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# Standard Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method[1]

This standard is issued under the fixed designation D 3687; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This practice covers the applications of methods for the ~~desorption~~extraction and gas chromatographic determination of organic vapors that have been adsorbed from air in sampling tubes packed with activated charcoal.

1.2 This practice is complementary to Practice D 3686.

~~1.3This practice is applicable for analysis of samples taken from workplace or other atmospheres, provided that the contaminant adsorbs onto charcoal and that it can be analyzed by gas chromatography. A partial list of organic compounds for which this method is applicable is given in A1 in Practice D3686~~

1.3 This practice is applicable for analysis of samples taken from workplace or other atmospheres provided that the contaminant adsorbs onto charcoal, that it can be adequately extracted from the charcoal, and that it can be analyzed by gas chromatography (GC). Other adsorbents and other extraction techniques are described in Practice D 6196.

1.4 Organic compounds of multicomponent samples may mutually interfere during analysis. Methods to resolve interferences are given in Section 6.

1.5 The values stated in SI units are to be regarded as the standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* ~~Specific precautions are given in 8.1.4.2 and Annex A1.~~ Specific precautions are given in 8.4, 9.2, and in A1.2.3.



## 2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres

D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)

D 6196 Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air

E 355 Practice for Gas Chromatography Terms and Relationships

2.2 *NIOSH Standards:*

CDC-99-74-45 Documentation of NIOSH Validation Tests[3]

~~Manual of Analytical Methods, 2nd Ed.[3]~~ NIOSH Manual of Analytical Methods, 4th Ed.[4]

2.3 ~~*OSHA Standard:*~~ *OSHA Standards:*

29 CFR 1910 ~~General and Industrial OSHA Safety and Health Standard~~ Code of Federal Regulations, Regulations Relating to Labor, Occupational Safety and Health Administration, Department of Labor [5]

OSHA Sampling and Analytical Methods [6]

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[1] This practice is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittees D22.04 on Workplace Atmospheres.
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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from the U.S. Department of Commerce, National Technical Information Service, Port Royal Road, Springfield, VA 22161.

~~[4] Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.~~

[4] NIOSH Manual of Analytical Methods (NMAM). http://www.cdc.gov/niosh/nmam/ (accessed 1/2007).

~~[5] The boldface numbers in parentheses refer to the list of references at the end of this standard.~~

[5] Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

~~[6] Benzene is used in this practice as the reference chemical for the purposes of illustration, but a less toxic chemical such as toluene could be used.~~

[6] OSHA Sampling and Analytical Methods, http://www.osha.gov/dts/sltc/methods/index.html (accessed 1/2007).

2.4 *UK Health and Safety Executive (HSE):*[7]
Methods for the Determination of Hazardous Substances (MDHS)
2.5 *Berufsgenossenschaftliches Institut für Arbeitsschulz (BGIA):*[8]
GESTIS Analytical Methods

## 3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this practice, refer to ~~Terminology D1356,~~ the terminology specified in D 1356 and E 355.

~~3.1.2*relative retention time (RRT)*—a ratio of RTs' for two chemicals for the same chromatographic column and carrier gas flow rate, where the denominator represents a reference chemical.~~

~~3.1.3*retention time (RT)*—time to elute a specific chemical from a chromatographic column, for a specific carrier gas flow rate, measured from the time the chemical is injected into the gas stream to when it appears at the detector.~~

## 4. Summary of Practice

~~4.1Organic vapors, which have been collected on activated charcoal and eluted therefrom with carbon disulfide or other appropriate desorbent, are determined by gas-liquid chromatography, using a flame ionization detector and other appropriate detectors.~~

~~4.2Interferences resulting from the analytes having similar retention times during gas-liquid chromatography are resolved by improving the resolution or separation, such as by changing the chromatographic column or operating parameters, or by fractionating the sample by solvent extraction.~~

~~4.3Peaks are identified using techniques such as GC/MS and dual column chromatography.~~

4.1 Organic vapors that have been collected on activated charcoal are extracted with carbon disulfide or another appropriate solvent and are determined by GC using a flame ionization detector (FID). Carbon disulfide is a relatively small molecule that can penetrate the "ink-bottle" shaped pores of activated charcoal, it has a high heat of adsorption on activated charcoal which helps in displacing other adsorbed molecules, and it is a reasonably good solvent for most, especially non-polar, organic molecules. Polar modifiers (such as *N,N-dimethylformamide*) are frequently added to enhance the recovery of polar organic compounds. Other advantages to using carbon disulfide include an early elution time on most GC columns and a small FID response.

4.2 Interferences resulting from the analytes having similar retention times during GC analysis are resolved by changing the GC column, by changing the operating parameters, or by fractionating the sample using solvent extraction as described in Section A1.1.

4.3 Peak purity and identity can be confirmed using techniques such as GC/MS.

## 5. Significance and Use

5.1 Promulgations by the Federal Occupational Safety and Health Administration (OSHA) in 29 CFR 1910 designate that certain organic compounds must not be present in workplace atmospheres at concentrations above specified values.

5.2 This practice, when used in conjunction with Practice D 3686, will promote needed accuracy and precision in the determination of airborne concentrations of many of the organic chemicals given in 29 CFR 1910, CDC-99-74-45~~, and the Manual of Analytical Methods. It can be used to determine worker exposures to these chemicals, provided appropriate sampling periods are used.~~

~~5.3A partial list of chemicals for which this practice is applicable is given in A1 of Practice D3686, along with their OSHA Permissible Exposure Limits.~~ , NIOSH Manual of Analytical Methods, OSHA Sampling and Analytical Methods, HSE Methods for the Determination of Hazardous Substances, and BGIA GESTIS Analytical Methods. It can be used to determine worker exposures to these chemicals, provided appropriate sampling periods are used.

5.3 Most laboratories are equipped with apparatus similar to that described in Section 7. Other apparatus can be used when analytical procedures suitable for that equipment are employed. The analytical techniques (or variations thereof) described in Sections 9-11 are in general use to analyze volatile organic compounds extracted from charcoal. Other procedures can be used when appropriate.

## 6. ~~Interferences~~

~~6.1Any gas chromatographic separation that involves a mixture of polar and nonpolar compounds is confronted with serious problems due to peak superimposition. In many industrial operations, both nonpolar compounds, such as mixed aliphatic petroleum hydrocarbons, and polar substances, such as aromatic hydrocarbons, amines, oxygenated compounds and sometimes halogenated compounds, may be used and found in the workplace atmosphere. It is rarely the case that a single organic solvent vapor may be expected in a workplace atmosphere where organic solvents are being used.~~

~~[7] The 1-mL volume of $CS_2$ is used when analyzing 150-mg charcoal tubes. If larger charcoal tubes are being analyzed, a proportionately larger volume of $CS_2$ should be used.~~

[7] HSE Methods for the Determination of Hazardous Substances (MDHS). http://www.hse.gov.uk/pubns/mdhs/index.htm# (accessed 1/2007).

[8] GESTIS Analytical Methods. http://www.hvbg.de/e/bia/gestis/analytical_methods/index.html (accessed 1/2007).

6.2Such interferences are frequently resolved by changing the type of column, length of column, or operating conditions, to improve resolution of separation of compounds.

6.3General approaches which can be followed are given below:

6.3.1Generally unknown samples are analyzed using at least two columns of different polarity.

6.3.2As a general guide to practice, nonpolar substrates, such as the silicones, tend to separate according to the boiling points of the compounds, whereas polar column separations are influenced more by the polarity of the compounds.

6.3.3A single wide bore capillary column can replace several specialized packed columns and provide better sample resolution in significantly less time. Application of these columns minimizes operational changes required to achieve peak resolution.

6.4Selective solvent stripping techniques have been used successfully to make clean and fast separations of polar, nonpolar and oxygenated compounds. A general guideline is given in Annex A1 and detailed procedures are given in Refs **Interferences**

6.1 Any chemical that produces an FID response and has a similar retention time as the analyte is a potential interference. If potential interferences were reported when the samples were received they should be considered before the samples are extracted. Generally, gas chromatographic conditions such as the type of GC column (phase) or operating parameters can be changed to resolve interferences.

6.2 Selective solvent stripping techniques have been used successfully to make clean and fast separations of polar, nonpolar and oxygenated compounds. A general guideline is given in A1.1 and detailed procedures are given in Refs[9] **(1 and 2).** ).

6.3 When necessary, the identity or purity of an analyte peak can be confirmed by GC/mass spectrometry.

6.4 The presence of co-adsorbed chemicals can affect the recovery (extraction efficiency) of a particular analyte. Suspected effects can be tested by spiking the analytes on charcoal as in Section 11.

## 7. Apparatus

7.1 *Gas Chromatograph*(GC), having a flame ionization detector and either an isothermally controlled or temperature programmed heating oven.

7.2A variety of packed and capillary columns are suitable. Two suitable packed columns are a 10 ft stainless steel column, ⅛ in. ID packed with 10% free fatty acid phase (FFAP) substrate on 80/100 mesh acid washed diatomaceous earth and a nonpolar column containing 10% methyl silicone substrate on the same support material in a similar column as given above. Alternatively, 35% diphenyl, 65% dimethyl polysiloxane and polyethylene glycol wide bore capillary columns (0.53 and 0.75 mm) may be used in place of the packed columns. These columns are available in 30 and 60 m lengths. Gas chromatograph, equipped with a flame ionization detector (FID), a temperature-programmable oven, and an automatic sample injector (autosampler). Sample injection may be performed manually if necessary. Other detectors (such as electron capture, flame photometric, nitrogen phosphorous detectors) can be used when appropriate but the extraction solvent may have to be modified.

7.2 *Electronic data system*, or other suitable means to record and measure detector response, to prepare calibration curves, and to process sample results.

7.3 *Microsyringes*, two or more 10-µL volume.

7.4*Vials*, 5-mL serum, fitted with caps lined with TFE-fluorocarbon. GC columns, required to separate the complex mixture of possible organic chemicals. Examples of the most common and useful GC columns are 60-m long, 0.32-mm i.d. fused silica capillary GC columns with 0.1 to 1-µm thick (df) phases such as 100 % dimethyl polysiloxane, 95 % dimethyl-5% diphenyl polysiloxane, and polyethylene glycol.

7.4 *Laboratory glassware*, calibrated syringes, calibrated solvent dispensers, assorted Class A pipets and volumetric flasks and glass automatic sample injector (autosampler) vials with PTFE septum caps to contain analytical standards and samples.

## 8. Calibration Reagents

8.1 *Preparation of Gas Chromatograph* :

8.1.1Install the selected column.

8.1.2Check the system for leaks as prescribed by GC manufacturer.

8.1.3Select a carrier gas flow compatible with the detector and column selected for the separation.

8.1.4Calibrate the chromatographic column to determine the relative retention times (RRTs) of the various compounds of interest.

8.1.4.1Select a reference solvent which will serve as a benchmark.

8.1.4.2Prepare a 0.05% solution of this solvent (volume/volume) in chromatographic grade carbon disulfide ($CS_2$). When kept in a properly closed container (see 7.4) and refrigerated when not in use, some solutions will keep for several weeks **(3).**

NOTE1—**Warning:**Carbon disulfide is toxic and explosive, as are many of the organic compounds to be analyzed. Work with these chemicals must be done in a properly operating laboratory hood.

8.1.4.3Into a clean 10-µL syringe draw 2 µL of $CS_2$. Draw the $CS_2$ into the barrel of the syringe until the air bubble appears at the 1-µL mark. Check the nominal volume of $CS_2$; it should be about 2 µL. If it is not, repeat the process until the proper volume is present.

[9] The boldface numbers in parentheses refer to the list of references at the end of this standard.

8.1.4.4Draw 2 µL of 0.05% benzene (or other reference chemical) in $CS_2$ into the syringe and then into the barrel in accordance with 8.1.4.3. The barrel should now contain 2µ L of $CS_2$, a small bubble of air, and 2 µL of 0.05% solution of benzene in $CS_2$.

NOTE2—Two microlitres of an 0.05% v/v solution of any solute in a solvent will contain, in micrograms, the numerical equivalent of the density of the solute. For example, 2 µL of an 0.05% solution of benzene contains 0.879 µg of benzene. The practical density of benzene is 0.879 at 25°C.

8.1.4.5Inject the contents of the syringe into the gas-chromatographic column. (See 8.1.4.3-8.1.4.5 describing the solvent-flush technique referred to in this practice.) Injection by means of a GC autosampler is acceptable in most cases.

8.1.4.6Record the chromatogram of the 0.05% benzene standard in $CS_2$ using an integrator or strip chart recorder.

8.1.4.7The time between the injection of benzene onto the chromatographic column and peak maximum is the retention time (RT) for benzene.

8.1.4.8Retention times may be determined manually by observing the time required for a compound to pass through the chromatographic column using a stop watch or by measuring the distance from the starting point to peak maximum shown on the strip chart. Alternatively an electronic integrator may be used to determine RTs. Most modern gas chromatographs are equipped with electronic integrators that can accurately measure RTs' within a hundredth of a minute.

8.1.4.9For the same conditions of operation (carrier gasflow rate, column temperature, column characteristics) the RT may be considered a constant.

8.1.4.10Maintain a continuing record of RTs for the reference compound in a laboratory log. This log record should include the date, the concentration and volume of the reference compound, the operating conditions of the gas chromatograph, the carrier gas flow rate, the recorder constants, and the degree of signal attenuation. It should also include the flow rate of air and hydrogen to the detector flame.

8.1.4.11Prepare 0.05% solutions (or other concentrations) of organic solvents of interest and develop a set of RTs for them. It is preferable to run more than one analysis for each solvent.

8.1.4.12Record both the RT and the detector response. For general analytical usage these data provide a quick means of ascertaining crude concentration levels. (When precise information is necessary, fresh standards are run to prepare a standard curve.)

8.1.4.13Using the RT of the reference compound as the denominator and the RT of the solute as the numerator, calculate the relative retention time (RRT). This parameter is a constant for a given set of operating conditions. It may be used for rapid and accurate qualitative analysis when there is no reason to believe that there are peak superimpositions. A separate laboratory log for RRTs should be developed and maintained, using at least two columns of different polarities. (A list of such values is given in Table 1, for example only.) A gas chromatograph interfaced with a mass spectrometer provides the most positive means of peak identification.

8.1.4.14It is good practice to ascertain periodically the relative standard deviation of this parameter for all solutes of interest.

8.1.5The quantitative response of a GC detector may be determined by the peak height measurement or peak area integration using an electronic integrator or a data system. A detailed description of these techniques can be found in Practice E355.

8.2For any compound of interest a set of standards should be prepared in the eluent to be used for the samples (usually $CS_2$). The concentration levels of the standards should be such as to embrace the concentration of the unknown quantity.

8.2.1Prepare at least three standard solutions that bracket the expected concentration of the analyte in the sample.

8.2.2At least three runs of each standard should be done.

8.2.3When there is initial variability in the detector response of standards, so that the calculated relative standard deviation or the mean is greater than a value considered acceptable by the analyst (generally this should not exceed 5% for a good chromatographic system), a series of at least five points should be run and at least five peaks per point measured. Outliers should be eliminated by the application of statistical methods **(4).** If the variability does not comply with the performance criteria described in this paragraph, check the stability system (flow, temperature, column, etc.) before proceeding further.

8.2.4A fresh set of standards should be prepared for each analytical series. Generally standards kept in properly closed vials, sealed with TFE-fluorocarbon lined screw caps, will keep for at least a week if refrigerated **(5).** Standards kept in containers capped by glass stoppers will not keep longer than a day and should be discarded after that time.

8.2.5This practice does not recommend the use of small, standard-taper centrifuge tubes, sealed with standard taper stoppers, for preparation of either standards or samples. Carbon disulfide ($CS_2$) is highly volatile and will be lost from such vials. No attempt should be made to replace the evaporated loss by addition of $CS_2$ to a fixed volume line in such a container.

8.3Desorption efficiencies for organic compounds trapped on activated charcoal must be determined for each batch of charcoal or charcoal samplers. For purpose of reference, reported desorption efficiencies for a number of organic compounds are given in A1 of Practice D3686.

8.3.1Open a charcoal sampling tube of the same lot used for collecting the samples.

8.3.2Inject a known amount (2 to 20 µL/100 mg charcoal) of one or more solvents below the surface of and directly onto the activated charcoal, and cap the tube immediately. It is useful to chill the sampling tube during this operation, or to have chilled the capped tube and contents immediately prior to its being charged with solvent, since the heat of adsorption may be sufficient to volatilize some of the material and to cause loss. The amount injected should approximate realistically that quantity which would be found in 10 L of air containing the exposure limit designated in 29 CFR 1910.

8.3.3Tubes should be prepared for each of the following amounts: 0.5, 1.0, and 2.0 times the amount determined in 8.3.2.