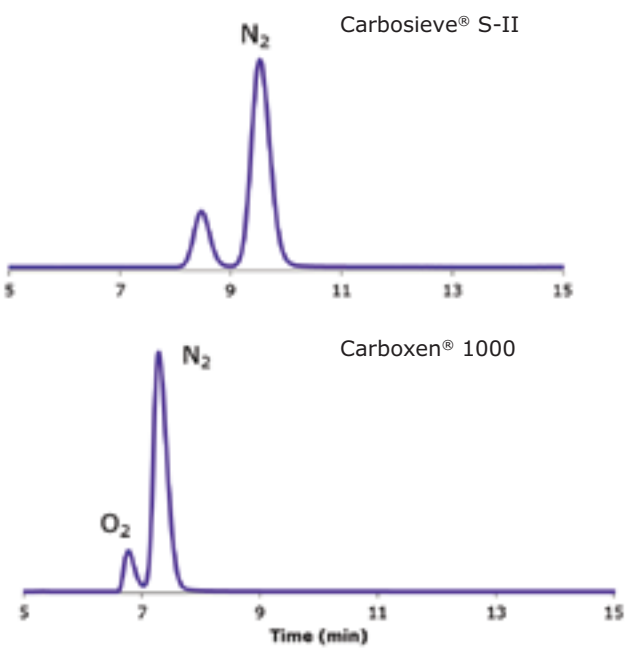


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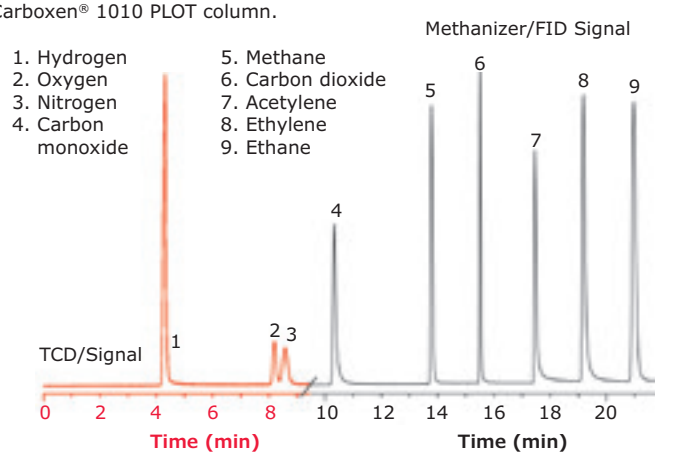
Figure 4. Separation of permanent gases and light hydrocarbons with a Carboxen® 1010 PLOT column.

column:	Carboxen® 1010 PLOT, 30 m x 0.53 mm I.D., 30.0 µm (25467)
oven:	35 °C (7.5 minutes) to 250 °C at 24 °C/minute
injector:	200 °C
detector:	TCD/methanizer-FID, 230 °C
flow:	Argon, 3.0 mL/min
valve:	150 °C
injection:	10.0 µL valve injection
sample:	transformer gas for ASTM method D3612-96

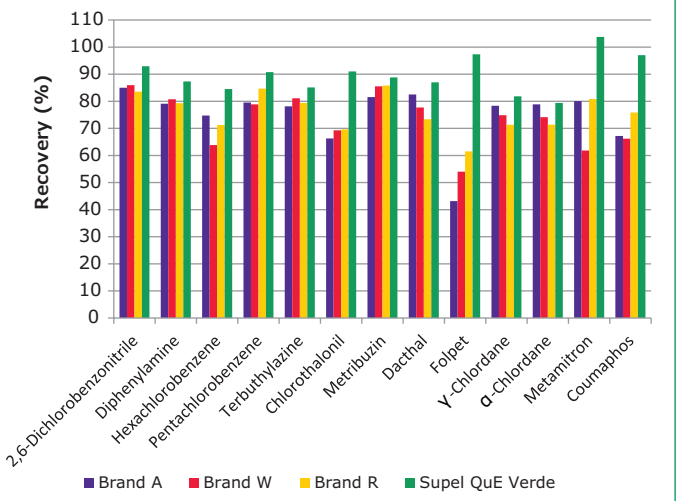


Sample Preparation

SPE

These carbon adsorbents are also be widely used in sample preparation techniques. Carbon removes matrix interferences in SPE cartridge applications, so a clean sample can be injected and precisely analyzed by HPLC or GC. For this application, carbons with larger particle and pore sizes like Carbopack™ and Graphsphere™ are effective for cleaning samples without retaining the molecules of interest. ENVI-Carb™ and ENVI-Carb™ Y are carbons from the family of Carbopacks that are used in SPE products such as ENVI-Carb™ and Supel™ QuE Verde, respectively. ENVI-Carb™ is highly effective in removing chlorophyll and carotenoids; similarly, the product Supel™ QuE Verde removes chlorophyll and gives a high recovery of planar pesticides (see **Figure 5**).

Figure 5. Recoveries of planar pesticides for different QuEChERS brands compare to Supel™ QuE Verde

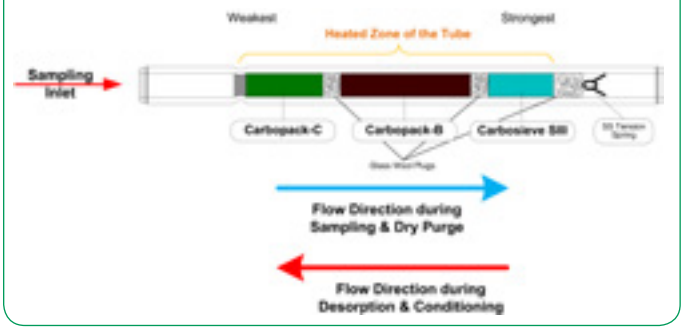


Recoveries between 70% and 120% are typically considered to be acceptable.

Air Sampling

Single bed and multi-bed carbon adsorbent tubes have become significant tools for air sampling analysts. One example is the Carbotrap® 300 3-bed tube (i.e. Carbotrap® C, Carbotrap® B and Carbosieve® S-III) which was the first tube developed for the US EPA for monitoring toxic, volatile, and semi-volatile organic compounds (see **Figure 6**). The development of a 2-bed tube containing Carbopack™ B and Carboxen® 1000 was key for the 61 compounds list of airborne contaminants established later by the EPA.

Figure 6. Multi-bed tube for air sampling (Carbotrap® 300)



Additional efforts with the EPA focused on the development of a single bed tube containing a mesoporous graphitized carbon black, Carbopack™ X, for 72-hour passive sampling of 1,3-butadiene and various other airborne organic compounds (see **Figure 7**).

Solid Phase Microextraction (SPME)

Carbons with particle sizes of 2.0 µm have been adhered, using a Merck patented adhesive, to SPME fibers for the extraction of organic compounds from aqueous and atmospheric environments (see **Figure 8**).

Figure 7. Carbopack™ X passive sampling tube data

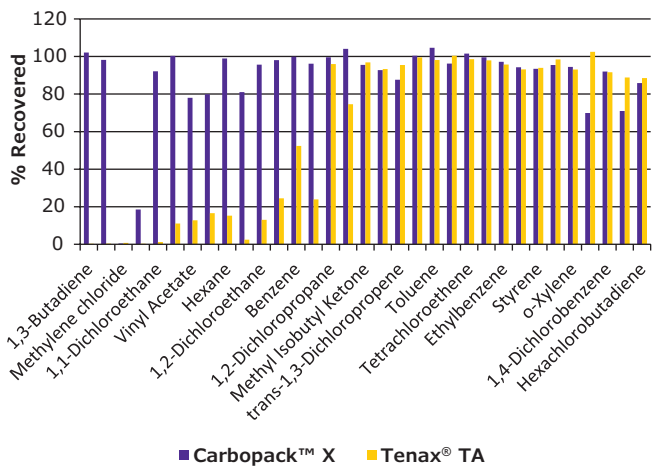
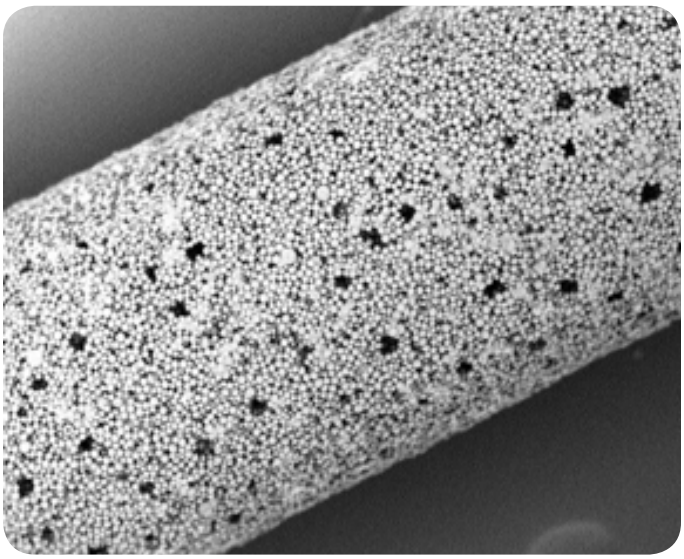


Figure 8. SPME fiber with Carboxen® 1006



Conclusion

Supelco has a 40+ year commitment to carbon adsorbent research and product development. Evidence of this can be seen in our high purity, specialty carbon adsorbents, which are currently used for:

- Collection media in air sampling devices
- Packings in SPE hardware, purge traps, and GC columns
- Purification of gas or liquid streams
- Recovery of synthesized compounds from reaction mixtures
- And many more exciting applications

If you are interested in a new adsorbent and know the target physical specifications (surface area, porosity, pore diameter, particle size range, etc.), let us know and we can investigate the possibility of manufacturing it. You can also try one of our ready-made sample kits, which you can find at **SigmaAldrich.com/carbon**

However, most requests require a specialty carbon adsorbent that can perform a specific task. In that case, tell us the type of sample (gas, liquid, or paste) you are working with, what analytes you want to adsorb and analyze, and if there is a need to recover the analytes after adsorption. Our R&D group will investigate whether an existing adsorbent is appropriate, or if a new adsorbent needs to be developed.

To learn more about our portfolio of specialized carbon adsorbents and/or download the "Supelco® Specialty Carbon Adsorbent" brochure, visit us at **SigmaAldrich.com/carbon**

To request a quote, contact Supelco_Quotes@sial.com