Designation: D3687 – 07

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 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.

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 Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds 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]

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,

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

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

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

[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).

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.

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

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.

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 $mg/m^3 \times 0.012\ m^3 = 9.04$ 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] 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.