

Carbotrap Carbon Black: An Excellent Adsorbent for Solvent or Thermal Desorption/GC Analyses of Airborne Organic Compounds

Carbotrap adsorbent traps and releases a wider range of airborne organic compounds than Tenax GC or Amberlite XAD-2 resin. Compounds adsorbed by Carbotrap adsorbent can be completely recovered through either solvent or thermal desorption. Carbon disulfide, a highly effective desorbing solvent, degrades Tenax GC and Amberlite XAD-2, forcing you to use potentially less effective desorbing solvents. Thermal desorption releases adsorbates undiluted from the adsorbent, enabling you to monitor small amounts of analytes that might be undetected with solvent desorption. Tenax GC and Amberlite XAD-2 resins release residues during thermal desorption, but Carbotrap adsorbent is stable at high temperatures ($\geq 400^{\circ}\text{C}$). Carbotrap adsorbent also is more hydrophobic than the resins, and its performance is unaffected by humidity.

Key Words

- airborne organic compounds ● air contaminants
- air sampling

Carbotrap™ high purity, graphitized carbon black can adsorb, then release, a wide range of airborne organic contaminants. A Class I adsorbent (1), it has no surface ions or active functional groups. The entire surface is available for interactions that depend solely on dispersion (London) forces (2). In contrast, two other widely used adsorbents, Tenax® GC and Amberlite® XAD®-2 resins, have localized surface charges for specific adsorbent/adsorbate interactions. Furthermore, Carbotrap adsorbent is more hydrophobic than either of the resins. Thus, its performance is unaffected by humidity. Carbotrap adsorbent is free of contaminants and is not susceptible to solvent degradation.

We evaluated Carbotrap adsorbent for airborne organic compounds, using procedures that parallel work described by the United States Environmental Protection Agency (3). We introduced a known *challenge* concentration of adsorbate onto a Carbotrap bed, then passed air through the bed. The specific retention or *breakthrough* volume (V_g^t) of air needed to elute the adsorbate was determined. The larger the V_g^t value, the better the retention of the adsorbate.

To determine the range of molecular sizes that can be trapped successfully, then desorbed, from Carbotrap adsorbent (the *functional trapping/desorbing range*), we used 38 straight chain and ring compounds ranging from C2 to C14. To characterize the nonspecific surface properties of Carbotrap adsorbent, adsorbates with diverse functional groups were chosen. We established the lower end of the functional range by setting 1.0 liter as the lowest acceptable breakthrough volume. The upper end of the range was determined by evaluating Carbotrap adsorbent's

ability to release large molecules, such as polynuclear aromatic hydrocarbons or pesticides, through thermal desorption. A 2.0 minute migration time and 350°C desorption temperature were considered maximum allowable conditions for proper thermal desorption.

Table 1. Breakthrough Volumes for Organic Adsorbates on Carbotrap Adsorbent

Adsorbate	V_g^t 20°C (mL/g)	Correlation Coef.*
Ethane	1.73×10^1	1.00000
n-Propane	5.49×10^1	0.99412
n-Butane	4.06×10^2	0.99875
Ethanol	4.93×10^2	0.99219
Acetic acid	7.16×10^2	0.99690
Propionic acid	1.66×10^3	0.98410
1,2-Dichloroethane	1.94×10^3	0.99848
2-Butanone	3.76×10^3	0.99611
n-Pentane	5.89×10^3	0.99994
2-Methyl-2-propanol	6.52×10^3	0.98650
Benzene	1.17×10^4	0.99802
1,1,2-Trichloroethylene	1.27×10^4	0.99939
n-Butanol	1.92×10^4	0.99643
1,1,2-Trichloroethane	2.47×10^4	0.99986
n-Hexane	7.99×10^4	0.99871
n-Pentanoic acid	4.31×10^5	0.97190
Phenol	6.16×10^5	0.99941
Toluene	6.50×10^5	0.99972
Chlorobenzene	1.58×10^6	0.99999
Cyclohexanone	2.04×10^6	0.99581
n-Butylamine	2.08×10^6	0.99935
4-Heptanone	2.44×10^6	0.99991
1,4-Dichlorobenzene	1.34×10^7	0.99925
n-Octane	1.61×10^7	0.99989
Ethylbenzene	2.03×10^7	0.99989
p-Cresol	2.06×10^7	0.99948
Benzylamine	2.23×10^7	0.99990
p-Xylene	4.27×10^7	0.99963
Acetophenone	6.40×10^7	0.99971
Isopropylbenzene	1.70×10^8	0.99999
n-Propylbenzene	1.72×10^9	0.99993
n-Decane	4.79×10^9	0.99971
n-Butylbenzene	5.83×10^9	0.99937
Biphenyl	3.74×10^{12}	0.99999
n-Hexylbenzene	7.00×10^{12}	0.99989
n-Dodecane	1.63×10^{14}	0.99903
n-Octylbenzene	1.31×10^{15}	0.99985
n-Tetradecane	8.32×10^{16}	0.96309

*For temperature/breakthrough volume. V_g^t values for high boiling adsorbates must be determined at elevated temperatures, then calculated for 20°C (by linear regression) for comparison. These correlation coefficients show that the regression plots used in this investigation were linear.

Functional range for Carbotrap adsorbent.

Larger compounds that can be desorbed if higher desorption temperatures are used.

Table 2. Breakthrough Volumes (V_g^t), Adsorption Coefficients (K_a), and Equilibrium Sorption Capacity (Q_g) Values for Carbotrap, Tenax GC, and Amberlite XAD-2 Adsorbents

Adsorbate	V_g^t 20°C*			K_a			Q_g		
	Carbotrap	Tenax GC	XAD-2	Carbotrap	Tenax GC	XAD-2	Carbotrap	Tenax GC	XAD-2
n-Decane	4.79×10^9	1.56×10^7	3.63×10^7	2.60	3.61×10^{-2}	5.40×10^{-3}	28.0	9.14×10^{-2}	2.12×10^{-1}
Benzylamine	2.23×10^7	3.57×10^6	1.63×10^7	1.21×10^{-2}	8.23×10^{-3}	2.42×10^{-3}	9.81×10^{-2}	1.57×10^{-2}	7.18×10^{-2}
Chlorobenzene	1.58×10^6	1.51×10^5	4.84×10^5	8.55×10^{-4}	3.49×10^{-4}	7.20×10^{-5}	7.30×10^{-3}	8.85×10^{-4}	2.24×10^{-3}
p-Xylene	4.24×10^7	3.88×10^5	7.95×10^6	2.30×10^{-2}	8.39×10^{-4}	1.18×10^{-3}	1.82×10^{-1}	1.66×10^{-3}	3.40×10^{-2}
p-Cresol	2.06×10^7	1.50×10^7	4.96×10^6	1.11×10^{-2}	3.45×10^{-2}	7.39×10^{-4}	9.14×10^{-2}	3.70×10^{-3}	2.21×10^{-7}
n-Pentanoic acid	4.31×10^5	9.78×10^5	1.01×10^5	2.34×10^{-4}	2.26×10^{-3}	1.51×10^{-5}	1.76×10^{-3}	3.99×10^{-3}	4.31×10^{-4}
Cyclohexanone	2.04×10^6	1.06×10^6	6.27×10^5	1.10×10^{-3}	2.45×10^{-3}	5.45×10^{-5}	8.19×10^{-3}	4.28×10^{-3}	1.47×10^{-3}
2-Methyl-2-propanol	6.52×10^3	6.86×10^2	5.42×10^3	3.53×10^{-6}	1.58×10^{-6}	8.06×10^{-7}	1.99×10^{-5}	2.09×10^{-6}	1.65×10^{-5}

*For the three adsorbents, correlation coefficients for breakthrough volume and temperature ranged from 0.97190 to 1.00000.

Carbotrap adsorbent's functional range for the compounds studied is indicated in Table 1. Extremely large sample volumes can be used with adsorbates larger than n-decane and n-butylbenzene. In comparison, the lower end of the functional range for Amberlite XAD-2 resin is similar to that for Carbotrap adsorbent, but the upper limit is restricted by the resin's limited ability to withstand certain solvents, or temperatures above 150°C. The lower end of the range for Tenax GC appears to be a linear C6 molecule or equivalent structure (e.g., butanoic acid: C-C-C-O-O). For Tenax GC, as for Amberlite XAD-2, desorption of larger molecules, and of certain molecules within the functional range, is hampered by solvent and temperature effects.

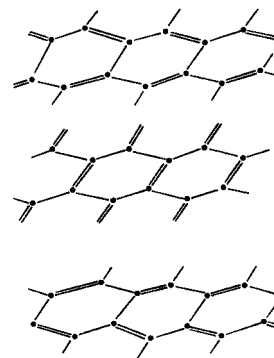
We used adsorbates representing eight classes of compounds to compare the adsorptive properties of Carbotrap, Tenax GC, and Amberlite XAD-2 adsorbents. Carbotrap adsorbent shows greater adsorbing capacity for linear and cyclic molecules (Table 2) – an expression of the carbon's unique surface area properties (area: 100m²/g, density: 0.38g/mL) and delocalized surface charge, a combination that permits greater interaction between the adsorbent surface and the adsorbate. Tenax GC adsorbent's greater adsorbing power for n-pentanoic acid is due to localized surface charges specific for interaction with acid groups (Figure A).

From the breakthrough volume, V_g^t , two other values can be calculated to characterize the adsorbent/adsorbate relationship. The adsorption coefficient, K_a , describes the distribution of the adsorbate between the gas and solid phases and relates the retention volume to the adsorbent surface area. The equilibrium sorption capacity, Q_g , describes the adsorbent's capacity for the adsorbate. Large values of K_a and Q_g indicate good retention characteristics. The large Q_g values for Carbotrap adsorbent in Table 2 reflect the ability of the entire surface to participate in the interaction (Figure A). V_g^t values also can be used to predict the relationship between the adsorbent and untested adsorbates in the same chemical class as a tested adsorbate.

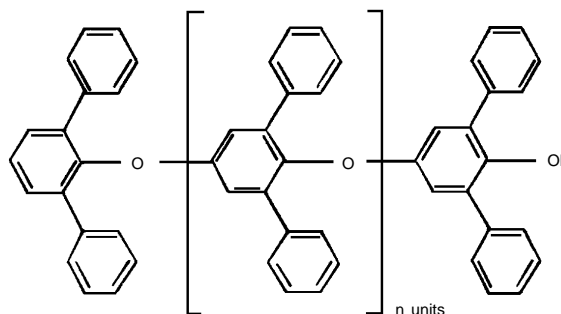
Adsorbates were recovered from tubes containing Carbotrap adsorbent through both solvent desorption and thermal desorption techniques. Our initial studies showed 1-butanol, 2-butanone, and 2-ethoxyethylacetate are difficult to desorb from some adsorbents. The electron-rich oxygen atoms in these molecules form covalent bonds with metal and salt impurities on an adsorbent's surface. These adsorbates, then, are a stringent test of adsorbent surface purity. Similarly, the active groups on chlorobenzene (halogen), n-pentanoic acid (carboxyl), and benzylamine (amino) reveal specific, localized charges on an adsorbent surface. Adsorbate volumes in Table 3 represent the quantity of adsorbate in 5.0 liters of air at 0.5 times the Occupa-

Figure A. The Entire Surface of Carbotrap Adsorbent is Available for Adsorbent/Adsorbate Interactions

A1. Surface Model for Carbotrap Adsorbent (Surface Area ~ 100m²/g). Charges are uniformly distributed around the carbon atom centers.



A2. Surface Model for Tenax GC Resin (Surface Area ~ 23.5m²/g). Surface is nonuniform in charge – charge is localized to oxygen atoms.



A3 – Surface Model for Amberlite XAD-2 Resin (Surface Area ~ 364m²/g). Surface is nonuniform in charge and is less polar than Tenax GC.

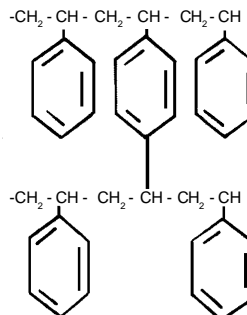


Figure A1 adapted from (4), Figures A2 and A3 from (3).

797-0673, 0674, 0675

tional Safety and Health Administration (OSHA) threshold limit value (TLV[®]). When a TLV was not available, 1.0µL was used.

For activated charcoal, 60% recovery of 1-butanol and 2-ethoxyethylacetate is typically cited as an acceptable value. For Carbotrap adsorbent, recovery of these and other compounds is virtually complete by either solvent or thermal desorption (Table 3), due to the high purity of the sorbent and the nonspecific nature of its graphitized surface.

We used two desorbing solvents in this evaluation (Table 3). Carbon disulfide was chosen because it is commonly used as a desorbing solvent for charcoal, and because its high heat of adsorption allows it to readily displace adsorbed compounds. Carbon disulfide *cannot* be used with polymeric adsorbents, such as Tenax GC or Amberlite XAD-2, because it degrades them. Thus, with these materials you are forced to use other solvents that may less effectively remove adsorbates. We also used acetonitrile as a desorbing solvent, because it is widely used in liquid chromatographic analyses.

Table 3. Desorption Efficiency for Carbotrap Adsorbent

Adsorbate	Volume (µL)	Desorption Efficiency (%)		
		Solvent Desorption		Thermal Desorption
		Acetonitrile	Carbon Disulfide	
Toluene	2.2	102	—	111
2-Butanone	1.8	108	109	105
1-Butanol	0.9	106	102	116
2-Ethoxyethylacetate	1.4	104	102	109
n-Decane	1.0	100	—	111
Chlorobenzene	1.6	93	—	113
n-Pentanoic acid	1.0	110	103	111
Benzylamine	1.0	108	—	109

Thermal desorption has gained acceptance because of more demanding regulations from the USEPA, the National Institute for Occupational Safety and Health (NIOSH), and other agencies. When recovered by solvent desorption, a trapped adsorbate is diluted. In contrast, when a suitable adsorbent is heated, adsorbates are released effectively and undiluted.* Thus, with thermal desorption, you can monitor small amounts of airborne contaminants that otherwise might be undetectable.

Tenax GC resin releases toluene, benzene, and trichloroethylene residues during thermal desorption. Similarly, residues are evolved from Amberlite XAD-2 resin at 150°C, and at 250°C the resin will completely pyrolyze. Thus, Amberlite XAD-2 is poorly suited to thermal desorption, and Tenax GC must be carefully conditioned to prevent artifact formation. In contrast, Carbotrap adsorbent is stable at temperatures of 400°C or higher.

We use Carbotrap adsorbent in a number of the thermal desorption tubes (Carbotrap tubes) and solvent desorption tubes (ORBO™ tubes) we offer from stock – for a complete list of these tubes, refer to the current Supelco catalog. We also offer Carbotrap adsorbent in bulk, and we can prepare Carbotrap tubes to your unique specifications. For additional information about Carbotrap and thermal desorption, contact our Technical Service Group.

* Strong polar and/or ionic groups on an adsorbent surface can cause disassociation of an adsorbate, or of the adsorbent's surface bonds, forming artifacts.

Ordering Information:

Thermal Desorption Tubes

For Dynatherm Instruments

All tubes are 11.5cm in length. Standard air sampling tubes are 4mm ID x 6mm OD glass; 7mm ID x 10mm OD tubes are used only for continuous on-line monitoring with the ACEM.

Tube ID x OD (mm)	Model 850/890 TDU Only Cat. No.	Model 850/890 TDU and ACEM 900/901-FF Cat. No.	ACEM 900/901-FF Only Cat. No.
Carbotrap 100 (Carbotrap B) for C5-C12 compounds in air			
7 x 10	—	—	custom
4 x 6	20238	20872*	—
Carbotrap 150 (glass beads, Carbotrap C) for large molecules in air or aqueous samples			
7 x 10	—	—	custom
4 x 6	—	20381*	—
Carbotrap 200 (glass beads, Carbotrap B, Carbosieve S-III*) for C2-C14 compounds in air			
7 x 10	—	—	custom
4 x 6	20242	20873*	—
2 x 6 [■]	20244	—	—
Carbotrap 217 (Carbotrap B, Carboxen-1000) for TO-17 compounds, other volatiles in air			
7 x 10	—	—	20724*
4 x 6	—	20895-U*	—
Carbotrap 300 (Carbotrap C, Carbotrap B, Carbosieve S-III) for C2 and larger compounds in air			
7 x 10	—	—	custom
4 x 6	20379	20875*	—
2 x 6 [■]	20382	—	—
Carbotrap 317 (Carbotrap C, Carbotrap B, Carboxen-1000) for TO-17 compounds, other volatiles and semivolatiles in air			
7 x 10	—	—	20881*
4 x 6	—	20877*	—
Carbotrap 400 (Carbotrap F, Carbotrap C, Carbotrap B, Carboxen 569) for C2 and larger compounds in aqueous samples			
7 x 10	—	—	custom
4 x 6	20359	20882*	—

*glass frit at sample inlet

■ For focusing semivolatile compounds.

*Patented (see "Legally Speaking" in our catalog)

For descriptions of additional Carbotrap tubes and other thermal desorption products, please refer to our catalog.

References

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References not available from Supelco.

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Tenax – Enka Research Institute, Arnhem

TLV – Occupational Safety and Health Administration

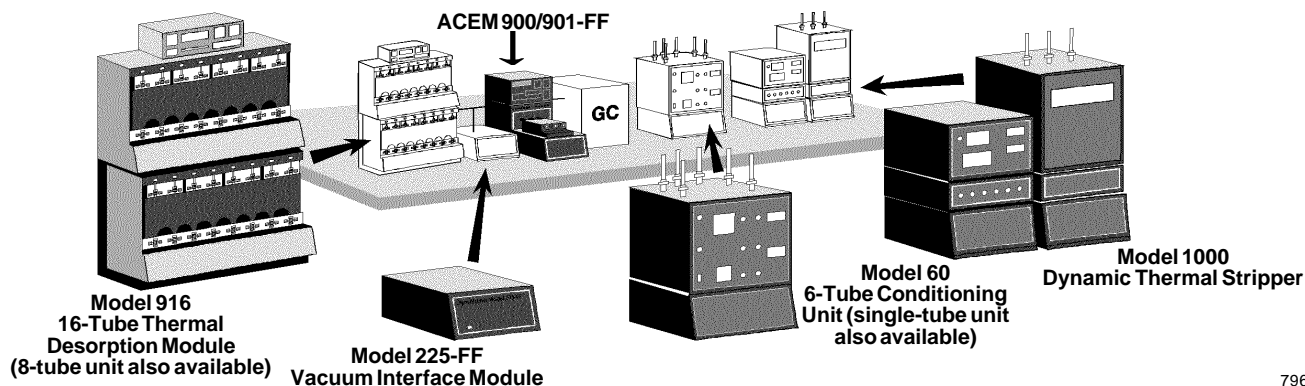
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The core of our system, the ACEM desorber, will transfer a sample from a thermal desorption tube to almost any gas chromatograph. You can effectively concentrate analytes from air, water, soil, foods, etc. with optimal moisture control, ensuring maximum analytical sensitivity. An effective, convenient dry purge system replaces cryogenic cooling of the GC oven: analytes collected on a 4mm ID tube are transferred to a 1mm ID

refocusing tube, then are swiftly desorbed onto the capillary column in a very tight band. In conjunction with our hydrophobic adsorbent tubes, this dry purge capability enables you to deliver 100% of even high-humidity samples to the GC. Units that rely on cryogenic refocusing typically require a 4:1 split of high-humidity samples to control water in the system – the column receives only a small fraction of the sample.

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Modular add-on units broaden and expedite your sample handling ability.



796-0478

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When interfaced with a GC, this factory-assembled system provides complete, unattended, continuous on-line monitoring.



996-0300

Versatility and value – installs in about 5 minutes! The ACEM and the Vacuum Interface Module are plumbed, wired, and attached to a mounting plate. Simply connect the carrier gas supply and the fused silica transfer line, and plug in the AC power cable (115VAC).

Description	Cat. No.
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■CE approved

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Modular thermal desorber prepares narrow-band injection into a GC column.



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Description	Cat. No.
ACEM Model 900/901-FF*	22587
Replacement Ferrules, pk. of 10	22393

*Includes a 30" fused silica transfer line for connection to most manufacturers' GCs, adsorbent tubes, a VOC test standard, copper tubing and fittings to connect a carrier gas supply, and an operating manual.

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