Designation: ~~D3687 – 07 (Reapproved 2012)~~ D3687 – 19

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

This standard is issued under the fixed designation D3687; 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 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 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 D6196.~~

~~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 8.4, 9.2, and in A1.2.3.~~

~~1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*~~

~~2. Referenced Documents~~

~~2.1 *ASTM Standards:*[2]~~
~~D1356 Terminology Relating to Sampling and Analysis of Atmospheres~~
~~D3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)~~
~~D6196 Practice for Choosing Sorbents, Sampling Parameters and Thermal Desorption Analytical Conditions for Monitoring Volatile Organic Chemicals in Air~~
~~E355 Practice for Gas Chromatography Terms and Relationships~~

~~2.2 *NIOSH Standards:*~~
~~CDC-99-74-45 Documentation of NIOSH Validation Tests[3]~~
~~NIOSH Manual of Analytical Methods, 4th Ed.[4]~~

~~2.3 *OSHA Standards:*~~
~~29 CFR 1910 Code of Federal Regulations, Regulations Relating to Labor, Occupational Safety and Health Administration, Department of Labor [5]~~

[1] This ~~practice~~ test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittees D22.04 on Workplace Air Quality.

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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.

[4] Available from the U.S. Department of Commerce, National Technical Information Service, ~~Port Royal~~5301 Shawnee Road, ~~Springfield,~~Alexandria, VA ~~22161.~~22312, https://www.ntis.gov.

[5] ~~NIOSH Manual of Analytical Methods (NMAM), http://www.cdc.gov/niosh/nmam (accessed 1/2007).~~Available from the Centers for Disease Control and Prevention (CDC), https://www.cdc.gov/niosh/nmam.

[6] Available from ~~Superintendent of Documents,~~ U.S. Government Printing Office, ~~Washington, DC 20402.~~Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, http://www.access.gpo.gov.

OSHA Sampling and Analytical Methods[6]
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 the terminology specified in D1356 and E355.

4. Summary of Practice

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 D3686, 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, 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

6.1 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,* 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.

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[7] OSHA Sampling and Analytical Methods, http://www.osha.gov/dts/sltc/methods/index.html (accessed 1/2007).Available from Occupational Safety and Health Administration (OSHA), 200 Constitution Ave., NW, Washington, DC 20210, https://www.osha.gov/dts/sltc/methods/index.html.

[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).Available from Health and Safety Executive (HSE), Redgrave Court, Merton Road, Bootle, Merseyside, L20 7HS, http://www.hse.gov.uk/pubns/mdhs/index.htm.

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

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 *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. Reagents

8.1 *Analytical standards,* reagent grade or better, typically 97-99+%.

8.2 *Carbon disulfide,* reagent grade or better, typically 99.9 % with low benzene content.

8.3 *Internal standard,* reagent grade or better, typically 99+%, *p*-cymene and 1-phenyl hexane are often used. Other internal standard reagents can be used providing that they not appear in air samples and that they are fully tested.

8.4 *Extraction solvent,* usually consists of 0.25 microlitres of internal standard per milliliter of carbon disulfide. Other extraction solvents can be used provided they are fully tested. (**Warning—**Carbon disulfide is toxic and extremely flammable, as are many of the organic chemicals to be analyzed. Work with these chemicals in a properly functioning laboratory hood.)

9. Calibration

9.1 In general, follow the manufacturer's manual and safety instructions to set up the gas chromatograph. Always use high purity gases and high quality gas purifiers.

9.2 Install the selected GC column and set the linear velocity of the carrier gas following manufacturer's instructions. Set the injector split ratio at 10:1 or at some other appropriate ratio. The most commonly used capillary GC carrier gas is hydrogen. Set the injector, detector, and column oven temperatures appropriate for the selected GC column. It is often useful to heat the GC column at 10-20°C below the expected maximum operating temperature of the column for about two hours before any analysis is performed. Before analyzing standards or samples, place a fresh septum into the injection port of the chromatograph. Replace the septum daily or when necessary. Septum failure is a frequent cause of inconsistent FID response and changes in chromatography. (**Warning—**Hydrogen gas is explosive and extremely flammable. It is absolutely essential that the gas chromatograph be leak free.)

9.3 Make sure that the electronic data system is properly set to collect analytical data.

9.4 Prepare separate solutions containing 1 mL of each analyte per 1 mL of extraction solvent. These solutions are used to determine GC column retention time of the analytes.

9.5 Analyze these solutions and a reagent blank (without charcoal) using an appropriate GC column and an appropriate oven temperature program to determine GC column retention times for each analyte and for the internal standard. It may be useful to create an in-house "column map" for each GC column listing retention times for each analyte determined using a standard temperature program and a standard carrier gas linear velocity.

9.6 Prepare analytical standards that bracket the expected range of sample results for each of the analytes by injection of microliter amounts of the analytes into the extraction solution. For example: if the requested analyte is toluene, the air volume sampled with a charcoal tube is 12 L, the density of toluene is 0.866 g/mL, the purity of the analytical standard is 99 %, and the exposure limit (target concentration) is 200 ppm (753 mg/m^3). Calculate the mass of toluene equivalent to the target concentration by multiplying the exposure limit by the charcoal sample air volume (753 mg/m^3 × 0.012 m^3 = 9.04 mg per sample). Prepare a standard at approximately the target concentration by diluting 10.00 µL of toluene to 1.00 mL with extraction solvent. This standard will contain 8.57 mg/mL toluene (10.00 µL × 0.866 mg/µL × 0.99 pure /1.00 mL). Prepare additional analytical standards at the reporting limit, 0.25×, 0.5×, 1.5×, and 2.0× the target concentration. Standards for other analytes can be prepared similarly to toluene using their respective exposure limits, densities, purities of analytical standards, and sample air volume (or average air volume for multiple samples). Different analytes can be prepared in the same solution if applicable. Prepare independent analytical standards with material obtained from a separate vendor to test the purity of the source material and the accuracy of the standard preparation.

9.7 Analyze the standards using the same temperature program used in 9.5. Compare the chromatograms to be certain the analytes are resolved. Generally, chromatographic conditions can be altered to separate interferences.

9.8 Use an internal standard (ISTD) calibration method for most organic compounds. An internal standard calibration function is incorporated with most electronic data systems. Calibration curves for each analyte can be constructed by plotting detector response of standards (*y* axis) against mass per standard (*x* axis). FID response is usually linear; therefore, linear regression is generally appropriate to find the equation of the best-fit line for the calibration curve. Program the data system to calculate results in terms of micrograms per sample. This is appropriate because both standards and samples are prepared in 1.00 mL of extraction

solvent. Typically, results for standards (other than for the reporting limit) calculated from the calibration curve will deviate from their theoretical amounts by not more than ±10 %. Usually, deviation for the reporting limit is no more than ±25 %. Prepare and analyze fresh standards as necessary. Analyze a fresh set of calibration standards with each sample set, or with a day's sequence of sample sets.

10. Sample Preparation

10.1 Consider potential analytical interferences that were reported when the samples were received. Make certain that the extraction efficiency (also called desorption efficiency) for all requested analyses has been determined (as described in Section 11) before extracting the samples.

10.2 Most charcoal tubes have two sections and each section is quantitively transferred to a separate labeled autosampler vial. Some charcoal tubes have three sections and each of the three sections should be similarly transferred to a separate labeled autosampler vial.

10.3 Remove the plastic cap from end of the charcoal with the back-up section(s) of the sampling tube.

10.4 Remove the plug that holds the back-up section in place and transfer the charcoal to an appropriately labeled vial and close the vial. Similarly transfer the second back-up section (if present) to a separate labeled vial and close the vial. (A small 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-gauge) steel wire or a 3-in. (76-mm) No. 20 hypodermic needle.)

10.5 Remove the plug and transfer the front section of charcoal to an appropriately labeled vial and close the vial. Check the plugs to make sure that no charcoal adheres to them. Discard the plugs and empty glass tube.

10.6 Continue this process until all of the samples have been transferred appropriately to vials. Prepare laboratory media blanks for analysis in addition to the field media blanks. Laboratory media is identical to field media except that these charcoal tubes have been set aside for use in the laboratory.

10.7 For some highly volatile compounds such as methylene chloride, it may be useful to refrigerate the vials containing the charcoal sections before addition of the extraction solvent. Loss can occur due to heat generated by addition of the extraction solvent. Use a calibrated 1.00-mL solvent dispenser or a 1.00-mL Class A volumetric pipet to transfer the extraction solvent to the sample vials. It is sometimes necessary to use a larger volume of extraction solvent to adequately extract samples. Prepare analytical standards with the same volume of extraction solvent used to extract samples.

10.8 With this dispenser or pipet, transfer 1.00 mL of extraction solvent to each of the vials, taking care to seal them securely after the solvent has been added.[10]

10.9 From time to time (at approximately 5 min intervals), agitate the samples. Let the extraction process continue for at least 30 min, however, some analytes require longer times (3). Use of a mechanical shaker or other device to agitate the samples may enhance extraction.

10.10 Ensure that the electronic data system is properly set to collect analytical data.

10.11 Analyze the samples using the same temperature program as used for the standards in Section 9. Place autosampler vials containing reagent blanks between samples and standards when "carry-over" from a previous injection is suspected.

10.12 Perform replicate injections as necessary.

11. Extraction Efficiency

11.1 Each analytical laboratory must determine its own extraction efficiencies because techniques and reagents can vary from one laboratory to another. Extraction efficiency can usually be considered constant for each laboratory, but it should be confirmed whenever the sample extraction process is significantly changed. Perform preliminary tests to determine the minimum amount of time required to completely extract the analyte from the charcoal, and also if some form of mechanical agitation or other action is necessary. Extraction efficiency should be determined separately for each analyte. Other extraction solvents and internal standards than listed in this practice can be used provided they are tested. Confirm that recovery of the internal standard from charcoal is sufficiently high (at least 95 %) by analyzing charcoal tube and reagent blanks. Select another chemical to be used as the internal standard if recovery of the internal standard is not at least 95 %. Low internal standard recovery will cause extraction efficiency results to be artificially high.

11.2 Determine extraction efficiency for four samples at each of the following levels: the reporting limit, 0.25×, 0.5×, 1×, 1.5× and 2.0× times the target concentration masses as determined in Section 9. Perform a test at 1× the target concentration with wet samplers that were prepared by spiking the charcoal with 50 µL of water a day before spiking the analyte. A 100-mg section of activated charcoal is saturated after collecting approximately 50 mg of water. The "wet test" is performed to determine if the

[11] The 1.00-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.

analyte partitions in the water phase resulting from extraction of wet samples collected in humid atmospheres. This undesirable situation can sometimes be resolved by using drying reagents such as magnesium sulfate or by using alternative extraction solvents.

11.3 Transfer a sufficient number of front sections of charcoal tubes to autosampler vials and securely seal the vials. If the back-up section contains half the amount in the front section then two back-up sections can be combined in the same vial to prepare the equivalent of a front section. Charcoal used as received from the manufacturer is knows as "dry" media.

11.4 Spike each vial with the appropriate amount of analyte and allow the vials to stand at room temperature overnight.

11.5 Extract the vials by removing the caps and adding 1.00 mL (or larger volume if necessary) of extraction solvent as in Section 10. Agitate the samples manually as in Section 10, or mechanically agitate the samples if it is determined to be necessary in preliminary tests. Allow the samples to extract for the amount of time determined in the preliminary tests.

11.6 Analyze the four extracted samples at each level plus three separate analytical standards prepared at each level. The standards should be prepared from the same solution used to spike the samples.

11.7 Calculate results for each level separately after using one of the three standards to perform a single point ISTD calibration. Average the results for the standards and divide each sample result by that average and multiply by 100 to calculate the extraction efficiency. The average of the results is the extraction efficiency at that level.

11.8 Repeat the process in 11.6 for each level performing a new single point ISTD calibration at each level.

11.9 The extraction efficiency should be high and constant at all levels. An alternative extraction solvent and technique should be considered if the extraction efficiency is less than 75 % or if it is not constant. Average the extraction efficiencies for the six levels providing they are constant (less than ±5 % difference between levels). Repeat the test for any level that appears to be an outlier and be wary of discarding results. Do not include results from the "wet test" in the average because this would bias the average.

11.10 Low or inconsistent extraction efficiencies can often be resolved by use of a different extraction solvent or by using mechanical agitation.

11.11 Determine if extracted samples are stable by reanalyzing the dry 1× times target concentration samples about 24 hours after they were extracted. Use fresh analytical standards.

11.12 Sometimes it is necessary to use low or non-constant extraction efficiencies if they are determined to be reproducible and if they are greater than 75 %. This situation should be avoided if possible.

12. Sample Results

12.1 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 they should be considered before the samples are extracted. Alternative GC columns may help resolve interferences. When necessary, the identity or purity of an analyte peak can be confirmed by GC/mass spectrometry.

12.2 Obtain analytical results in terms of micrograms per sample with the electronic data system that was programmed to produce calibration curves that were prepared using analytical data from the analytical standards prepared and analyzed as in Section 9. Dilute the samples with extraction solvent or analyze additional standards if sample results are not within the range of prepared standards.

12.3 Determine if field media blank samples were contaminated by comparison of analytical results with results from laboratory media blanks. Do not subtract laboratory media blank media results from field sample results. If the field media blank sample has been severely contaminated then it is possible that the field samples have been similarly contaminated. Do not perform blank subtractions using severely contaminated field media blanks, but report analytical results in terms of mass per sample for the field media blank along with results for the field samples and then qualify all results as "possibly contaminated". Do not calculate air concentration for these samples, but allow the person performing sampling to make such calculations.

12.4 Calculate total micrograms of an analyte per sample by adding results for the charcoal tube front section and results for the back-up section(s) together. Correct this total amount by subtracting the total amount of analyte (if any) found on the field media blank sample. If the sample back-up section contains more than 10 % of the analyte mass found on the front section, report this fact along with sample results. Divide the total blank-corrected result by the decimal equivalent of the extraction efficiency (that is, 98.5 % = 0.985) to calculate corrected µg per sample.

12.5 Calculate air concentrations as follows:

$$mg/m^3 = \frac{corrected\ \mu g\ per\ sample}{litres\ of\ air\ sampled} \quad (1)$$

$$ppm = 24.47 \times \frac{mg/m^3}{molecular\ weight\ of\ analyte} \quad (2)$$

13. Quality Assurance

13.1 Analytical laboratory accreditation (such as American Industrial Hygiene Association Laboratory Quality Assurance Programs) and laboratory proficiency testing programs can help establish and maintain high standards of laboratory performance quality.

13.2 It is beyond the scope of this practice to prescribe how a quality assurance program should be organized and function. The overall purpose of quality assurance is to ensure that reported laboratory results are sufficiently accurate and precise for their intended purpose. To this end, most laboratories have a quality assurance program to estimate combined sampling and analytical uncertainty. Sampling uncertainty, often estimated from sampling pump uncertainty, is usually assumed to be ±5 %. Analytical uncertainty is generally estimated from the results of spiked quality control samples that are analyzed along with field samples. Analytical uncertainty is then statistically combined with sampling uncertainty to estimate overall sampling and analytical uncertainty. The generally accepted limit for sampling and analytical uncertainty is no more than ±25 %.

14. Keywords

14.1 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 carbon disulfide 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 carbon disulfide with one wash of laboratory grade water.

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 carbon disulfide (**1**).

A1.2.3 Dimethyl sulfate will extract nitrated aromatic compound from a mixture of aromatics and alkyl hydrocarbon solvents in carbon disulfide. (**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 carbon disulfide with one wash.

A1.2.5 A10 % solution of hydroxylamine hydrochloride will extract selectively acetone, methyl ethyl ketone, isobutyl ketone, methyl propyl ketone and methyl butyl ketone from solution in carbon disulfide in three separate washes.

A1.3 The usual semimicrochemical techniques and precautions should be taken when such manipulations of the carbon disulfide eluate are undertaken, and it should be recognized that carbon disulfide is highly toxic, volatile, and flammable.