Designation: D 3687 – 01

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 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.

1.3 This 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 D 3686.

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.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[2]

D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)[2]

E 355 Practice for Gas Chromatography Terms and Relationships[3]

2.2 *NIOSH Standards:*

CDC-99-74-45 Documentation of NIOSH Validation Tests[4]

Manual of Analytical Methods, 2nd Ed.[4]

2.3 *OSHA Standard:*

29 CFR 1910 General and Industrial OSHA Safety and Health Standard[5]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this practice, refer to Terminology 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

4.1 Organic 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.

4.2 Interferences 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.

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

5. Significance and Use

5.1 Promulgations by the Federal Occupational Safety and Health Administration (OSHA) in 29 CFR 1910 designate that

[1] This practice is under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres, and is the direct responsibility of Subcommittees D22.04 on Workplace Atmospheres.

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[2] *Annual Book of ASTM Standards*, Vol 11.03.

[3] *Annual Book of ASTM Standards*, Vol 03.06.

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

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

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.

5.3 A partial list of chemicals for which this practice is applicable is given in A1 of Practice D 3686, along with their OSHA Permissible Exposure Limits.

6. Interferences

6.1 Any 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.

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

6.3 General approaches which can be followed are given below:

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

6.3.2 As 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.

6.3.3 A 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.

6.4 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 Annex A1 and detailed procedures are given in Refs **(1 and 2).**[6]

7. Apparatus

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

7.2 A 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.

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

7.4 *Vials*, 5-mL serum, fitted with caps lined with TFE-fluorocarbon.

8. Calibration

8.1 *Preparation of Gas Chromatograph*:

8.1.1 Install the selected column.

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

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

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

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

8.1.4.2 Prepare 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).**

NOTE 1—**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.

8.1.4.3 Into 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.

8.1.4.4 Draw 2 µL of 0.05 % benzene (or other reference chemical)[7] 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.

NOTE 2—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.

8.1.4.5 Inject 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.

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

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

8.1.4.8 Retention times may be determined manually by observing the time required for a compound to pass through the

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

[7] 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.

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.

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

8.1.4.10 Maintain 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.

8.1.4.11 Prepare 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.

8.1.4.12 Record 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.)

8.1.4.13 Using 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.

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

8.1.5 The 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 E 355.

8.2 For 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.

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

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

8.2.3 When 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.

TABLE 1 Relative Retention Times (RRTs) for a Group of Common Organic Compounds

NOTE 1—Column: 20-ft, ⅛-in. outside diameter, stainless steel column (20 m) packed with 10 % Carbowax on 80/100 mesh Chromosorb W. Oven: Isothermal at 95°C.

(All data relative to the Retention Time of Benzene = 1.000. RRTs are a mean of three or more determinations.)

Compound	Mean RRT	Standard Deviation	Relative Standard Deviation, %
Acetone	0.676	0.014	2.1
Amyl acetate	2.156	0.047	2.18
Isoamyl acetate	2.228	0.107	4.8
Benzene	1.000		
Butanol	2.945	0.155	5.3
Isobutanol	2.146	0.935	43.6
2-Butanone (MEK)	0.930	0.085	9.14
Butyl acetate	1.739	0.026	1.5
Isobutyl acetate	1.37		
Carbon tetrachloride	0.74	0.014	1.9
Cellosolve	5.27		
Cellosolve acetate	6.51		
Chloroform	1.298	0.03	2.3
Ethanol	1.078	0.001	0.1
Ethyl acetate	0.812	0.027	3.3
Ethyl benzene	2.183	0.002	0.1
Ethylene chloride	1.408	0.33	23.4
Methyl acetate	0.639	0.015	2.4
Methanol	1.020	0.028	2.7
Methylene chloride	0.875	0.005	0.57
Methyl isobutyl ketone	1.382	0.009	0.7
Pentanol	5.11		
Perchloroethylene	1.335	0.019	1.4
Propanol	1.659	0.018	1.1
Isopropanol	1.033	0.0099	1.0
Propyl acetate	1.16	0.028	2.4
Isopropyl acetate	0.828	0.017	2.1
Styrene	4.467	0.270	6.0
Toluene	1.505	0.016	1.06
Trichloroethylene	1.162	0.03	2.6
Trimethyl benzene	3.72		
1,1,1-Trichloroethane	0.78		
m-Xylene	2.309	0.107	4.6
o-Xylene	2.964	0.058	1.96
p-Xylene	2.315	0.04	1.7

8.2.4 A 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.

8.2.5 This 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.

8.3 Desorption 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 D 3686.

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

8.3.2 Inject 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.

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

8.3.4 Let the tubes stand at room temperature for a minimum of 8 h.

8.3.5 Treat these charcoal tubes exactly as described in Section 9 of this practice, eluting the chemical with CS_2 (or other appropriate eluent) and analyzing the eluate for its contents.

8.3.6 The percentage of chemical recovered from the charcoal (calculated by dividing the quantity recovered by the quantity applied, times 100) is the desorption efficiency. The datum obtained for the analyte of concern should be corrected by using the decimal fraction of the determined desorption (elution) efficiency.

8.3.7 When the desorption efficiency of a chemical is less than 75 %, an alternative sampling and analytical method should be considered.

9. Procedure

NOTE 3—**Warning:** Perform in a properly ventilated fume hood.

9.1 Prepare a set of empty vials by placing appropriate labels on them, indicating the identification number and designating whether they will contain the front (F) of the sampler or the back-up (B) portion.

9.2 Remove the plastic caps from the sampling tubes, or score and break the tubes just above the plug.

9.3 Remove the plug of glass wool which holds the front portion of charcoal in place and transfer the charcoal to the appropriate vial and close the vial. (A crochet hook is a convenient device for removing the plugs from the samplers, or a hook can be fashioned from a fine (18 to 20-gage) steel wire or a 3-in. (76-mm) No. 20 hypodermic needle.)

9.4 Repeat the same procedure for the back-up portion.

9.5 Continue this process until all of the samples have been transferred appropriately to vials.

9.6 Fit a 1-mL hypodermic syringe with a 3 or 4-in. (76 or 100-mm) No. 20 or No. 22 hypodermic needle.

9.7 With this syringe transfer 1 mL of CS_2 to each of the vials, taking care to cap them securely after the CS_2 has been added.[8]

9.8 From time to time agitate the samples. Let the elution process continue for at least 30 min. A longer period of time is desirable **(3).** (Some methods given in the reference in 2.2.2 require up to 4 h.)

9.9 Using the solvent-flush injection technique described in 8.1.4.3-8.1.4.5, accomplish the chromatography of the samples.

NOTE 4—**Caution:** Before beginning any analytical program, place a fresh septum into the injection port of the chromatograph. As a matter of good practice, replace the septum daily or when necessary. Septum failure is the most frequent cause of inconsistent detector response for a given standard or sample.

9.10 Repeat the analysis at least three times.

9.11 The volume parameters specified in 8.1.4.3-8.1.4.5 should be maintained. Two microlitres of sample, followed by 2 µL of solvent-flush in the microsyringe, have been found practical and completely adequate for all needs by at least one compliance laboratory **(5).**

9.12 After the analytical series has been completed, the reference solvent should be run as a performance standard. (See 8.1.4.)

9.13 Data reduction, either by peak height, area, or mass measurement, may now be performed.

10. Calculation

10.1 *Determination of µg per Sample*:

10.1.1 The actual concentration, in micrograms of analyte per millilitre of sample solution, can be taken from a standard curve plotted on linear paper, where peak height (or peak area or mass) is plotted as the ordinate and concentration in micrograms per 1 mL of CS_2 as the abscissa. If the instrumental response is known to be linear (from the performance of the standards) a single concentration level may be chosen as a calculation constant, if desired.

10.1.2 From the standard curve, determine the micrograms of analyte standard equivalent to the peak area (or height) from a particular compound. When 1 mL of CS_2 has been used for desorption, no volume corrections are needed; the standard curve is based on µg/mL CS_2 and the volume of the sample injected is identical to the volume of the standard injected.

10.1.3 Ascertain whether the field blank has been contaminated. If the blank has been contaminated, the sampling series must be held suspect. (See paragraph 9.7.3 of Practice D 3686.)

10.1.4 The total microgram amount found in the sample is corrected for desorption efficiency and laboratory blank as follows:

$$\mu g, \text{corrected} = \frac{\mu g \text{ in sample} - \mu g \text{ in blank}}{\text{desorption efficiency}} \quad (1)$$

Sum quantities for front and back-up sections.

[8] 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.

10.1.5 If the back-up section contains more than 10 % of that of the front section, discard the sample as unreliable (see section 7.1.2.2 of Practice D 3686).

NOTE 5—A break-through to the back-up section of 10 % of that of the front section usually suggests that some of the contaminant in the sampled air was not retained by the charcoal, and the calculated airborne concentration results will be lower than the actual concentrations. In cases where the calculated airborne concentrations exceed the health standard, despite break-through, it is meaningful and proper to report the results as greater than the calculated value.

10.2 *Determination of Air Concentration*:

10.2.1 Correct air volume of the sample to standard temperature and pressure (see appropriate paragraph of Practice D 3686).

10.2.2 If the criteria for a proper sample have been met, calculate the concentration of solvent vapor in a cubic metre of air as follows:

$$\frac{\text{Total analyte (µg/sample)}}{\text{Sampled air volume (L/sample)}} = \frac{\mu g}{L} = \frac{mg}{m^3} \quad (2)$$

10.2.3 If it is desired to convert this value to parts per million (v/v) in air:

$$ppm = 24.47 \times \frac{mg/m^3}{\text{molecular weight of solvent}} \quad (3)$$

11. Precision and Bias

11.1 Precision and bias in this type of analytical procedure are dependent upon the precision and bias of the analytical procedure for each solvent analyte of concern, and the precision and bias of the sampling process.

11.2 When the errors involving determination of desorption efficiency, sampling, analysis, and pump calibration are combined, the state of the art indicated a relative precision of ± 15 % at the 95 % confidence level for most solvent vapors.

12. Keywords

12.1 activated charcoal tube; air monitoring; charcoal tube; organic vapors; sampling and analysis; workplace atmospheres

ANNEX

(Mandatory Information)

A1. SELECTIVE SOLVENT-STRIPPING TECHNIQUES

A1.1 Organic compounds are soluble, or react with a number of solvents in a selective manner. Advantage of these phenomena may be taken in the analysis of solvent systems in CS_2 when there is peak overlap **(1).**

A1.2 The following criteria are generally useful:

A1.2.1 Certain amines and amides are water soluble. Dimethylformamide is rapidly extracted from CS_2 with one wash of laboratory grade water **(5).**

A1.2.2 Oxygenated hydrocarbons such as esters, ketones, alcohols, and ethers are extracted by a solution consisting of 2 parts by volume of concentrated sulfuric acid and one of phosphoric acid (85 %). A volume of 0.5 to 1 mL of this solution is sufficient to effect a quantitative extraction of an oxygenated hydrocarbon compound from CS_2 **(1).**

A1.2.3 Dimethyl sulfate will extract nitrated aromatic compound from a mixture of aromatics and alkyl hydrocarbon solvents in CS_2.

NOTE A1.1—**Warning:** Dimethyl sulfate is a suspected carcinogen and is extremely corrosive.

A1.2.4 A saturated solution of sodium metabisulfite will extract selectively acetone and methyl ethyl ketone from a mixture of oxygenated and other carbon compounds in CS_2 with one wash.

A1.2.5 A 10 % solution of hydroxylamine hydrochloride will extract selectively acetone, methyl ethyl ketone, isobutyl ketone, methyl propyl ketone and methyl butyl ketone from solution in CS_2 in three separate washes.

A1.3 The usual semimicrochemical techniques and precautions should be taken when such manipulations of the CS_2 eluate are undertaken, and cognizance should be taken of the fact that CS_2 is highly volatile and flammable.

REFERENCES

(**1**) Levadie, B., and MacAskill, S. M.," Analysis of Organic Solvents Taken on Charcoal Tube Samplers by a Simplified Technique," *Analytical Chemistry*, Vol 48, No. 1, 1976, pp. 76–78.
(**2**) Levadie, B., and MacAskill, S. M., addendum to Ref **(1)**, Vol 48, No. 11, p. 1656.
(**3**) White, I. D., Taylor, D. G., Mauer, P. A., and Kupel, R. E., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in Industrial Atmosphere," *American Industrial Hygiene Association Journal*, Vol 31, 1970, p. 225.
(**4**) Dean, R. B., and Dixon, W. J., "Simplified Statistics for Small Numbers of Observations," *Analytical Chemistry*, Vol 23, 1951, pp. 636–638.
(**5**) Levadie, B., Vermont Division of Occupational Health Laboratory, Personal Communication on File at ASTM Headquarters, July 1976.