3.7.12 B 8-7-92

Site: Oak Landfill
Break: 3.7
Other:

METHOD TO2
Volatile Organic Compounds in Air Tubes

DATE: July 2, 1992

1.0 **SCOPE AND APPLICATION:** This method describes the analytical procedures used to determine the amount of volatile organic compounds trapped on Supelco, Inc. Carbotrap air tubes using a gas chromatograph ion trap detector.

This method is intended to meet the quality control requirements of USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA-600 14-84-041, April 1984, Method TO2.

2.0 **SUMMARY OF METHOD:** Carbotrap tubes are heated in order to transfer the captured organics onto a fused silica capillary column. An ion trap detector is used for analyte detection. Analytes are confirmed by spectral identification. See Table 1 for the list of compounds and reporting limits.

The Carbotrap 300 tube contains 3 types of absorbent material. Flu sections from front to back are Carbotrap C graphitized carbon black, carbotrap graphatized carbon black and Carbosieve S-III molecular sieve. The back bed of Carbosieve S-III traps gases such as vinyl chloride, the middle bed, carbotrap traps C_5-C_8 compounds, and the front bed, Carbotrap C traps the heavier compounds. See Appendix A for published literature from Supelco, Inc.

3.0 **APPARATUS AND MATERIALS:**

A. Instrumentation
   1. Varian 3400 Gas Chromatograph equipped with split/splitless injector.
   2. Finnigan ITS40 Ion Trap Detector
   3. Envirochem Model 851 Thermal Desorber
   4. Tekmar LSC-2 Purge and Trap

B. Fused Silica Capillary Column
   DB-624, 75 x 0.53, 3.0 um film thickness

C. Data System - The data system being used is the Finnigan ITS40 software, version 2.00.

4.0 **REAGENTS:**

A. Solvents
   1. Methanol - purge and trap quality
   2. Reagent Water - organic free water

B. Stock Standards

Standards for this method are purchased from Restek Corporation and Chem Serv with the necessary data packages or standards are made from pure materials. The stock standards for this method are the following:

a. Restek VOA Calibration Mix #4 - Catalog No. 30009 2000 mg/l in methanol
b. Restek VOA Calibration Mix #5 - Catalog No. 30010 2000 mg/l in methanol
c. Aquatec 602 Mix (11199102) 500 mg.l in methanol
d. Aquatec GCMS VOA Calibration Mix #3 (06/18/91) 2000 mg/l in methanol
e. Aquatec Trichlorofluoromethane Standard (05079104) 5000 mg/l in methanol
g. Restek VOA Internal Mix Catalog No. 30011 2500 mg/l in methanol

C. Working Standards

a. 100 mg/l working standard

500 ul Restek Mix #4 2000 mg/l
500 ul Restek Mix #5 2000 mg/l
2000 ul 602 Mix 500 mg/l
500 ul GCMS Mix #3 2000 mg/l
200 ul Trichlorofluoromethane Standard 5000 mg/l
6300 ul methanol

b. 20 mg/l working standard

2000 ul 100 mg/l working standard
8000 ul methanol

c. 5 mg/l working standard

2500 ul 20 mg/l working standard
7500 ml methanol

D. Standards for calibration are introduced to the analytical system via the thermal desorber to replicate the flow pattern of the sample analytes. A known amount of standard is injected onto the front bed of Carbotrap C and thermally desorbed as the samples are performed.

5.0 **INSTRUMENT SET-UP:** The thermal desorber transfer line is directly connected to the inlet of the purge and trap vessel. The helium carrier gas containing the organic analytes is purged through 2 ml of reagent water in order to scrub polar organics such as the methanol, used for standards from the sample. The organics are refocused on the LSC-2 trap and thermally desorbed onto the GC column.

A. Thermal Desorber
   Desorb Temp. - 400°C
   Desorb Time - 5 min.
   Bake Temp. - 400°C
   Bake Time - 5 min.

B. LSC-2 Purge & Trap - Two milliliters of reajent water is transferred in the 5 ml purge vessel.
   Purge Time - 7.0
   Day Purge Time - 2.0
   Predesorb Temp. - 40°
   Desorb Temp. - 180°
   Desorb Time - 2.0
   Bake Temp. - 220
   Bake Time - 7.0
   - The trap used consists of 2/3 Tenax, 1/3 carbosieve S-II.
   - The purge and trap transfer line is directly connected to the capillary column.

C. Varian 3400 Gas Chromatograph
   Initial Temp. - 40°C
   Initial Time - 4 min.
   Ramp Rate - 10°/min.
   Final Temp. - 200°C
   Final Time - 1 min.

6.0 CARTRIDGE PREPARATION: Cartridges are prepared by purging ultra high purity helium at a flow of 50ml/mm through each tube thermally heated to 400°C for 10 minutes. After 10 minutes, the tube is cooled to room temperature while still connected to the helium gas. The tube is removed and stored in a Teflon lined screw glass tube. The cartridges must be used within 2 weeks of being baked.

Prior to field sampling 5% of the tubes must be analyzed for blank contamination. The batches of tubes are acceptable if there are no analytes of interest greater than 10ng.

7.0 INITIAL CALIBRATION:

A. Before analysis may begin, the ion trap detector must be toned using bromofluorobenzene (BFB). BFB is used instead of FC-43 in order to tune the detector the same as in the USEPA Methods 624 and 524, which are purge and trap methods for volatile organic compounds.

Bromofluorobenzene (BFB) must meet the following specifications:

Mass	Ion Abundance Criteria
50	8.0 - 40.0 percent of mass 95
75	30.0 - 66.0 percent of mass 95
95	base peak, 100 percent of mass 95
96	5.0 - 9.0 percent of mass 95 (see note)
173	less than 2.0 percent of mass 174
174	50.0 - 120.0 percent of mass 95
175	4.0 - 9.0 percent of mass 174
176	93.0 - 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

Note: All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

B. A 5 point curve containing all analytes of interest must be analyzed at the following amounts: 10, 20, 50, 200, and 500 ng. Using a quadratic equation, the correlation coefficient of each compound used for quantitation must be greater than 0.990.

C. The asymmetry factor should be between 0.8 and 2.0 for the following analytes:
   1. benzene
   2. methylene chloride
   3. tetrachloroethene

D. A Quality Control Check Standard at 30 ng should be analyzed after the 5 point calibration. See Table 1 for acceptable recovery limits. The quality control standard is prepared the same as the standards are prepared.

E. Instrument Blank - Before analysis of samples should start, an acceptable instrument blank must be acquired. An acceptable method blank contains all analyte at less than one half the reporting limit.

F. The initial calibration sequence is as follows:
   1. VIBLK##
   2. 10 ng
   3. 20 ng
   4. 50 ng
   5. 200 ng
   6. 500 ng
   7. QCS##
   8. VIBLK##

8.0 CONTINUING CALIBRATION

A. The mid-level standard must be analyzed within 12 hours of the previous standard. The response factor must be ± 20% of the initial mid-level standard to continue analysis.

The first 12 hour time period after the calibration curve starts at the injection of the 500 ng standard. For the following analytical windows the start time of the 12 hour window is at the injection of the instrument blank prior to the 50ng check standard.

B. Instrument Blanks - Instrument blanks must be analyzed every 10 samples. Instrument blank must not have any analytes above one half the reporting limit. If an instrument blank fails previous analysis must be reviewed for possible contamination.

C. The continuing analysis is as follows:

6. 500 ng - start time of first analytical 12 hour window (Note: This is the 500ug standard at the end of the calibration)
7. QCS##
8. VIBLK##

9-18 samples

19 VIBLK##

20-29 samples

30 VIBLK## - start of second analytical 12 hour window

31 50ng Check Standard - must be analyzed before first 12 hour window ends.

9.0 SAMPLE ANALYSIS: Before samples, blanks and standards are analyzed they are fortified with surrogate and internal standard compounds.

Internal Standard Spike	Amount
1,4-difluorobenzene	100 ng
Chlorobenzene-d_5	100 ng
Bromochloromethane	100 ng

Surrogate Spike	Amount
1,2-dichloroethane-d_4	200 ng
Toluene-d_8	200 ng
Bromofluorobenzene	200 ng

The internal standard recovery should be within 50 to 150% of the average area counts from the five point calibration.

The surrogate standard recovery should be 75-125% of the true value.

Matrix/Matrix Duplicate Analysis - In general samples for matrix and matrix spike analysis will be spike data 100 ng. The recovery limits are 75-125% of the true value. The reproducibility of the results should be ± 25%.

10.0 IDENTIFICATION: Identification of analytes is performed by comparing retention times of the standards with the samples. Analytes are confirmed by spectral identification.

11.0 QUANTITATION: Sample results will be reported in ng/tube or ppb v/v depending on information received with the tubes. The calculation for reporting the result in ppb(v/v) is:

$$\frac{\frac{\text{ng}}{\text{tube}} \times \frac{1\ \text{ug}}{1000\ \text{ng}} \times \frac{1\ \text{umole}}{\text{m.w.}} \times \frac{24.45\ \text{ul(g) at 1 atm, 25C}}{1\ \text{umole}}}{\frac{\text{L(g) sampled at 1 atm, 25C}}{\text{tube}} \times \frac{\text{m}^3}{1000\ \text{L(g)}}} = \text{ppb(v/v)}$$

Table 1 Target Compound List

Compound	Reporting Limit ng/tube	QCS Recovery Limits %
Chloromethane	10	60-141
Bromomethane	10	59-142
Vinyl chloride	10	69-132
Chloroethane	10	77-123
Methylene chloride	10	78-123
Trichlorofluoromethane	10	67-134
1,1-Dichloroethene	10	63-137
1,1-Dichloroethane	10	84-116
trans-1,2-Dichloroethene	10	64-136
cis-1,2-Dichloroethene	10	60-120
1,2-Dichloroethane	10	72-129
1,1,1-Trichloroethane	10	71-129
Carbon tetrachloride	10	69-132
Bromodichloromethane	10	76-124
1,2-Dichloropropane	10	74-126
cis-1,3-Dichloropropene	10	64-136
Trichloroethene	10	77-123
Dibromochloromehtane	10	66-135
1,1,2-Trichloroethane	10	79-122
Benzene	10	77-123
trans-1,3-Dichloropropene	10	64-136
Bromoform	10	74-127
1,1,2,2-Tetrachloroethane	10	49-151
Tetrachloroethene	10	70-130
Toluene	10	78-123
Chlorobenzene	10	80-120
Ethylbenzene	10	63-137
Styrene	10	60-120
1,2-Dichlorobenzene	10	68-132
1,3-Dichlorobenzene	10	72-128
1,4-Dichlorobenzene	10	70-130
Total Xylenes	10	60-120

Note: QCS limits are derived from USEPA methods 601/602

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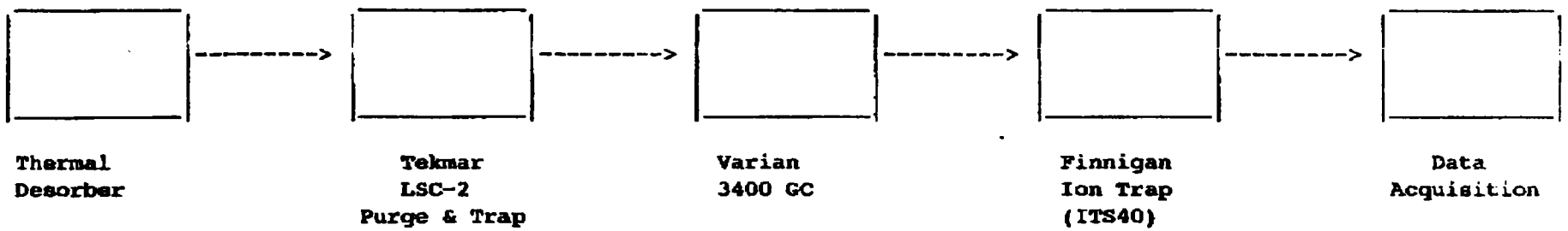


Figure 1. GC/MS Analysis System. The sample tube is thermally baked at 400°C. The organic compounds are transferred using helium carrier gas and refocused on the Tekmar LSC-2 absorbent trap. This trap is then heated and the organic compounds are transferred to the gas chromatagraphic column and detected by the Ion Trap.

APPENDIX A

Carbotrap™ — an Excellent Adsorbent for Sampling Many Airborne Contaminants

GC Bulletin 846B

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 in nature 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 US 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^1) of air needed to elute the adsorbate was determined. The larger this value, the better the adsorbate was retained.

Carbotrap adsorbent traps and releases a wider range of airborne organic compounds than Tenax GC or XAD-2 resins

To determine Carbotrap adsorbent's functional trapping range (the range of molecular sizes that can be trapped successfully, then desorbed), we used 38 compounds ranging from C2 to C14 straight chain and ring compounds. 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 the Carbotrap adsorbent's ability to release large molecules (e.g., PAHs or pesticides) through thermal desorption. A 2.0 minute migration time and 350°C temperature were considered the maximum allowable conditions for proper thermal desorption.

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.

As a 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 Amberlite XAD-2 resin's limited ability to withstand certain solvents and temperatures above 150°C. The lower limit for Tenax GC appears to be a linear C6 backbone or equivalent struc-

Table 1 — Breakthrough Volumes for Organic Adsorbates on Carbotrap Adsorbent

Adsorbate	V_g^1 20°C (ml/g)	Correl. Coef.*
Ethane	1.73×10^1	1.00000
n-Propane	5.49×10^1	0.99412
n-Butane	4.06×10^2	0.99975
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	8.40×10^7	0.99971
Isopropylbenzene	1.70×10^8	0.99998
n-Propylbenzene	1.72×10^8	0.99993
n-Decane	4.79×10^8	0.99971
n-Butylbenzene	5.83×10^8	0.99937
Biphenyl	3.74×10^{12}	0.99999
n-Hexylbenzene	7.00×10^{12}	0.99989
n-Dodecane	1.53×10^{14}	0.99903
n-Octylbenzene	1.31×10^{15}	0.99985
n-Tetradecane	8.32×10^{16}	0.96309

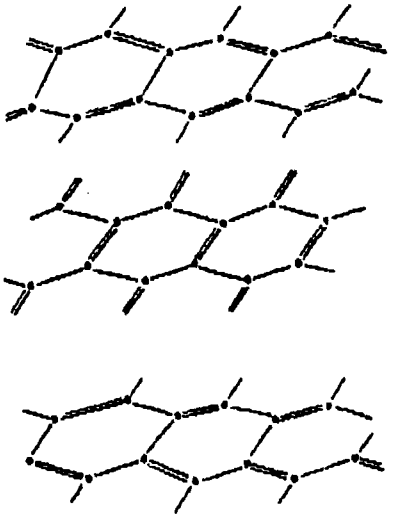
*V_g^1 values for high boiling adsorbates must be determined at elevated temperatures, then calculated for 20°C (by linear regression) for comparison. These temperature/breakthrough volume correlation coefficients show regression plots used in this investigation were linear.

☐ Functional range for Carbotrap adsorbent

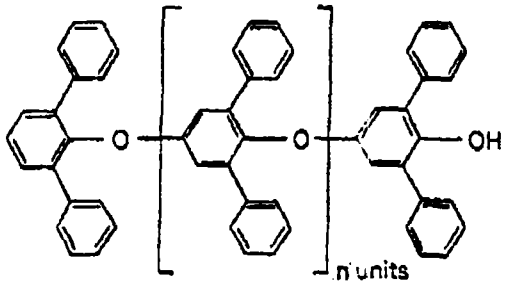
☒ Larger compounds that must be desorbed at higher temperatures.

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.

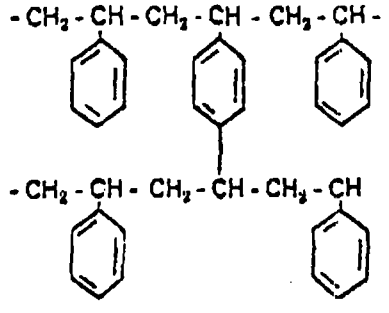


Figure A1 adapted from (4), Figures A2 and A3 from (3).

ture (e.g., butanoic acid: C-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 restricted by solvent and temperature effects.

We used adsorbates representing eight classes of compounds to compare the adsorptive properties of the Carbotrap, Tenax GC, and Amberlite XAD-2 adsorbents. Carbotrap adsorbent shows greater adsorbing capacity for linear and cyclic molecules (Table 2). This results from its 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 interactions with acid groups (Figure A).

From the breakthrough volume, V_g, 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, relating 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 values can also be used to predict the relationship between the adsorbent and untested adsorbates in the same chemical class as a tested adsorbate.*

You can completely recover adsorbed compounds from Carbotrap adsorbent by either solvent or thermal desorption

Adsorbates were recovered from Carbotrap adsorbent tubes by both solvent and thermal desorption techniques. *Our previous studies showed 1-butanol, 2-butanone, and* 2-ethoxyethylacetate were 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. The active groups on chlorobenzene (halogen), n-pentanoic acid (carboxyl), and benzylamine (amino) similarly 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 *Occupational Safety and Health Administration's 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 both methods of desorption (Table 3). This is due to the high purity of the sorbent and the nonspecific nature of its graphitized surface.

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

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

Adsorbate	V^t_g 20°C■			K_a			G_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^{-4}	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^{-3}	8.23×10^{-3}	2.42×10^{-3}	9.21×10^{-7}	1.57×10^{-6}	7.12×10^{-7}
Chlorobenzene	1.58×10^8	1.51×10^5	4.64×10^5	8.65×10^{-4}	3.49×10^{-1}	7.20×10^{-5}	7.30×10^{-3}	8.35×10^{-4}	2.24×10^{-3}
p-Xylene	4.24×10^7	3.68×10^5	7.95×10^6	2.30×10^{-2}	8.39×10^{-1}	1.18×10^{-3}	1.62×10^{-1}	1.66×10^{-3}	3.40×10^{-2}
p-Cresol	2.06×10^7	1.50×10^7	4.96×10^8	1.11×10^{-3}	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	9.78×10^4	1.01×10^5	2.34×10^{-4}	2.26×10^{-3}	1.51×10^{-3}	1.76×10^{-3}	3.99×10^{-4}	4.31×10^{-4}
Cyclohexanone	2.04×10^8	1.06×10^6	6.27×10^5	1.10×10^{-3}	2.45×10^{-2}	5.45×10^{-5}	8.19×10^{-3}	4.26×10^{-3}	1.47×10^{-3}
2-Methyl-2-propanol	6.52×10^3	6.66×10^3	5.42×10^3	3.53×10^{-6}	1.58×10^{-5}	9.06×10^{-7}	1.99×10^{-5}	2.09×10^{-6}	1.65×10^{-5}

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

Table 3 — Desorption Efficiency for Carbotrap Adsorbent by Solvent and Thermal Desorption

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

Thermal desorption has now gained acceptance because of more demanding regulations from the *US Environmental Protection Agency*, the *National Institute for Occupational Safety and Health*, 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 would otherwise be undetectable.

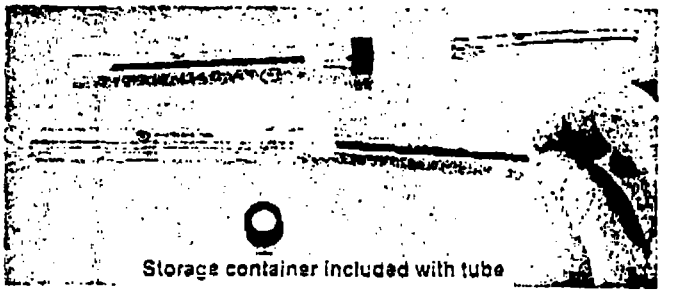
Tenax GC resin releases toluene, benzene, and trichloroethylene residues during thermal desorption. Residues are evolved from Amberlite XAD-2 resin at 150°C. At 250°C the resin will completely pyrolyze. Thus, Amberlite XAD-2 is poorly suited to thermal desorption, and Tenax GC must be carefully conditioned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

Although Carbotrap adsorbent once came with wide particle size distribution, we now offer the uniform sized, large particle material (20/40 mesh). This further reduces back pressure.

Carbotrap adsorbent is available in 7mm OD x 5mm ID x 10cm long ORBO™-100 solvent desorption tubes (350mg/175mg bed weights), or in tubes for three widely used thermal desorption units. It also comes in bulk. Of course, we can prepare custom Carbotrap tubes to your specifications. For information about thermal desorption, or details on custom Carbotrap tubes, call our Technical Service Department.

►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.

Carbotrap 100 Thermal Desorption Tubes



Thermal Desorption Unit	Tube Specifications	Cat. No.
Supelco	glass, 6mm OD x 4mm ID x 11.5cm long	2-0238
Tekmar®	stainless steel, 1/4" OD x 7" long	2-0241
	5/8" OD x 7" long	2-0239
CDS	stainless steel, 1/4" OD x 3" long	2-0240

ORBO-100 Solvent Desorption Tubes (pack of 25)	2-0255
Carbotrap adsorbent (20/40 mesh), 5g	2-0287

For descriptions of additional Carbotrap thermal desorption tubes and the Supelco™ Thermal Desorption Unit, please refer to our catalog.

References

1. Kiselev, A.V. and Y.I. Yashin Gas Adsorption Chromatography, Plenum Press, New York, pp. 11-13 (1969).
2. Atkins, P.W., Physical Chemistry (2nd Ed.), W.H. Freeman & Co., San Francisco (1982).
3. Characterization of Sorbent Resins for Use in Airborne Environmental Sampling, US EPA Document No. 600/7-78-054 (1978).
4. Wood, Keenan, and Bull, Fundamentals of College Chemistry (2nd Ed.), Harper and Row (1968).

References not available from Supelco.

Supelco™ Thermal Desorption Unit

If your analyses involve . . .

- Industrial Hygiene
- Ambient Air Monitoring
- Indoor Air Pollution
- Sampling Hazardous Waste Sites
- Water Pollution Samples
- Alcoholic Beverages
- Petroleum
- Plastics

. . . the Supelco Thermal Desorption Unit offers you the most value at the lowest price.

Accurate, ballistic heating — Samples are delivered rapidly to the analytical column for sharp, symmetrical peaks. Cooldown time is <2 minutes via a high speed fan.

Temperatures attained:
30°C → 400 ±4°C in 26 ±2 seconds
30°C → 300 ±1°C in 20 ±2 seconds
30°C → 200 ±1°C in 16 ±2 seconds
30°C → 100 ±1°C in 12 ±2 seconds

Temperature programming capability — Program at variable rates for thermal fractionation of contaminants, residue/pyrolysis analyses of polymers, etc.

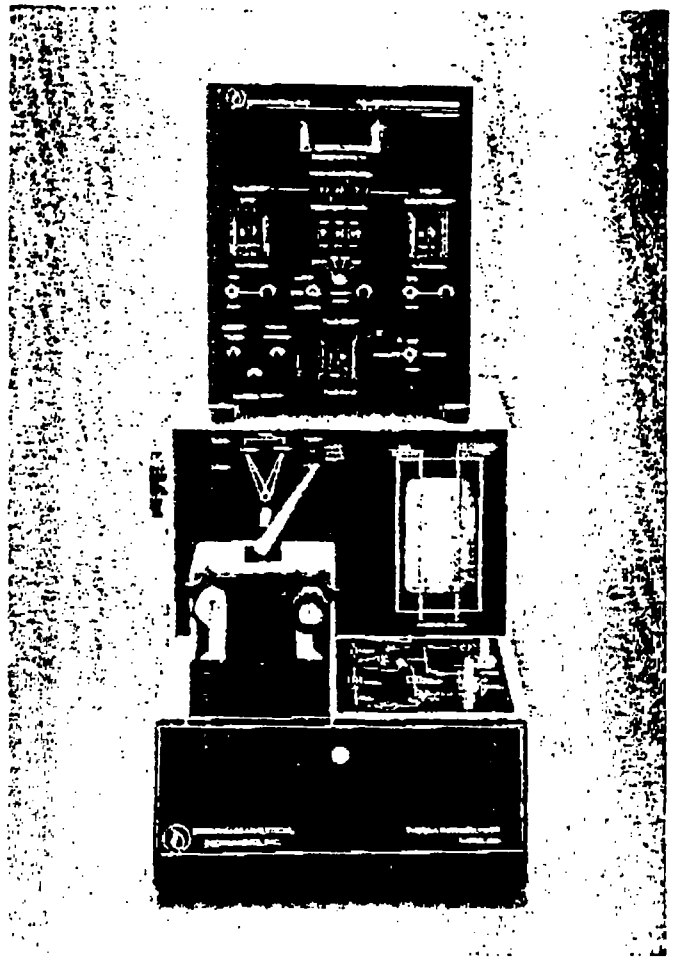
Exclusive sample saving device — A splitter and a secondary adsorbent trap saves you 0 to 99% of the sample for a second analysis. The splitter incorporates a shut-off valve and a fine metering valve.

Accepts reusable Carbotrap thermal desorption tubes — For long term economy.

Secondary trap/water removal port — Accelerate water migration through the adsorbent bed by applying minimal heat to the adsorbent tube. This protects the analytical column from water damage, while higher boiling compounds remain on the adsorbent. Or place a secondary trap in the port, to collect materials from the primary chamber during ballistic or temperature programmed desorption.

Heated nickel transfer line — Prevents sample adsorption or condensation during transfer to a glass or metal packed column, narrow bore (0.25 - 0.32mm ID) capillary column, or wide bore (0.5+ mm ID) capillary column. Each transfer line is custom prepared for the GC system it will be used with. (Fused silica transfer line available upon request.)

Electronics interface with the GC — You can automatically start the analytical and integrating systems.



2-2895 Supelco Thermal Desorption Unit (110 VAC)

For current product prices, and a complete explanation of Supelco's limited warranty, please see our most recent catalog.

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SUPELCO
A ROHM AND HAAS COMPANY

Efficiently Monitor Toxic Airborne Compounds by Thermal Desorption

GC Bulletin 849A

Described in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* are US Environmental Protection Agency methods for monitoring volatile and semivolatile organic compounds in air samples (1). Each of the first three methods calls for a different sampling technique, followed by thermal desorption to a capillary GC column for analysis.

In Method TO-1, compounds are trapped on a porous polymer adsorbent, transferred to a cold trap, and desorbed to the column. In Method TO-2, they are trapped on a carbon molecular sieve adsorbent, transferred to a cold trap, and desorbed to the column. In Method TO-3, they are trapped on a cold trap and desorbed to the column.

To perform all three methods you need two different adsorbent traps — plus a cold trap — to obtain your samples. Even if you follow only *one* of these methods, you need a highly efficient system for trapping, desorbing, and analyzing your samples.

We recommend a reusable Carbotrap™ 300 thermal desorption tube, a Supelco™ Thermal Desorption Unit, and either a SUPELCOWAX™ 10 capillary column or a Carbopack™ packed column. This system ensures high efficiency for trapping, transferring, and analyzing samples for *each* of the above mentioned methods.

This three component system ensures excellent analyses for TO-1, TO-2, or TO-3 toxic compounds. A Carbotrap 300 multi-bed tube (Figure A) efficiently adsorbs and releases *all* compounds listed in these methods — even when they are present in complex mixtures. The back bed, Carbosieve☆ S-III carbon molecular sieve, traps vinyl chloride and other light compounds. The middle bed (Carbotrap graphitized carbon black) traps the C5-C8 compounds. The front bed (Carbotrap C graphitized carbon black) traps the heaviest compounds (Table 1). Desorption for all compounds is nearly 100% (Table 2).

Our Supelco Thermal Desorption Unit (Figure B) efficiently and rapidly transfers the adsorbed compounds from the Carbotrap 300 tube to the GC column. The unit desorbs the com-

Figure A — Carbotrap 300 Tubes Trap a Wide Range of Airborne Compounds

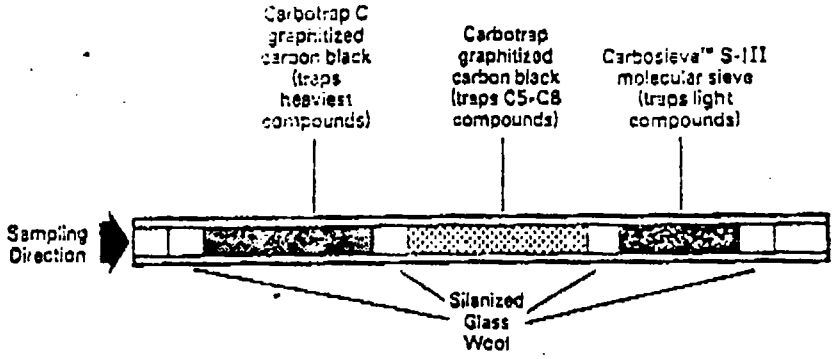


Table 1 — Breakthrough Volumes (in Liters) for US EPA TO-1 Hydrocarbons on a Carbotrap 300 Thermal Desorption Tube

Hydrocarbon	Carbosieve™ S-III	Carbotrap	Carbotrap C
Vinyl Chloride	158		
Chloroform		1.1■	
1,2-Dichloroethane		0.4	
1,1,1-Trichloroethane		2.7■	
Carbon tetrachloride		4.7■	
1,2-Dichloropropane		6.6	
Trichloroethylene		2.5	
Bromoform		1.7	
Tetrachloroethylene		2.2	
Chlorobenzene		31.6	
n-Heptane		26.2	
1-Heptene		26.4■	
Benzene		2.3	
Toluene		13.0	
Ethylbenzene			12.9
p-Xylene			11.2
m-Xylene			11.0■
o-Xylene			11.0■
Cumene			27.8■

■Theoretical value, calculated from predictive model established for sampling volumes.

pounds ballistically, raising the tube temperature from 35°C to 330°C in 16 seconds. All valves and tubing in the unit are inert. The transfer line between the tube and column is heated, eliminating cold spots where analytes could condense. As a result, samples are sharply focused at the column inlet and the compounds can be efficiently separated. Peaks are symmetrical, ensuring accurate qualitative and quantitative analyses *without a cold trap.*

To calibrate the thermal desorption unit or evaluate desorption efficiency of the adsorbent tube, you can inject control samples into the unit's injection port. These are delivered onto the GC column through the same pathway that *desorbed samples follow. Furthermore,* you can use the unit with either capillary or packed columns. (This is important, because both column types are needed to perform a complete analysis of the TO-1 compounds.)

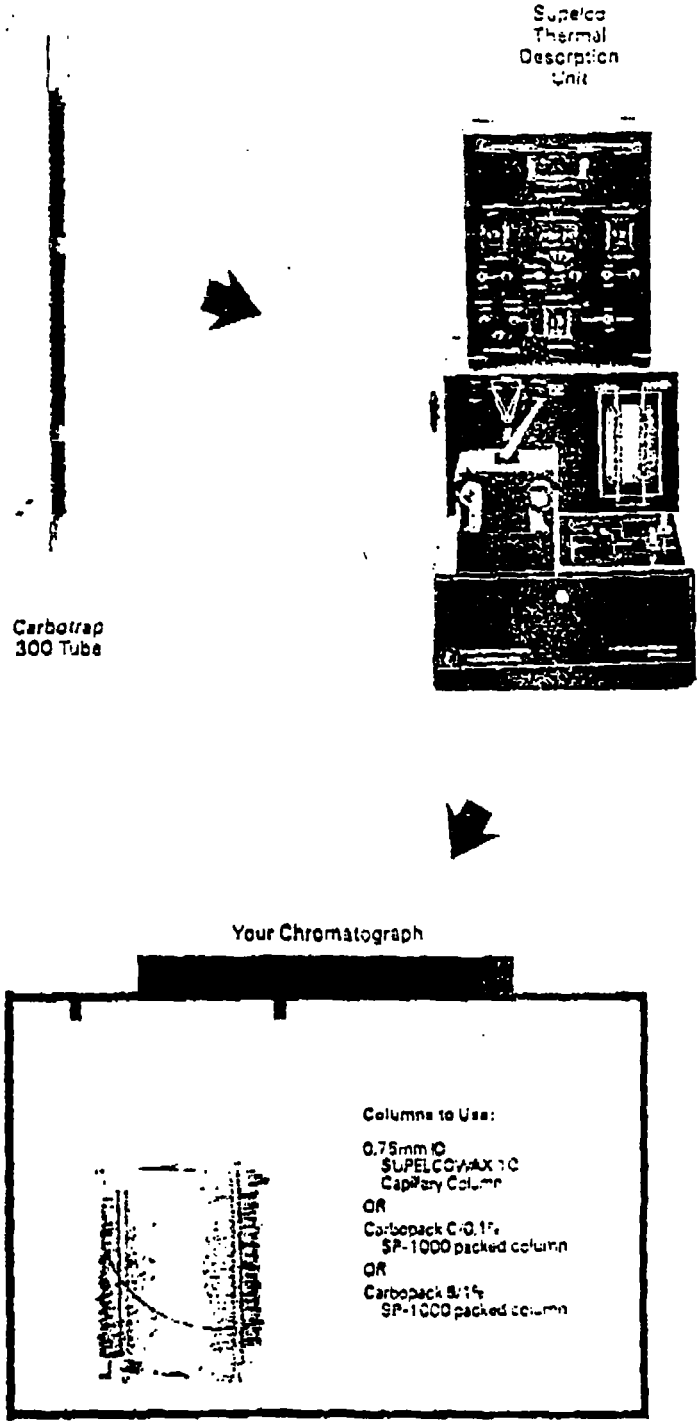
Choose a 0.75mm ID SUPELCOWAX 10 capillary column or one of two Carbopack packed columns to effectively refocus the thermally desorbed compounds, then resolve them as symmetrical peaks. The wide bore capillary column accepts samples with a wide range of component concentrations (<1 to >10,000ng on-column). It can be used with the same injection, flow control, and detection equipment as packed columns.■ Of all the packings we tested, Carbopack packings provided the best analyses of the TO-1, TO-2, and TO-3 compounds. The high surface area of the Carbopack graphitized carbon black packings ensures excellent refocusing capability.

Table 2 — Toxic Compounds Efficiently Desorbed from Carbotrap 300 Tubes

4mm ID Tube to GC Column	
Adsorbate	Desorption Efficiency* ± Rel. Std. Dev. (%)
Benzene	100 ±5.5
Bromoform	100 ±2.1
Carbon tetrachloride	99 ±3.6
Chlorobenzene	100 ±0.7
Chloroform	94 ±5.2
3-Chloropropene	100 ±3.2
Cumene	99 ±3.6
1,2-Dichloroethane	102 ±4.1
1,1-Dichloroethylene	101 ±0.6
Dichloromethane	98 ±1.0
Ethylbenzene	100 ±3.0
n-Heptane	99 ±4.2
1-Heptene	99 ±4.7
Tetrachloroethylene	99 ±2.9
Toluene	99 ±4.2
1,1,1-Trichloroethane	100 ±3.0
Trichloroethylene	101 ±2.6
Vinyl chloride	101 ±2.5
o-Xylene	99 ±3.6
m-Xylene	100 ±3.8
p-Xylene	99 ±3.6
4mm ID Tube to 2mm ID Tube to Column	
Adsorbate	Desorption Efficiency* ± Rel. Std. Dev. (%)
Acrylonitrile	100 ±0.6
3-Chloropropene	101 ±2.1
1,1-Dichloroethylene	99 ±1.7
Methylene chloride	101 ±1.5
Vinyl chloride	99 ±1.5

*Mean for three evaluations.

Figure 8 — Complete System for Trapping and Analyzing TO-1, TO-2, and TO-3 Compounds



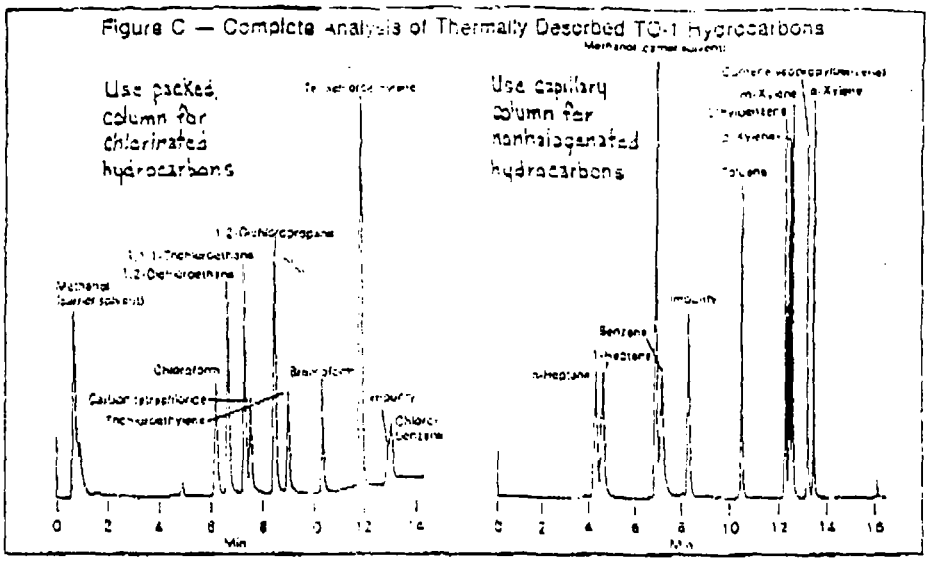
If your samples contain all of the eighteen TO-1 compounds, use a SUPELCOWAX 10 wide bore capillary column and a Carbopack C/0.1% SP™-1000 packed column (Figure C). Two pairs of nonhalogenated hydrocarbons (n-heptane and toluene, o-xylene and cumene) coelute from the packed column. The capillary column resolves these compounds. Similarly, two pairs of chlorinated hydrocarbons (carbon tetrachloride and 1,1,1-trichloroethane, chloroform and tetrachloroethylene) coelute from the capillary column, but are resolved on the packed column.

Either a 0.75mm ID SUPELCOWAX 10 column or a Carbopack B/1% SP-1000 packed column provides excellent separations and sharp peaks for the TO-2 and TO-3 compounds (Figure D). When using the capillary column, you can obtain the sharpest vinyl chloride peak by trapping the sample on a 4mm ID Carbotrap 300 tube, transferring it to a 2mm ID tube, then desorbing it to the capillary column (Figure D). The Supelco Thermal Desorption Unit makes this transfer easy. Simply put the 2mm ID tube in the exclusive sample saver chamber and quantitatively transfer the sample from the 4mm ID tube (Table 2). With the packed column, the vinyl chloride peak will be sharp from the 4mm tube and this transfer procedure is unnecessary.

If you are following all three methods, you can use a Carbopack B/1% SP-1000 column for the TO-1 compounds, as well as for the TO-2 and TO-3 compounds. Analysis time for the TO-1 compounds will be a little longer on a Carbopack C/0.1% SP-1000 column, but the samples will be resolved well.

We also prepare standards to help you perform these analyses. Toxic Organics Mix TO-1A contains 2mg of each compound in the capillary chromatogram in Figure C in methanol. Toxic Organics Mix TO-1B contains 2mg of each of the other compounds in Figure C, plus allyl chloride, acrylonitrile, bromobenzene, 1,3-dichloropropane, and ethylene dibromide

Figure C — Complete Analysis of Thermally Desorbed TO-1 Hydrocarbons

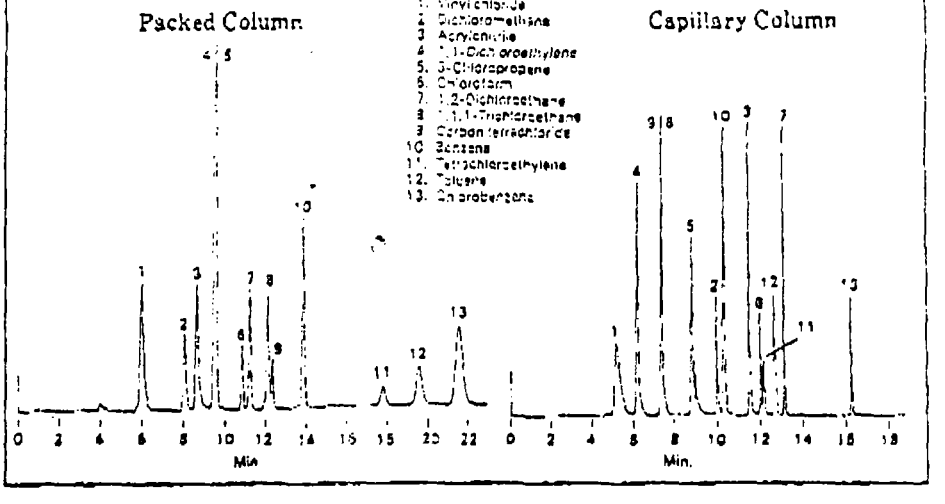


Analytical Conditions — 80/100 Carbopack C/0.1% SP-1000, 6' x 1/8" SS, Col. Temp.: 35°C for 2 min., then to 220°C at 16°C/min., Flow Rate (4mm ID desorp. tube to column): 20ml/min., He, Det.: FID (8 x 10^{11} AFS), Sample: 2ng each component.

SUPELCOWAX 10, 60m x 0.75mm ID (1.0µm film), Col. Temp.: 35°C for 4 min., then to 220°C at 8°C/min., Flow Rate (4mm ID desorp. tube to column): 10ml/min., He, Make-up Gas: 40ml/min., N_2, Det.: FID (80 x 10^{11} AFS), Sample: 0.2ng each component.

Desorption Conditions — Tube Desorb Temp./Time: 330°C/4 min., Valve Compart. & Trans. Line Temp.: 220°C.

Figure D — Thermally Desorbed TO-2 and TO-3 Compounds



Analytical Conditions — 80/60 Carbopack B/1% SP-1000, 8' x 1/8" SS, Sample: 1-5ng each component, conditions same as for Figure B.

SUPELCOWAX 10, 60m x 0.75mm ID (1.0µm film), Col. Temp.: 35°C for 4 min., then to 180°C at 8°C/min., Flow Rate (2mm ID desorp. tube to column): 5ml/min., He, Make-up Gas: 50ml/min., N_2, Det.: FID (8 x 10^{11} AFS), Sample: 1-5ng each component.

Desorption Conditions — see Figure C.

in methanol. Toxic Organics Mix TO-2A contains 2mg each of the TO-2 compounds vinyl chloride, vinylidine chloride, and methylene chloride in methanol.

To monitor all airborne TO-1, TO-2, and TO-3 toxic compounds, use Carbotrap 300 tubes, a Supelco Thermal Desorption Unit, and a SUPELCOWAX 10 wide bore capillary column or a Carbopack packed column. You will get consistent and reliable analyses for these compounds, and for many other airborne compounds as well.

Reference

1 *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, US EPA Document No. 600/4-84-041 (April, 1984).
Reference not available from Supelco.

Carbotrap 300 Thermal Desorption Tubes
11.5cm x 6mm OD
4mm ID 2-0379
2mm ID 2-0382

Supelco Thermal Desorption Unit**
110 VAC
2-2895

SUPELCOWAX 10
Capillary Column
60m x 0.75mm ID, 1.0 µm film
2-3723

Carbopack Packings
60/80 Carbopack B/1% SP-1000, 15g 1-1815
80/100 Carbopack C/0.1% SP-1000, 15g 1-1820

Standards
Toxic Organics Mix TO-1A, 1 ml 4-8896
Toxic Organics Mix TO-1S, 1 ml 4-8897
Toxic Organics Mix TO-2A, 1 ml 4-8898

**Manufactured by Dynatherm, Inc. Marketed exclusively by Supelco, Inc.

For stock and custom-prepared columns, refer to our catalog or call our Sales Department.

For information about the Supelco Thermal Desorption Unit, please call our Technical Service Department.

*Manufactured by Dynatherm, Inc. Marketed exclusively by Supelco, Inc.

*For information on using wide bore capillary columns in packed column instruments, request Bulletin 814.

*British Pat. No. 1310422, German Pat. No. 1935800

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the SUPELCO reporter

Vol. VII, No. 3
May 1988

A Digest of GC, HPLC and Chemical Standard Articles of Current Interest to Chromatographers

Carbotrap™ — an Excellent Adsorbent for Sampling Many Airborne Contaminants

SAMPLE HANDLING

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 in nature 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 US 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_g) of air needed to elute the adsorbate was determined. The larger this value, the better the adsorbate was retained.

Carbotrap adsorbent traps and releases a wider range of airborne organic compounds than Tenax GC or XAD-2 resins

To determine Carbotrap adsorbent's functional trapping range (the range of molecular sizes that can be trapped successfully, then desorbed), we used 38 compounds ranging from C2 to C14 straight chain and ring compounds. 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 the Carbotrap adsorbent's ability to release large molecules (e.g., PAHs or pesticides) through thermal desorption. A 2.0 minute migration time and 350°C temperature were considered the maximum allowable conditions for proper thermal desorption.

Carbotrap adsorbent's functional range for the compounds studied is indicated in Table 1. Extremely large

(cont'd on page 2)

Table 1 — Breakthrough Volumes for Organic Adsorbates on Carbotrap Adsorbent

Adsorbate	V^g_g 20°C (ml/g)	Correl. Coeff.[▲]
Ethane	1.72 x 10[1]	1.00000
n-Propane	5.49 x 10[1]	0.99472
n-Butane	4.06 x 10[2]	0.99875
Ethanol	4.93 x 10[2]	0.99219
Acetic acid	7.16 x 10[2]	0.99090
Propionic acid	1.06 x 10[3]	0.99410
1,2-Dichloroethane	1.94 x 10[3]	0.99848
2-Butanone	3.75 x 10[3]	0.99911
n-Pentane	5.89 x 10[3]	0.99994
2-Methyl-2-propanol	6.52 x 10[3]	0.98030
Benzene	1.17 x 10[4]	0.99802
1,1,2-Trichloroethylene	1.27 x 10[4]	0.99989
n-Butanol	1.92 x 10[4]	0.99913
1,1,2-Trichloroethane	2.47 x 10[4]	0.99956
n-Hexane	7.99 x 10[4]	0.99871
n-Pentanoic acid	4.81 x 10[5]	0.97190
Phenol	6.16 x 10[5]	0.99941
Toluene	6.50 x 10[5]	0.99972
Chlorobenzene	1.58 x 10[6]	0.99999
Cyclohexanone	2.04 x 10[6]	0.99981
n-Butylamine	2.09 x 10[6]	0.99935
1-Heptanone	2.44 x 10[6]	0.99991
1,4-Dichlorobenzene	1.34 x 10[7]	0.99925
n-Octane	1.01 x 10[7]	0.99999
Ethylbenzene	2.03 x 10[7]	0.99959
p-Cresol	2.06 x 10[7]	0.99948
Benzylamine	2.23 x 10[7]	0.99990
p-Xylene	4.27 x 10[7]	0.99993
Acetophenone	6.40 x 10[7]	0.99971
Isopropylbenzene	1.70 x 10[8]	0.99999
n-Propylbenzene	1.72 x 10[8]	0.99998
n-Decane	4.79 x 10[8]	0.99971
n-Butylbenzene	5.53 x 10[8]	0.99997
Biphenyl	9.74 x 10[9]	0.99999
n-Hexylbenzene	7.00 x 10[10]	0.99989
n-Dodecane	1.63 x 10[10]	0.99903
n-Octylbenzene	1.31 x 10[11]	0.99985
n-Tetradecane	5.32 x 10[10]	0.96309

[▲] V^g_g values for high boiling adsorbates must be determined at elevated temperatures, then calculated for 20°C (by linear regression) for comparison. These temperature/breakthrough volume correlation coefficients show regression plots used in this investigation were linear.

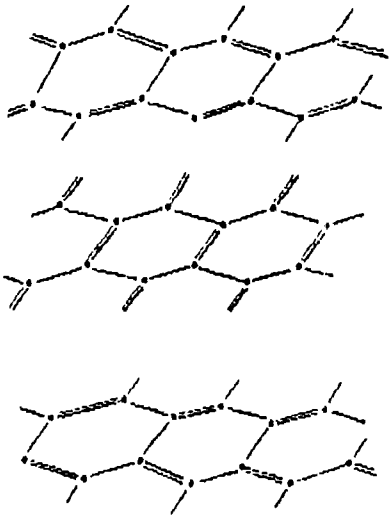
▨ Functional range for Carbotrap adsorbent.

□ Larger compounds that must be desorbed at higher temperatures.

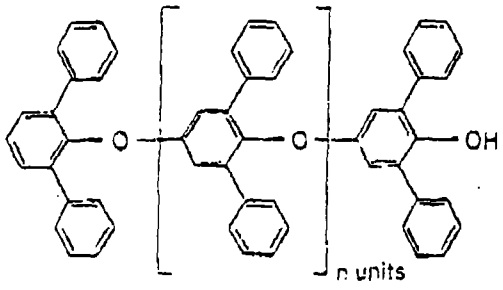
Carbotrap — an Excellent Adsorbent for Sampling Many Airborne Contaminants

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.

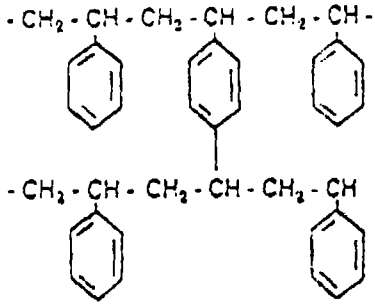


Figure A1 adapted from (4). Figures A2 and A3 from (3).

sample volumes can be used with adsorbates larger than n-decane and n-butylbenzene.

As a 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 Amberlite XAD-2 resin's limited ability to withstand certain solvents and temperatures above 150°C. The lower limit for Tenax GC appears to be a linear C6 backbone or equivalent structure (e.g., butanoic acid: C-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 restricted by solvent and temperature effects.

We used adsorbates representing eight classes of compounds to compare the adsorptive properties of the Carbotrap, Tenax GC, and Amberlite XAD-2 adsorbents. Carbotrap adsorbent shows greater adsorbing capacity for linear and cyclic molecules (Table 2). This results from its 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 interactions with acid groups (Figure A).

From the breakthrough volume, V^0_g, 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, relating 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^0_g values can also be used to predict the relationship between the adsorbent and untested adsorbates in the same chemical class as a tested adsorbate.

You can completely recover adsorbed compounds from Carbotrap adsorbent by either solvent or thermal desorption

Adsorbates were recovered from Carbotrap adsorbent tubes by both solvent and thermal desorption techniques. Our previous studies showed 1-butanol, 2-butanone, and 2-ethoxyethylacetate were 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. The active groups on chlorobenzene (halogen), n-pentanoic acid (carboxyl), and benzylamine (amino) similarly 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 *Occupational Safety and Health Administration's* 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 both methods of desorption (Table 3). This is due to the high purity of the sorbent and the nonspecific nature of its graphitized surface.

Two desorbing solvents were used in this evaluation (Table 3). Carbon disulfide was chosen because it is commonly used as a desorbing solvent for charcoal. Also, its high heat of adsorption allows it to readily displace adsorbed compounds. Carbon disulfide *cannot* be used with polymeric adsorbents, such as Tenax GC and Amberlite XAD-2, because

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

	V^t_g 20°C■			K_a			Q_g		
Adsorbate	Carbotrap	Tenax GC	XAD-2	Carbotrap	Tenax GC	XAD-2	Carbotrap	Tenax GC	XAD-2
n-Decane	4.70×10^6	1.56×10^7	3.68×10^7	2.60	3.51×10^{-2}	5.40×10^{-2}	28.0	9.14×10^{-2}	2.12×10^{-2}
Benzylamine	2.23×10^7	3.57×10^6	1.63×10^7	1.21×10^{-3}	8.26×10^{-3}	2.42×10^{-3}	3.51×10^{-3}	1.57×10^{-4}	7.28×10^{-4}
Chlorobenzene	1.58×10^6	1.51×10^5	4.84×10^5	5.55×10^{-4}	3.48×10^{-4}	7.20×10^{-4}	7.80×10^{-4}	8.55×10^{-4}	2.24×10^{-3}
p-Xylene	4.24×10^6	3.83×10^5	7.96×10^6	2.80×10^{-3}	8.36×10^{-4}	1.18×10^{-3}	1.52×10^{-3}	1.66×10^{-3}	3.40×10^{-3}
p-Cresol	2.06×10^7	1.50×10^7	4.96×10^6	1.11×10^{-4}	3.45×10^{-7}	7.89×10^{-4}	9.14×10^{-3}	3.70×10^{-3}	2.21×10^{-3}
n-Pentanoic acid	4.31×10^5	9.75×10^5	1.01×10^6	2.34×10^{-4}	2.26×10^{-5}	1.51×10^{-4}	1.76×10^{-3}	3.99×10^{-4}	4.31×10^{-4}
Cyclohexanone	2.04×10^6	1.05×10^6	6.27×10^5	1.10×10^{-3}	2.45×10^{-3}	5.45×10^{-3}	5.19×10^{-3}	4.28×10^{-3}	1.47×10^{-2}
2-Methyl-2-propanol	6.62×10^3	6.56×10^3	5.42×10^3	3.54×10^{-5}	1.56×10^{-4}	8.06×10^{-5}	1.99×10^{-5}	2.09×10^{-4}	1.65×10^{-5}

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

Table 3 — Desorption Efficiency for Carbotrap Adsorbent by Solvent and Thermal Desorption

		Desorption Efficiency (%)		
		Solvent Desorption		
Adsorbate	Volume	Acetonitrile	Carbon Disulfide	Thermal Desorption
Toluene	2.2 µl	102	—	111
2-Butanone	1.8 µl	103	109	105
1-Butanol	0.9 µl	106	102	116
2-Ethoxyethylacetate	1.1 µl	104	102	103
n-Decane	1.0 µl	100	—	111
Chlorobenzene	1.0 µl	94	—	113
n-Pentanoic acid	1.0 µl	110	104	111
Benzylamine	1.0 µl	108	—	109

it degrades them. Thus, you are forced to use other solvents that may not remove the adsorbates effectively. The other solvent, acetonitrile, is often used in liquid chromatographic analyses.

Thermal desorption has now gained acceptance because of more demanding regulations from the *US Environmental Protection Agency*, the *National Institute for Occupational Safety and Health*, 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 would otherwise be undetectable.

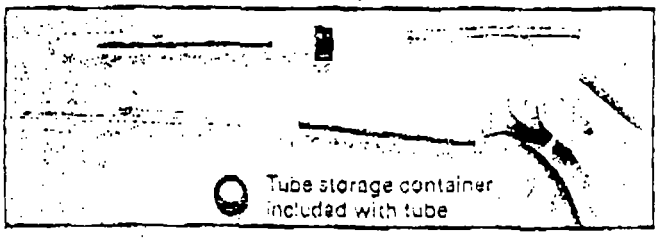
Tenax GC resin releases toluene, benzene, and trichloroethylene residues during thermal desorption. Residues are evolved from Amberlite XAD-2 resin at 150°C. At 250°C the resin will completely pyrolyze. Thus, Amberlite XAD-2 is poorly suited to thermal desorption, and Tenax GC must be carefully conditioned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

Although Carbotrap adsorbent once came with wide particle size distribution, we now offer the uniform sized, large particle material (20/40 mesh). This further reduces back pressure.

Carbotrap adsorbent is available in 7mm OD x 5mm ID x 10cm long ORBO™-100 solvent desorption tubes (350mg/175mg bed weights), or in tubes for three widely used thermal desorption units. It also comes in bulk. Of course, we can prepare custom Carbotrap tubes to your specifications. For information about thermal desorption, or details on custom Carbotrap tubes, call our Technical Service Department.

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

Carbotrap 100 Thermal Desorption Tubes



Thermal Desorption Unit	Tube Specifications	Cat. No.	Price/tube
Supelco	glass, 6mm OD x 4mm ID x 11.5cm long	2-0238	$2.25
Tekmar®	stainless steel, 1/4" OD x 7" long	2-0241	30
	5/8" OD x 7" long	2-0239	70
CDS	stainless steel, 1/4" OD x 3" long	2-0240	24

ORBO-100 Solvent Desorption Tubes	2-0255	$95/25
Carbotrap adsorbent (20/40 mesh), 5g	2-0287	$30

For descriptions of additional Carbotrap thermal desorption tubes and the Supelco™ Thermal Desorption Unit, please refer to our catalog.

References

1. Kiselev, A.V. and Y.I. Yashin, Gas Adsorption Chromatography, Plenum Press, New York, pp. 11-16 (1969).
2. Atkins, P.W., Physical Chemistry (2nd Ed.), W.H. Freeman & Co., San Francisco (1982).
3. Characterization of Sorbent Resins for Use in Airborne Environmental Sampling, US EPA Document No. 600/7-78-054 (1978).
4. Wood, Keenan, and Hall, Fundamentals of College Chemistry (2nd Ed.), Harper and Row (1968).

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November, 1986

the Supelco Reporter

Chromatography and Chemical Standards News

A Digest of GC, HPLC and Chemical Standard Articles of Current Interest to Chromatographers.

New Thermal Desorption Tube for Monitoring Hazardous Airborne Hydrocarbons

GC

Carbotrap 300 tubes efficiently trap and release US EPA TO-1 chlorinated and nonchlorinated hydrocarbons

Are you required to monitor air levels of the aliphatic, aromatic, and chlorinated hydrocarbons listed in US Environmental Protection Agency TO-1 methodology (1)? If so, you'll appreciate our new multi-bed thermal desorption tube. This new tube efficiently adsorbs and releases *all* of these compounds, whether present individually (as in some industrial environments) or in complex mixtures (like the ambient air at toxic waste sites).

The new *Carbotrap™ 300 thermal desorption tube* was designed to retain vinyl chloride, a chlorinated hydrocarbon with a small retention volume, while efficiently adsorbing and releasing the higher molecular weight compounds (*e.g., alkyl benzenes*). *The back bed*, 125mg of Carbosieve® S-III, traps vinyl chloride and other light compounds. The *middle* bed, 200mg of Carbotrap, traps the C5-C8 compounds. The *front* bed, 300mg of Carbotrap C, traps the heaviest compounds (Table 1). In total, the design of the Carbotrap 300 tube allows sampling volumes of up to 10 liters to be used without breakthrough by any of these compounds.

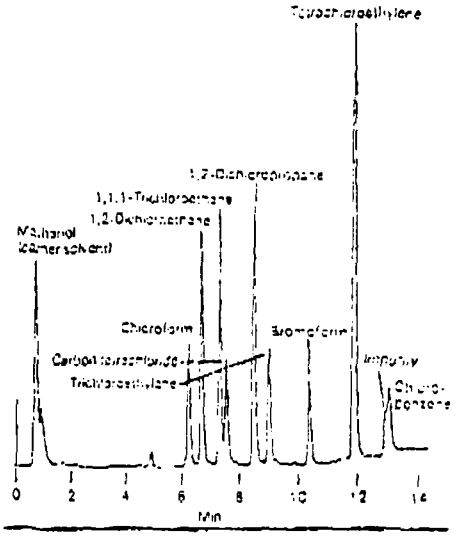
To successfully monitor EPA TO-1 hydrocarbons and chlorinated hydrocarbons, you must use a reliable system. We suggest our reusable thermal desorption tube, a suitable analytical column, and an efficient thermal desorption unit to transfer the samples from the tube to the column.

We selected two GC columns (a packed column and a capillary column) on the basis of their ability to refocus the thermally desorbed compounds, then effectively resolve them with good *peak symmetry. We evaluated graphitized* carbon black materials as packings because their high surface areas exhibit excellent refocusing capability.

The packing we chose, Carbopack C/0.1% SP-1000™ (Figure A), provided

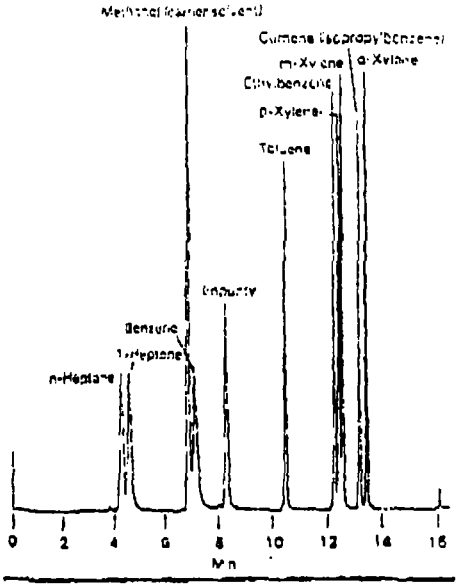
(cont'd on page 3)

Figure A — TO-1 Chlorinated Hydrocarbons by Thermal Desorption and Analysis on a Packed Column



Analytical Conditions — 60/80 Carbopack C/0.1% SP-1000, 6' x 1/8" SS, Col. Temp.: 35°C for 2 min., then to 220°C at 10°C/min., Inj. & Det. Temps: 220°C, Flow Rate (desorption tube to column): 20ml/min., He, Det.: FID, Sens.: 8 x 10⁻¹¹ AFS, Sample: 1.0µl containing 2.0µg/ml each component.
Thermal Desorption Conditions — Tube Desorp. Temp./Time: 350°C/4 min., Valve Compart. & Trans. Line Temps: 220°

Figure B — *TO-1 Nonhalogenated* Hydrocarbons by Thermal Desorption and Analysis on a 0.75mm ID Capillary Column



Analytical Conditions — SUPELCOWAX 10, 60m x 0.75mm ID (1.0µm film), Col. Temp.: 35°C for 4 min., then to 220°C at 5°C/min., Inj. & Det. Temps: 220°C, Flow Rate (desorption tube to column): 10ml/min., He, Make-up Gas Flow: 40ml/min., N, Det.: FID, Sens.: 80 x 10⁻¹¹ AFS, Sample: 1.0µl containing 0.2µg/ml each component.
Thermal Desorption Conditions — Tube Desorp. Temp./Time: 350°C/4 min., Valve Compart. & Trans. Line Temps: 220°C.

(cont'd from front page)

New Thermal Desorption Tube for Monitoring Hazardous Airborne Hydrocarbons

the best performance among several materials. On the other hand, a 60m x 0.75mm ID SUPELCOWAX™ 10 capillary column was needed to resolve the xylene isomers (Figure B). The wide bore capillary column accepts samples with a wide range of component concentrations (<1 to >10,000ng on-column). It can also be used with the same injection, flow control and detection equipment used with the packed column.

To analyze the entire complement of TO-1 compounds, you should use both the packed and capillary columns. Two pairs of nonhalogenated hydrocarbons (n-heptane and toluene, o-xylene and cumene) coelute from the packed column. These compounds can be resolved by using the capillary column. Similarly, two pairs of chlorinated hydrocarbons (carbon tetrachloride and 1,1,1-trichloroethane, chloroform and tetrachloroethylene) coelute from the capillary column, but are resolved by the packed column.

To successfully transfer the hydrocarbons from the thermal desorption tube to the column, we used a *Supelco*™ *Thermal Desorption Unit (Figure C).* This unit desorbs the hydrocarbons ballistically at a rate of approximately 18°C/second, raising the tube temperature from 35°C to 320°C in 16 seconds. All segments of the transfer system (valving, tubing, and transfer line) between the tube and column are inert. The entire transfer system is also heated, eliminating cold spots where analytes could condense. Thus, the sample is sharply focused at the column inlet and the compounds can be efficiently separated.

Control samples for calibrating the thermal desorption unit and evaluating desorption efficiency can be injected into the unit's injection port. They are delivered onto the GC column through the same pathway desorbed samples follow. The thermal desorption unit can be used with either a packed column or a capillary column. Thus, it is ideal for TO-1 chemicals analyses because, with some samples, both column types may be needed to perform a complete analysis.

Our new multi-bed tube, in conjunction with a Supelco Thermal Desorption Unit and the columns described, can be used to monitor all airborne TO-1 compounds. We are now investigating the use of this tube for collecting similar and more volatile compounds, now trapped by purge and trap (TO-2) or cold trap (TO-3) procedures.

Figure C — The Supelco Thermal Desorption Unit Transfers Samples from the Adsorbent Tube to the Analytical Column

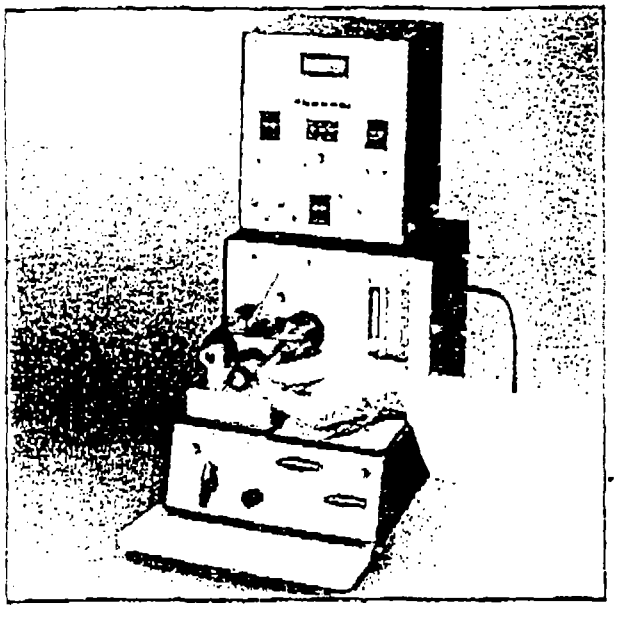


Table 1 — Breakthrough Volumes (in Liters) for US EPA TO-1 Hydrocarbons on the Carbosieve™ S-III/Carbotrap/Carbotrap C Thermal Desorption Tube

Hydrocarbon	Carbosieve S-III (125 mg)	Carbotrap (200mg)	Carbotrap C (300mg)
Vinyl Chloride	15[a]		
Chloroform		1.1■	
1,2-Dichloroethane		0.4	
1,1,1-Trichloroethane		2.7■	
Carbon tetrachloride		4.7■	
1,2-Dichloropropane		6.8	
Trichloroethylene		2.5	
Bromoform		1.7	
Tetrachloroethylene		2.2	
Chlorobenzene		316	
n-Heptane		262	
1-Heptene		284■	
Benzene		2.3	
Toluene		130	
Ethylbenzene		4060	12.9
p-Xylene			11.2
m-Xylene			11.0■
o-Xylene			11.0■
Cumene			27.8■

■Theoretical value calculated from predictive models observed for sampling volumes.

References

1. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.* US EPA Document No. 600/4-84-041 (April, 1984).

Reference not available from Supelco.

Carbotrap 300 Thermal Desorption Tube, 11.5cm x 6mm OD x 4mm ID
2-0379 $32/tube

80/100 Carbopack C/0.1% SP-1000, 15g
1-1820 $100

For stock and custom-prepared columns, refer to our catalog or call our Sales Department.

SUPELCOWAX 10 Capillary Column 60m x 0.75mm ID, 1.0μm film
2-3723 $499

Supelco Thermal Desorption Unit (110 VAC)
2-2895 $4500

For information about the Supelco Thermal Desorption Unit, or using our wide bore capillary columns in your packed column system, please call our Technical Service Department.