

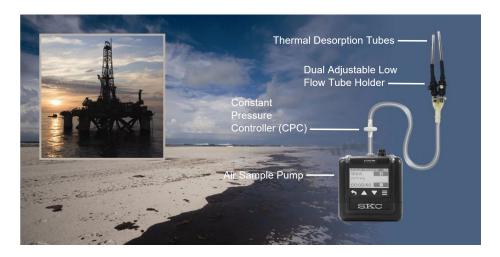
VOC METHOD UPDATE SKC APPENDICES TO EPA METHOD TO-17

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This method update has been written by SKC as a guideline for users. The sampling apparatus specified in this SKC update reflects new technology that may not have been available at the time of the original publication. This method update by SKC has not been officially endorsed or approved by U.S. EPA.

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN AMBIENT OR INDOOR AIR

SKC APPENDIX A
 Active Sampling Using SKC Solid Adsorbent Tubes



SKC APPENDIX B
 Passive Sampling Using SKC ULTRA Series Diffusive Samplers



1.Scope

- **1.1** This document is written by SKC as appendices to U.S. EPA Compendium Method TO-17, Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes (published in 1997). The samplers described, however, are suitable for sampling VOCs in ambient or indoor air. As such, this document also provides an update of EPA Compendium Method IP-1B, Determination of Volatile Organic Compounds in Indoor Air Using Solid Adsorbent Tubes (published in 1989).
- **1.2** Method TO-17 specifies the use of a solid adsorbent tube for sampling followed by thermal desorption (TD) and gas chromatography (GC) analysis. **SKC Appendix A**, presented in this document, provides a listing of solid sorbent tubes available from SKC for the compounds referenced in the original TO-17 method.
- **1.3 SKC Appendix B** describes a passive sampling method for VOCs using diffusive samplers manufactured by SKC. With these samplers, VOCs diffuse onto the sorbent at a fixed, defined rate determined by the specific chemical and the geometry of the samplers. The sorbent is transferred from the sampler into a tube for thermal desorption and gas chromatographic analysis.
- **1.4** Both the active and passive sampling methods are capable of measuring target compounds in the low parts-per-billion (ppb) and parts-per-trillion (ppt) concentration range.

2. Significance

- **2.1** Accurate risk assessment of human and ecological exposure to toxic VOCs is an important goal of the U.S. EPA. Of the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments (CAAA) of 1990, 97 are VOCs. Similarly, in the indoor environment, VOCs are high priority pollutants. Construction of more tightly sealed buildings and the use of synthetic building materials and furnishings can significantly increase the indoor levels of many VOCs. In addition, VOCs can migrate from buried waste and/or contaminated groundwater through subsurface solid into the air space of overlying buildings (vapor intrusion). These vapors may then accumulate, thereby reducing the indoor air quality and posing a health risk to building occupants. VOC vapor intrusion is a hot-button issue in the field of environmental science and regulatory policy. Therefore, measuring VOC levels is an essential part of evaluating potential health threats and identifying appropriate controls.
- **2.2** Historically, stainless steel canisters have been used to measure VOC exposures in ambient air. Canisters, however, do not have the size and portability for microenvironmental and human subject studies. In addition, the cost and logistics of canister sampling can be quite burdensome. (8)

- **2.3** Solid sorbent samplers offer users a simpler option for measuring VOCs. EPA Compendium Method TO-17 describes several advantages of solid sorbent samplers:
 - The small size and light weight of the sorbent sampler and attendant equipment
 - The availability of a large selection of sorbents to match the target compounds
 - The commercial availability of thermal desorption systems to release the sample from the sorbent and into the analytical system
 - The placement of the sorbent packing as the first element in the sampling train, thus reducing the possibility of contamination or losses from upstream elements
 - The large amount of literature on the use of sorbent sampling and thermal desorption for monitoring workplace air, particularly from the Health and Safety Executive (HSE) in the United Kingdom (UK).
- **2.4** The procedures described in these appendices provide the user with a choice of methodologies for the sampling and analysis of VOCs in ambient or indoor air using solid sorbent technologies: active sampling with a pump/sorbent tube or passive sampling with a diffusive sorbent sampler.

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR USING ACTIVE SAMPLING ONTO SORBENT TUBES

EPA METHOD TO-17 HIGHLIGHTS

Sampler - Glass or stainless steel tubes of various lengths and outer diameters (OD) with the central portion packed with ≥ 200 mg of solid adsorbent material(s). Tubes should be individually numbered and show the direction of flow.

Flow rates - Two tubes[§] with independent flow control should be run in parallel to achieve sample volumes of 1 and 4 liters[‡]. Typical flow rates include:

- 16.7 ml/min to collect 1 liter of air in 1 hour
- 66.7 ml/min to collect 4 liters of air in 1 hour
- § EPA requires the use of distributed volume pairs for monitoring to ensure high quality data. However, in situations where acceptable data have been routinely obtained through use of distributed volume pairs and the ambient air is considered well characterized, cost considerations may warrant single-tube sampling. Any attendant risk to data quality objectives is the responsibility of the individual.
- ‡ Appropriate proportional scaling of these volumes to fit the target list and monitoring objectives is acceptable.

Sample time - 1 hour

Sample temperature - The temperature of the sorbent tube must be the same (and not lower than) ambient temperature when sampling or moisture will be retained via condensation

Sample storage - Use sample tubes within 30 days after conditioning with heat and an inert gas. After sampling, place the tubes in a clean, cool (< 4 C), and organic solvent-free environment. Generally, analysis should occur within 30 days of sample collection as artifacts may be generated during sample storage. Some compounds, such as limonene and labile sulfur or nitrogen-containing volatiles, will require analysis within one week. Tubes with multiple sorbent beds should also be analyzed as soon as possible to avoid sample recovery errors. Blank tubes should be stored in a manner similar to the sample tubes to check background levels of the sorbent.

Analysis - Thermal desorption followed by gas chromatography

Background levels of samplers - Tubes packed with sorbent should be conditioned using elevated temperatures and a flow of ultra-pure inert gas. Table 2 in www.epa.gov/sites/default/files/2019-11/documents/to-17r.pdf provides guidelines on the recommended temperature and gas flow for conditioning. Analyze a conditioned tube to obtain a blank profile for target compounds.

Capacity of samplers - Method TO-17, Appendix 1, provides a list of safe sample volumes (SSV) for target compounds.

Typical limits of detection - A method detection limit of < 0.5 ppb is a required performance criterion for Method TO-17. Detection limits will vary depending on several factors.

Precision - Duplicate (analytical) precision should be within 20%.

Audit accuracy - The degree of agreement with a known audit standard that should be within 30%

Distributed volume pairs - The absolute value of the relative difference between the two tube samples should be within 25%.

VOC METHOD UPDATE

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT OR INDOOR AIR

EPA METHOD TO-17 – SKC APPENDIX A (Active Solid Sorbent Tube)

EPA Compendium Method TO-17 can be found in its entirety online at www.epa.gov/sites/default/files/2019-11/documents/to-17r.pdf. SKC Appendix A lists SKC sorbent tubes that are suitable for target compounds, type of sorbent contained in each tube, and the tube material. For further details on SKC thermal desorption tubes, see Thermal Desorption Tubes or the SKC Catalog and Sampling Guide, or visit www.skcinc.com.

HYDROCARBONS

Aliphatic, aromatic, and cyclic hydrocarbons less volatile than ethane and more volatile than nC_{20}

Target Compound		Sorbent Type*		Tube (G=Glass) (SS=Stainless	SKC Cat. No.
rarget compound	Bed 1	Bed 2	Bed 3	Steel)	Cat. No.
	Anasorb® GCB2	Carbosieve S-III		G	226-346
n-Butane	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
n-Pentane	Anasorb GCB1	Carbosieve S-III		SS	226-349
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Anasorb GCB2	Carbosieve S-III		G	226-346
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
n-Pentane	Anasorb GCB1	Carbosieve S-III		SS	226-349
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Chromosorb® 106			SS	226-358
	Tenax [®] GR	Anasorb GCB2		G	226-345
	Anasorb GCB2	Carbosieve S-III		G	226-346
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
	Tenax GR	Anasorb GCB1		SS	226-348
n-Hexane	Anasorb GCB1	Carbosieve S-III		SS	226-349
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Anasorb GCB1			SS	226-356
	Chromosorb 106			SS	226-358

^{*} Anasorb GCB1 is equivalent to Carbopack® B; Anasorb GCB2 is equivalent to Carbopack C.

HYDROCARBONS (continued)

Townst Commound		Soubout Time*		Tube (G=Glass) (SS=Stainless	SKC Cat. No.
Target Compound	Bed 1	Sorbent Type* Bed 2	Bed 3	Steel)	Cat. NO.
	Tenax GR	Anasorb GCB2	Бей 3	G	226-345
Benzene	Anasorb GCB2	Carbosieve S-III		G	226-346
n-Heptane	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-340
Toluene					
n-Octane	Tenax GR	Anasorb GCB1		SS	226-348
Ethylbenzene	Anasorb GCB1	Carbosieve S-III		SS	226-349
Xylenes n-Nonane	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
1,3,5-Trimethyl	Anasorb GCB1			SS	226-356
benzene	Tenax TA			SS	226-357
n-Decane	Chromosorb 106			SS	226-358
	Tenax TA			G	226-360
Styrene	Tenax GR	Anasorb GCB2		G	226-345
Isopropylbenzene n-Propylbenzene 1-	Anasorb GCB2	Carbosieve S-III		G	226-346
Methyl-3-	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
ethylbenzene 1-Methyl-4-	Tenax GR	Anasorb GCB1		SS	226-348
ethylbenzene	Anasorb GCB1	Carbosieve S-III		SS	226-349
Methyl styrene	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
Methyl-2-ethyl benzene	Anasorb GCB1			SS	226-356
1,2,4-Trimethyl	Tenax TA			SS	226-357
benzene 1,2,3-Trimethyl benzene n-Undecane	Tenax TA			G	226-360
	Tenax GR	Anasorb GCB2		G	226-345
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
	Tenax GR	Anasorb GCB1		SS	226-348
n-Dodecane	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Anasorb GCB1			SS	226-356
	Tenax TA			SS	226-357
	Tenax TA			G	226-360

^{*} Anasorb GCB1 is equivalent to Carbopack B; Anasorb GCB2 is equivalent to Carbopack C.

HALOGENATED HYDROCARBONS INCLUDING PCBs

Aliphatic, aromatic, and cyclic halogenated hydrocarbons more volatile than nC₂₀

				Tube (G=Glass) (SS=Stainless	SKC
Target Compound	Dodd	Sorbent Type*	D10	Steel)	Cat. No.
	Bed 1	Bed 2	Bed 3	-	226.246
	Anasorb GCB2	Carbosieve S-III	Cook order C. III	G	226-346
Dichloromethane	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
	Anasorb GCB1	Carbosieve S-III		SS	226-349
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
				_	
	Tenax GR	Anasorb GCB2		G	226-345
	Anasorb GCB2	Carbosieve S-III		G	226-346
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
	Tenax GR	Anasorb GCB1		SS	226-348
1,2-Dichloroethane	Anasorb GCB1	Carbosieve S-III		SS	226-349
1,2-Dictilor detriane	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Anasorb GCB1			SS	226-356
	Tenax TA			SS	226-357
	Chromosorb 106			SS	226-358
	Tenax TA			G	226-360
	Tenax GR	Anasorb GCB2		G	226-345
	Anasorb GCB2	Carbosieve S-III		G	226-346
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
1,1,1-Trichloro-	Tenax GR	Anasorb GCB1		SS	226-348
ethane	Anasorb GCB1	Carbosieve S-III		SS	226-349
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Anasorb GCB1			SS	226-356
	Chromosorb 106			SS	226-358
Carbon Tetra-	Tenax GR	Anasorb GCB2		G	226-345
chloride	Anasorb GCB2	Carbosieve S-III		G	226-346
Trichloroethylene	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
1,1,2-Trichloro-	Tenax GR	Anasorb GCB1		SS	226-348
ethane	Anasorb GCB1	Carbosieve S-III		SS	226-349
Tetrachloro-	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
ethylene	Anasorb GCB1			SS	226-356
Chlorobenzene	Tenax TA			SS	226-357
1,1,1,2-Tetra-	Chromosorb 106			SS	226-358
chloroethane					
1,1,2,2-Tetra- chloroethane	Tenax TA			G	226-360

^{*} Anasorb GCB1 is equivalent to Carbopack B; Anasorb GCB2 is equivalent to Carbopack C.

ALCOHOLS

Alcohols more volatile than nC_{20} and sufficiently stable to be analyzed by conventional GC techniques

Target Compound		Sorbont Typo*		Tube (G=Glass) (SS=Stainless	SKC Cat. No.
rarget Compound	Bed 1	Sorbent Type* Bed 2	Bed 3	Steel)	Cat. No.
	Anasorb GCB2	Carbosieve S-III			226-346
NA attacas at				G	226-346
Methanol	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	+	
Ethanol	Anasorb GCB1	Carbosieve S-III		SS	226-349
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Tenax GR	Anasorb GCB2		G	226-345
	Anasorb GCB2	Carbosieve S-III		G	226-346
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
n-Propanol	Tenax GR	Anasorb GCB1		SS	226-347
Isopropanol	Anasorb GCB1	Carbosieve S-III		SS	226-349
ізоргораної	Anasorb GCB1	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Anasorb GCB2			SS	226-356
	Chromosorb 106			SS	226-358
	CHIOHIOSOID 100			33	220-338
	Tenax GR	Anasorb GCB2		G	226-345
	Anasorb GCB2	Carbosieve S-III		G	226-346
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
	Tenax GR	Anasorb GCB1		SS	226-348
n-Butanol	Anasorb GCB1	Carbosieve S-III		SS	226-349
iso-Butanol	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
iso Datailo.	Anasorb GCB1			SS	226-356
	Tenax TA			SS	226-357
	Chromosorb 106			SS	226-358
	Tenax TA			G	226-360
	Tenax GR	Anasorb GCB2		G	226-345
	Anasorb GCB2	Carbosieve S-III		G	226-346
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
	Tenax GR	Anasorb GCB1		SS	226-348
Octanol	Anasorb GCB1	Carbosieve S-III		SS	226-349
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Tenax TA			SS	226-357
	Tenax TA			G	226-360

^{*} Anasorb GCB1 is equivalent to Carbopack B; Anasorb GCB2 is equivalent to Carbopack C.

ESTERS AND GLYCOL ETHERS

Esters and glycol ethers more volatile than nC_{20} and sufficiently stable to be analyzed by conventional GC techniques

Torget Compound		Sorbont Tures*		Tube (G=Glass) (SS=Stainless Steel)	SKC Cat. No.
Target Compound	Bed 1	Sorbent Type* Bed 1 Bed 2 Bed 3			
	Tenax GR	Anasorb GCB2	Beu 3	G	226-345
	Anasorb GCB2	Carbosieve S-III		G	226-346
Methyl acetate	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
Methyl-t-butyl	Tenax GR	Anasorb GCB1		SS	226-348
ether	Anasorb GCB1	Carbosieve S-III		SS	226-349
t-Butyl acetate	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
,	Anasorb GCB1			SS	226-356
	Chromosorb 106			SS	226-358
Ethyl acetate Propyl acetate	Tenax GR	Anasorb GCB2		G	226-345
Isopropyl acetate	Anasorb GCB2	Carbosieve S-III		G	226-346
Butyl acetate Isobutyl acetate Methyl acrylate Ethyl acrylate Methyl methacrylate Methoxyethanol Ethoxyethanol Butoxyethanol Methoxypropanol Methoxy- ethylacetate	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
	Tenax GR	Anasorb GCB1		SS	226-348
	Anasorb GCB1	Carbosieve S-III		SS	226-349
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Anasorb GCB1			SS	226-356
	Tenax TA			SS	226-357
	Chromosorb 106			SS	226-358
Ethoxyethylacetate Butoxyethylacetate	Tenax TA			G	226-360

^{*} Anasorb GCB1 is equivalent to Carbopack B; Anasorb GCB2 is equivalent to Carbopack C.

ALDEHYDES AND KETONES

Aldehydes and ketones more volatile than nC₂₀ and sufficiently stable to be analyzed by conventional GC techniques

Target Compound		Sorbent Type*		Tube (G=Glass) (SS=Stainless	SKC Cat. No.
rarget Compound	Bed 1	Bed 2	Bed 3	Steel)	Cat. No.
	Anasorb GCB2	Carbosieve S-III		G	226-346
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
Acetone	Anasorb GCB1	Carbosieve S-III		SS	226-349
Accione	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Chromosorb 106			SS	226-358
	Tenax GR	Anasorb GCB2		G	226-345
	Anasorb GCB2	Carbosieve S-III		G	226-346
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
2-Butanone	Tenax GR	Anasorb GCB1		SS	226-348
Methylisobutyl-	Anasorb GCB1	Carbosieve S-III		SS	226-349
ketone	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
Cyclohexanone	Anasorb GCB1			SS	226-356
	Tenax TA			SS	226-357
	Chromosorb 106			SS	226-358
	Tenax TA			G	226-360
	Tenax GR	Anasorb GCB2		G	226-345
	Anasorb GCB2	Carbosieve S-III		G	226-346
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
n-Butanal	Tenax GR	Anasorb GCB1		SS	226-348
n-Butanai	Anasorb GCB1	Carbosieve S-III		SS	226-349
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Anasorb GCB1			SS	226-356
	Chromosorb 106			SS	226-358
	Tenax GR	Anasorb GCB2		G	226-345
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
3,5,5-Trimethyl-	Tenax GR	Anasorb GCB1		SS	226-348
cyclohex-2-enone	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Anasorb GCB1			SS	226-356
	Tenax TA			SS	226-357

^{*} Anasorb GCB1 is equivalent to Carbopack B; Anasorb GCB2 is equivalent to Carbopack C.

ALDEHYDES AND KETONES (continued)

Target Compound		Sorbent Type*		Tube (G=Glass) (SS=Stainless Steel)	SKC Cat. No.
	Bed 1	Bed 2	Bed 3		
	Tenax GR	Anasorb GCB2		G	226-345
	Anasorb GCB2	Carbosieve S-III		G	226-346
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
	Tenax GR	Anasorb GCB1		SS	226-348
Furfural	Anasorb GCB1	Carbosieve S-III		SS	226-349
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Anasorb GCB1			SS	226-356
	Tenax TA			SS	226-357
	Tenax TA			G	226-360

^{*} Anasorb GCB1 is equivalent to Carbopack B; Anasorb GCB2 is equivalent to Carbopack C.

MISCELLANEOUS VOCs

These are most VOCs in air. Generally compatible with all organics less volatile than ethane, more volatile than nC_{20} , and sufficiently stable to be analyzed by conventional GC techniques.

Target Compound		Sorbent Type*		Tube (G=Glass) (SS=Stainless Steel)	SKC Cat. No.
	Bed 1	Bed 2	Bed 3		
	Anasorb GCB2	Carbosieve S-III		G	226-346
A t : t - : l -	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
Acetonitrile	Anasorb GCB1	Carbosieve S-III		SS	226-349
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Tenax GR	Anasorb GCB2		G	226-345
	Anasorb GCB2	Carbosieve S-III		G	226-346
Acrylonitrile	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
Propionitrile	Tenax GR	Anasorb GCB1		SS	226-348
Acetic acid	Anasorb GCB1	Carbosieve S-III		SS	226-349
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
	Anasorb GCB1			SS	226-356

^{*} Anasorb GCB1 is equivalent to Carbopack B; Anasorb GCB2 is equivalent to Carbopack C.

MISCELLANEOUS VOCs (continued)

Target Compound		Sorbent Type*		Tube (G=Glass) (SS=Stainless Steel)	SKC Cat. No.
	Bed 1	Bed 2	Bed 3		
	Tenax GR	Anasorb GCB2		G	226-345
	Anasorb GCB2	Carbosieve S-III		G	226-346
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
	Tenax GR	Anasorb GCB1		SS	226-348
Maleic anhydride	Anasorb GCB1	Carbosieve S-III		SS	226-349
Pyridine	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	SS	226-350
Aniline	Anasorb GCB1			SS	226-356
	Tenax TA			SS	226-357
	Chromosorb 106			SS	226-358
	Tenax TA			G	226-360
	Tenax GR	Anasorb GCB2		G	226-345
	Anasorb GCB2	Anasorb GCB1	Carbosieve S-III	G	226-347
Nitrobenzene	Tenax GR	Anasorb GCB1		SS	226-348
Nitrobenzene	Anasorb GCB1	Anasorb GCB1	Anasorb GCB1	SS	226-350
	Tenax TA			SS	226-357
	Tenax TA			G	226-360
	Tenax GR	Anasorb GCB2		G	226-345
Dhonal	Tenax GR	Anasorb GCB1		SS	226-348
Phenol	Tenax TA			SS	226-357
	Tenax TA			G	226-360

^{*} Anasorb GCB1 is equivalent to Carbopack B; Anasorb GCB2 is equivalent to Carbopack C.

VOC METHOD UPDATE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AND INDOOR AIR

EPA METHOD TO-17 – SKC APPENDIX B (Passive [Diffusive] Sampler)

SKC APPENDIX B HIGHLIGHTS

Sampler - A nylon sampler housing with a number of inlet holes is loaded with one of several sorbents. Sampling is started by removing or sliding the cover to expose the holes to the air and is stopped by replacing the cover (SKC Inc, Eighty Four, PA; ULTRA Series Passive Samplers, Cat. No. 690 Series). With these samplers, VOCs diffuse onto the sorbent at a fixed, defined rate determined by the specific chemical and the geometry of the samplers.

Sampling/Uptake rate - Varies by compound. SKC and the U.S. OSHA Testing Lab have experimentally verified the sampling or uptake rates of many chemicals using SKC passive samplers. See the online <u>Passive Sampling Guide</u> for compound-specific sampling/uptake rates. Despite differences in the outward appearance of samplers, the sampler housings maintain the same geometry; therefore, the sampling rates are equivalent for all models provided similar sorbents are used. Additional information on sampling rates using Chromosorb 106 is available. (5)

Face velocity and orientation - The SKC ULTRA Series passive samplers will work in face or wind velocities of 5 to 200 cm/sec. Wind velocities < 5 cm/sec may result in reduced sampling rates. Operation is proficient in a parallel or perpendicular orientation to wind. For more information, go to www.skcinc.com and enter "ULTRA" in the Google search box.

Sample time – 8 hours to 30 days

Sampling conditions - Temperature range: 10 to 40 C and relative humidity range: 20 to 80% RH (25 C)

Sample storage - **Before use:** Store at ≤ 39.2 F (4 C) for up to 30 days to reduce the formation of artifacts and spurious peaks in the sorbent. **After use:** Store at ≤ 39.2 F (4 C) and analyze within 21 days. Store in a clean and organic solvent-free environment.

Analysis - Sorbent is transferred directly from the sampler housing to a thermal desorption tube (0.25-inch OD and minimum 3.5-inch length). The tube is sealed until analysis. The VOCs thermally desorbed from the sorbent are analyzed by gas chromatography, typically with mass spectrometry (MS).

Background levels of samplers - Typically less than 25 ng per passive sampler

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AND INDOOR AIR

EPA METHOD TO-17 – SKC APPENDIX B (Passive [Diffusive] Sampler)

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1. Scope

- **1.1** This method describes a procedure for the determination of VOCs in ambient or indoor air in the low-ppb and ppt range. The procedure has been found to be suitable for 8-hour to 30-day indoor/ambient air studies targeting medium-to-high boiling compounds.
- **1.2** This method uses the same thermal desorption techniques and gas chromatographic analysis specified in active sampling Method TO-17. In this case, however, VOCs are collected through a passive process of controlled diffusion through inlet holes of a sampler loaded with solid sorbent (SKC Inc., Eighty Four, PA; ULTRA Series Passive Samplers, Cat. No. 690 Series). Samplers are available with five different sorbents. At the laboratory, sorbent is transferred to a thermal desorption tube with an outer diameter of 0.25 inch and a minimum length of 3.5 inches (see <u>ULTRA Operating Instructions</u>). The tube is sealed until analysis. VOCs are thermally desorbed from the sorbent and analyzed by gas chromatography, typically with mass spectrometry.
- **1.3** The uptake rate varies by compound. Uptake rates and other critical sampling parameters have been experimentally verified for many VOCs by SKC and other agencies. (1-2) See the online <u>Passive Sampling Guide</u> for compound-specific sampling/uptake rates. Despite differences in the outward appearance of samplers, the sampler housings maintain the same geometry; therefore, the sampling rates are equivalent for all models provided similar sorbents are used. Only reverse diffusion may differ based on the sorbent and the chemical being sampled.
- **1.3.1** SKC ULTRA Series passive samplers will work in face or wind velocities of 5 to 200 cm/sec. Operation is proficient in a parallel or perpendicular orientation to wind. When face velocities are < 5 cm/sec, the sampling rate may be reduced (commonly called "zero velocity sampling rates"). These lower velocity rates are typically found when sampling inside homes or buildings. For more information, go to www.skcinc.com and enter "ULTRA" in the Google search box.
- **1.4** Researchers at the Sahlgrenska Academy at Goteborg University and the National Institute of Working Life in Sweden have also validated the use of SKC passive sampler for 1,3-butadiene and benzene in ambient air for eight hours up to seven days. (3)
- **1.5** The passive samplers are marketed as the ULTRA Series Passive Samplers for thermal desorption and are manufactured by SKC Inc. (Eighty Four, PA; ULTRA Series Passive Samplers, Cat. No. 690 Series). Up to five sorbents are available.
- **1.6** This method may involve hazardous materials, operations, and equipment. This method does not purport to address all the safety problems associated with its use. It is the user's responsibility to develop and implement appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.

2. Applicable Documents

2.1 ASTM International Standards

D1356 Definition of Terms Relating to Atmospheric Sampling and Analysis E682 Practice for Liquid Chromatography Terms and Relationships

2.2 Other Documents

- Compendium of Methods for the Determination of Air Pollutants in Indoor Air
- Compendium of Methods for the Determination of Organic Compounds in Ambient Air
- Methods for the Determination of Hazardous Substances by the Health and Safety Laboratory - MDHS 88 Volatile Organic Compounds in Air
- Performance of SKC ULTRA Passive Samplers by the U.S. Department of Labor

3. Summary of Method

- **3.1** Sorbent is loaded in a sampler housing that contains multiple inlet holes. VOC vapor diffuses into the sampler at an experimentally determined rate and is collected onto the solid sorbent material. The samplers have been found to be suitable for 8 hours up to 30 days of indoor/ambient air sampling targeting medium-to-high boiling compounds.
- **3.2** After sampling, samplers are closed with the sampler covers (see \underline{ULTRA} $\underline{Operating\ Instructions}$). Samplers are sealed in the provided pouches and packed for shipment to a laboratory. Store samples at $\leq 39.2\ F(4\ C)$ in a clean and organic solvent-free environment followed by analysis within 21 days.
- **3.3** In the analytical laboratory, the sorbent is transferred from the sampler housing directly into a thermal desorption tube. The tube is then sealed with PTFE caps or Swagelok® fittings. Thermal desorption tubes must be an outer diameter of 0.25 inch and a minimum length of 3.5 inches, such as those manufactured by Perkin-Elmer.
- **3.4** The VOCs adsorbed onto the sorbent material are thermally desorbed and analyzed by GC or GC/MS. The blank samples are likewise desorbed and analyzed.
- **3.5** VOCs in the sample are identified and quantified by comparison with calibration curves for the analytes of interest.

4. Significance

- **4.1** This method uses a passive sampling system with an uptake rate that depends on the diffusion coefficient of the VOC of interest, and that is proportional to the cross-sectional area of the opening of the sampler and inversely proportional to the length of the diffusion zone of the sampler. SKC and other agencies have experimentally verified sampling/uptake rates for various compounds. The samplers are available commercially from SKC Inc. as the ULTRA Series Passive Samplers (see <u>ULTRA Samplers</u> for details). The sorbent material must be used within 30 days or repurged by the user to ensure acceptable background levels. Typical background levels of VOCs **are less than 25 ng** per sampler. The portable samplers allow for employment of this method in general areas with some minimal air movement or in micro-environments.
- **4.2** Thermal desorption and subsequent GC or GC/MS analysis provide a very accurate measure of low-level VOC concentrations.

5. Definitions

Note: Definitions used in this document and any user-prepared SOPs should be consistent with ASTM International Methods D1356 and E682. All pertinent abbreviations and symbols are defined within this document at point of use.

6. Interferences

- **6.1** The ULTRA Series Passive Samplers allow the user to select the best sorbent for the target compounds and transfer sorbent easily for analysis. The Marine Corps selected Tenax TA for the measurement of chemical warfare agents. **(4)** U.S. OSHA reported on the use of Carboxen 1016, Carbotrap Z[®], and Chromosorb 106 for a mixture containing 20 solvent analytes. **(5)** SKC has conducted studies on Tenax TA and Anasorb GCB1 sorbents **(6)** and Carbograph 5 TD sorbent. **(7)**
- **6.2** Interferences are not a problem if the sorbent selection and GC parameters are properly managed.

7. Apparatus

7.1 Sampling

7.1.1 Passive Diffusive Samplers

ULTRA (see Figure 1) – A housing loaded with sorbent with inlet holes (SKC Inc., Eighty Four, PA; Cat. Nos. 690-101, -103, -104, -105, and -106) that allows for controlled diffusion and collection of VOCs. The sampler contains discrete compartments for sample sorbent and blank/correction sorbent. A cover slides for opening and closing the sampler. Sample sorbent is transferred to a thermal desorption tube.

Uptake rate is dependent on the sorbent, the target compound, and sampling conditions. The housing has a clip for positioning during sampling. SKC manufactures ULTRA Series samplers to meet the following criteria:

Total VOC concentration: < 0.025 μg (25 ng) per sampler or vial

- **7.1.2** The samplers are shipped from the manufacturer in a pouch, which can be used after sampling for shipping the samplers or sorbent vials in an appropriate mailer to a laboratory.
- **7.1.3** Sorbent is typically conditioned by packing it inside a tube using elevated temperatures and a flow of ultra-pure inert gas. EPA Method TO-17, Table 2 (www.epa.gov/sites/default/files/2019-11/documents/to-17r.pdf) provides guidelines on the recommended temperature and gas flow for conditioning.
- **7.1.4** Use sorbent within 30 days after conditioning with heat and an inert gas.

7.2 Analysis

- **7.2.1** After sampling, place sampler with sorbent or sorbent vial in a clean, cool (\leq 4 C), and organic solvent-free environment. Generally, analysis should occur within 21 days of sample collection as artifacts may be generated during sample storage. Some compounds, such as limonene and labile sulfur or nitrogen-containing volatiles, will require analysis within one week. Blank samplers or sorbent vials (from the same lot as sample sorbent) should be stored in a manner similar to the samples to check background levels of the sorbent.
- **7.2.2** Analytes should be desorbed from the sorbent by back flushing the tubes with heat and an inert gas (typically 150 to 400 C for 5 to 15 minutes with a carrier gas flow of 30 to 100 ml/min). The VOCs thermally desorbed from the sorbent are analyzed by gas chromatography, typically with mass spectrometry. See sample chromatogram in Figure 2.
- 8. Reagents and Materials
- 9. Preparation of Reagents

Complete information for Sections 8 and 9 can be obtained in EPA Method TO-17 at www.epa.gov/sites/default/files/2019-11/documents/to-17r.pdf.

- 10. Sample Collection
- **10.1** See ULTRA Operating Instructions.
- 11. Analytical Procedure
- 11.1 Sample Preparation and Desorption
- 11.1.1 See ULTRA Analysis Instructions.
- **11.1.2** Analytes should be desorbed from the sorbent by back flushing the tubes with heat and an inert gas (typically 150 to 400 C for 5 to 15 minutes with a carrier gas flow of 30 to 100 ml/min). The VOCs thermally desorbed from the sorbent are analyzed by gas chromatography with the detector recommended for the compound(s) of interest, typically mass spectrometry.

See EPA Method TO-17 at www.epa.gov/sites/default/files/2019-11/documents/to-17r.pdf for complete information on analysis, calibration, and quality assurance procedures.

12. Method Detection Limits

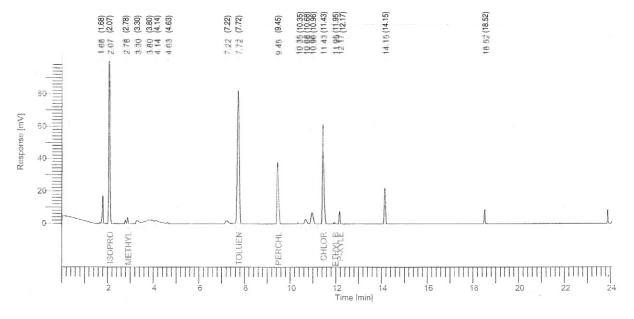
- **12.1** SKC researchers used the following procedure to determine detection limits.
- **12.1.1** Reporting limits were determined by running seven replicates of a standard at a level near the detection limit of the analyte. The standard deviation of the mean of these values was calculated and if the relative standard deviation was less than 25%, this was stated as the method reporting limit.

13. References

- 1. **SKC Inc.**: Passive (Diffusive) Sampler Research Reports. Eighty Four, PA. See online at www.skcinc.com/knowledgecenter/categories/research-reports
- U.S. Department of Labor: OSHA Analytical Methods Manual. Salt Lake City, Utah: U.S. Department of Labor, Occupational Safety and Health Division Directorate for Technical Support, 1990. See online at www.osha.gov/
- Strandberg, B., Olsson, K., Levin, J., et. al.: "Evaluation of Two Types of Diffusive Samplers and Adsorbents for Measuring 1,3-Butadiene and Benzene in Air," *Atmospheric Environment*, Vol. 39, Issue 22, July 2005, pp. 4101-4110
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- 4. **Hendricks, W.D., Roberts, J.L., Schultz, G.R.:** "Feasibility of Diffusive Sampling to Monitor U.S. Military Personnel for Exposure to Toxic Chemical Substances," Salt Lake City, Utah: U.S. Department of Labor, Occupational Safety and Health Division Directorate for Technical Support, 2001
- 5. U.S. Department of Labor: "Performance of SKC ULTRA Passive Samplers Containing Carboxen 1016, Carbotrap Z, or Chromosorb 106 When Challenged with a Mixture Containing Twenty of OSHA SLTC's Top Solvent Analytes," Salt Lake City, Utah: U.S. Department of Labor, Occupational Safety and Health Division Directorate for Technical Support, 2003. See online at www.osha.gov/sites/default/files/Performance-of-SKC-Ultra-Passive-Samplers.pdf
- Kuhlman, C., Coyne, L.: "Feasibility of a New Diffusive Sampler to Measure Sub-ppb Levels of VOCs," SKC Inc., presented at the AWMA Symposium on Air Quality Measurement Methods and Technology, April 2005
- 7. **Coyne, L., Kuhlman, C., Chada, J.:** "Validation of the 575-001 and the ULTRA Series Diffusive Samplers: Long-term Sampling in Indoor and Ambient Air Environments." *See online at* https://www.skcinc.com/knowledgecenter/resources/validation-of-the-575-001-and-the-ultra-series-diffusive-samplers-long-term-sampling-in-indoor-amb
- 8. **Hayes**, **H.**, **Mitzel**, **R.**: "AlHce 2011 Presentation: Field Evaluation of Diffusive Samplers for Indoor Air VOC Measurements (.pps)" at https://skcinc.sharepoint.com/:p:/s/knowledge/EeCYSOpKEopBiRy73PUXFVUBIvTGThPEoFaDi6yaEZV7hw?e=1QexIo



Figure 1. ULTRA Passive Sampler with Blank/Correction Compartment



Column: RTX-5, 30 m, 0.32 ID, 1 μ m df

Injection Temp.: 250 C
Detector Temp.: 250 C
Carrier Gas: Nitrogen

Flow:

 $N_2 = 2.5$ ml/min Air = 450 ml/min

 $H_2 = 45 \text{ ml/min}$

GC:

Perkin Elmer Clarus[®] 500

Integrator:

TotalChrom Software

Oven Program:

Initial Temp.: 35 C Initial Hold: 7 min

Ramp 1: 5 C/min to 100 C hold 0.5 min **Ramp 2:** 15 C/min to 175 C hold 0.0 min

Total Run Time: 25.5 min

Figure 2. Sample Chromatogram – VOCs on Tenax TA Sorbent