



Standard Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology)¹

This standard is issued under the fixed designation D 5197; 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 test method covers a procedure for the determination of formaldehyde (HCHO) and other carbonyl compounds (aldehydes and ketones) in air. Other carbonyl compounds that have been validated for determination by this method include acetaldehyde, acetone, propanal (propionaldehyde), methacrolein, 2-butanone (methyl ethyl ketone), butyraldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, o-tolualdehyde, m-tolualdehyde, p-tolualdehyde, hexanal, and 2,5-dimethylbenzaldehyde. Acrolein and crotonaldehyde may be quantified with good accuracy following special precautions (see 10.2.5).

1.2 This test method involves drawing air through a cartridge containing silica gel coated with 2,4-dinitrophenylhydrazine (DNPH) reagent. Carbonyl compounds readily form stable derivatives with the DNPH reagent. The DNPH derivatives are analyzed for parent aldehydes and ketones utilizing high performance liquid chromatography (HPLC). The sampling procedure is a modification of U.S. EPA Method TO-11A (see 2.2).

1.3 This test method is based on the specific reaction of carbonyl compounds with DNPH in the presence of an acid to form stable derivatives according to the reaction shown in Fig. 1, (where: both R and R^1 are alkyl or aromatic groups (ketones), or both, or either R or R^1 is a hydrogen atom (aldehydes)). The determination of formaldehyde and other carbonyl compounds, as DNPH derivatives, is similar to that of U.S. EPA Method TO-11A in that it utilizes HPLC with UV detection as the analytical finish. The detection limits have been extended to other carbonyl compounds that can be determined as outlined in Section 10.2.4. This test method is suitable for determination of formaldehyde and other carbonyl compounds in the concentration range from approximately 10 ppb to 1 ppm (v/v).

1.4 The sampling method gives a time-weighted average (TWA) sample. It can be used for long-term (1 to 24 h) or short-term (5 to 60 min) sampling of air for formaldehyde.

¹ This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.05 on Indoor Air.

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1.5 This test method instructs the user on how to prepare sampling cartridges from commercially available chromatographic grade silica gel cartridges² by the application of acidified DNPH to each cartridge.

1.6 The sampling flow rate, as described in this test method, has been validated for sampling rates up to 1.5 L/min. This flow rate limitation is principally due to the high pressure drop (>8 kPa at 1.0 L/min) across the user prepared silica gel cartridges which have a particle size of 55 to 105 μm . These cartridges are not generally compatible with battery-powered pumps used in personal sampling equipment (for example, those used by industrial hygienists).

1.7 Alternatively, pre-coated DNPH silica gel cartridges are also commercially available and may be substituted provided they can be demonstrated to perform equivalently.³ Some of these use silica gel of a larger particle size that results in a lower pressure drop across the cartridge. These low pressure drop cartridges may be more suitable for sampling air using battery-powered personal sampling pumps.

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

1.9 *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.*

2. Referenced Documents

2.1 ASTM Standards:⁴

D 1193 Specification for Reagent Water

² The cartridge used in the development and performance evaluation of this test method was the Sep-Pak Plus Silica cartridge. The sole source of supply of the cartridge known to the committee at this time is Waters Associates, 34 Maple Street, Milford, MA 01757. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

³ Tejada, S. B., "Evaluation of Silica Gel Cartridges Coated in situ with Acidified 2,4-Dinitrophenylhydrazine for Sampling Aldehydes and Ketones in Air," *International Journal of Environmental Analytical Chemistry*, Vol 26, 1986, pp. 167–185.

⁴ 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.

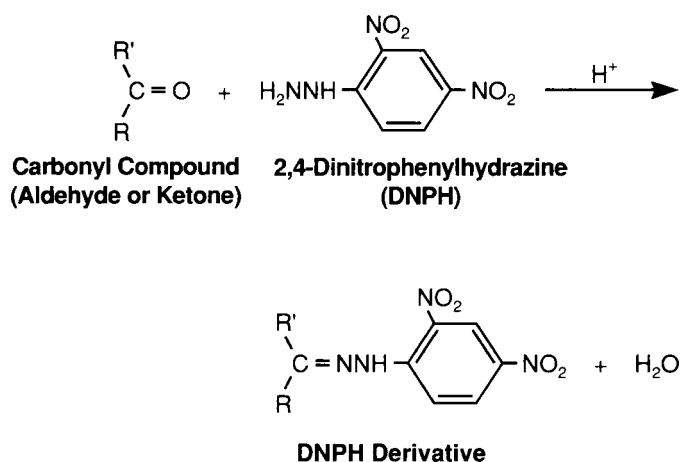


FIG. 1 Reaction of Carbonyl Compounds

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres

D 3195 Practice for Rotameter Calibration

D 3631 Test Methods for Measuring Surface Atmospheric Pressure

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

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E 682 Practice for Liquid Chromatography Terms and Relationships

2.2 EPA Methods:

Method TO-11A, EPA-625/R-96/010b, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1999⁵

EPA-600/R-98/004, Quality Assurance Handbook for Air Pollution Measurement Systems, Volume 2, Part 1—Ambient Air Quality Monitoring Program Quality System Development, U.S. Environmental Protection Agency, Research Triangle Park, NC, August 1998⁵

EPA-600/4-83-027, Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1983 (PB90-187 014/AS)⁵

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology **D 1356** and Practice **E 682**.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 All other pertinent abbreviations and symbols are defined when first cited in this test method.

4. Summary of Test Method

4.1 A known volume of indoor air is drawn through a prepacked silica gel cartridge coated with acidified DNPH, at a sampling rate of 0.5 to 1.2 L/min for an appropriate period of time. Both sampling rate and time are dependent upon carbonyl concentrations in the test atmosphere.

4.2 After sampling, the sample cartridges are individually capped and placed in individual bottles or other sealable containers. Sample identifying tags or labels are attached and the individual sample containers are then placed in a friction-top can or other suitable sealable secondary container with a pouch of charcoal for transport to the laboratory for analysis. The cartridges are placed in cold storage until analysis. Alternatively, the cartridges may be desorbed, diluted to a known volume, and refrigerated until analysis.

NOTE 1—A heat-sealable foil-lined plastic pouch of the type included with some commercial pre-coated DNPH cartridges may be used for storing a DNPH-coated cartridge after sampling, if appropriate.

4.3 The DNPH-carbonyl derivatives are determined using a gradient HPLC system, equipped with a C-18 reverse phase column and an ultraviolet (UV) absorption detector operated at 360 nm.

4.4 A blank cartridge is likewise desorbed and analyzed in accordance with 4.3.

4.5 Formaldehyde and other carbonyl compounds in the sample are identified and quantified by comparison of their retention times and peak heights or peak areas of their corresponding DNPH derivatives with those of standard solutions.

5. Significance and Use

5.1 This test method provides an analytical procedure for measuring formaldehyde and other carbonyl compounds in indoor or outdoor air.

6. Interferences

6.1 The solid sorbent sampling procedure is specific for sampling and analysis of carbonyl compounds. Interferences in this test method are certain isomeric aldehydes or ketones that may be unresolved by the HPLC system or coelute with DNPH derivatives of other aldehydes and ketones in the sample. Organic compounds that have the same retention time and significant absorbance at 360 nm as the DNPH derivatives of some carbonyl compounds will interfere. Such interferences can often be overcome by altering the separation conditions (for example, using alternative HPLC columns or mobile phase compositions).

6.2 Formaldehyde contamination of the DNPH reagent is a frequently encountered problem. The DNPH must be purified by multiple recrystallizations in UV-grade acetonitrile. Recrystallization is accomplished, at 40 to 60°C, by slow evaporation of the solvent to maximize crystal size. The purified DNPH crystals are stored under UV-grade acetonitrile until use. Impurity levels of carbonyl compounds in the DNPH are determined prior to use by HPLC and should be less than 0.15 µg per cartridge.

⁵ Available from the U.S. Environmental Protection Agency, <http://www.epa.gov/ttn/amtic/airtox.html>, or the U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Rd., Springfield, VA 22161.

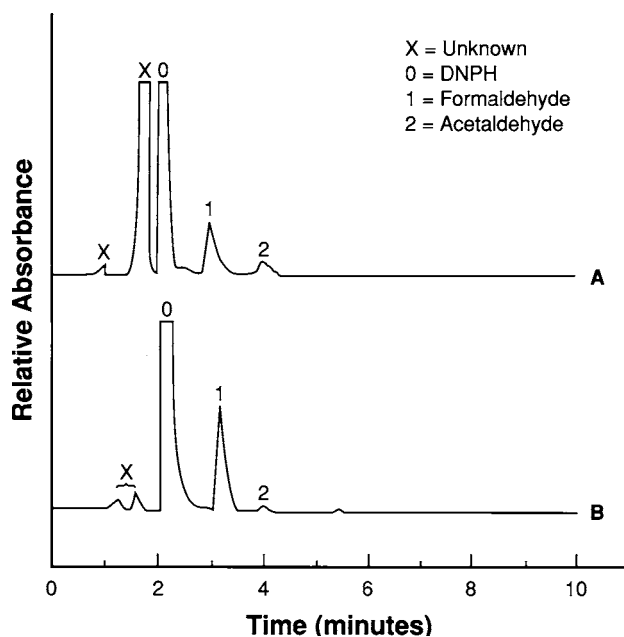


FIG. 2 Cartridge Samples of Formaldehyde in an Air Stream with (A) and without (B) Ozone

6.3 Exposure of the DNPH-coated sampling cartridges to direct sunlight may produce artifacts and should be avoided.⁶

6.4 Ozone at high concentrations (~120 ppb and above) has been shown to interfere negatively by reacting with both the DNPH and its carbonyl derivatives (hydrazones) in the cartridge.⁷ The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds and the duration of sampling. Significant (~45 %) negative interference from ozone was observed even at concentrations of formaldehyde and ozone typical of clean ambient air (2 and 40 ppbv, respectively) when air was sampled for three hours at 1 L/min. It is highly recommended that ozone be removed by means of the devices described in 6.4.2 and 6.4.4 before the sample reaches the cartridge.⁸

6.4.1 The presence of ozone in the sample stream is readily inferred from the appearance of new compounds with retention times shorter than that of the hydrazone of formaldehyde. Fig. 2 shows chromatograms of samples of a formaldehyde-spiked air stream with and without ozone.

6.4.2 The most direct solution to the ozone interference is to remove the ozone before the sample stream reaches the cartridge. This process entails constructing an ozone denuder or scrubber and placing it in front of the cartridge. The denuder is constructed of 1 m of 0.64-cm outside diameter by 0.46-cm inside diameter copper tubing, that is filled with a saturated

solution of KI in water, allowed to stand for a few minutes (~5), drained and dried with a stream of clean air or nitrogen for about 1 h. The capacity of the ozone denuder as described is about 100 ppm(v)-hour of ozone.

6.4.3 Test aldehydes (formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde, and *p*-tolualdehyde) that were dynamically spiked into an ambient sample air stream passed through the denuder with practically no losses.

6.4.4 Ozone scrubbers (cartridge filled with granular potassium iodide) are also commercially available from suppliers of pre-coated DNPH cartridges.

6.5 Special procedures must be followed if this test method is to be used for determination of acrolein or crotonaldehyde in air since the hydrazones of these compounds collected on DNPH-coated cartridge have been observed by HPLC to undergo transformation on storage to one or more compounds that have UV spectra suggesting the presence of the DNPH chromophore.^{9, 10} However, these daughter compounds can be linked with reasonable certainty to the disappearance of the corresponding parent hydrazones.

7. Apparatus

7.1 *Sampling System*, capable of accurately and precisely sampling 0.1 to 1.50 L/min.

NOTE 2—An example of a sampling system for ambient air consisting of a heated manifold/sample inlet, a denuder/cartridge assembly, a flow meter, a vacuum gage/pump, a timer and a power supply is shown in Fig. 3. In operation, ambient air is drawn through the denuder/cartridge assembly with a vacuum pump at a fixed flow rate between 0.1 to 2 Lpm.

NOTE 3—A pressure drop through the user-prepared sample cartridge of about 19 kPa at a sampling rate of 1.5 L/min has been observed. Some commercially available pre-coated cartridges may exhibit lower pressure drops, which will permit the use of battery-operated personal sampling pumps.

7.2 *HPLC System*, consisting of two or more mobile phase reservoirs; a single or a dual high-pressure pump system equipped with a mobile phase gradient programmer, an injection valve (automatic sampler with a 25- μ L or other convenient loop volume (10 μ L, 20 μ L)); a C18 reverse phase (RP) column (25-cm by 4.6-mm inside diameter); a UV detector operating at 360 nm; and a data system or strip chart recorder. A typical gradient HPLC system configuration is shown in Fig. 4.

NOTE 4—Most commercial HPLC analytical systems will be adequate for this application.

7.3 *Stopwatch*.

7.4 *Friction-Top Metal Can (for example, 4-L Paint Can) or Other Suitable Container*, with polyethylene air bubble packing or other suitable padding, to hold and cushion sample vials.

7.5 *Thermometer*, to record temperature.

7.6 *Barometer*, (Refer to Test Methods D 3631).

⁶ Grosjean, D., "Ambient Levels of Formaldehyde, Acetaldehyde, and Formic Acid in Southern California: Results of a One-Year Base-Line Study," *Environmental Science & Technology*, Vol 25, 1991, pp. 710-715.

⁷ Arnts, R. R., and Tejada, S. B., "2,4-Dinitrophenylhydrazine-Coated Silica Gel Cartridge Method for Determination of Formaldehyde in Air: Identification of an Ozone Interference," *Environmental Science & Technology*, Vol 23, 1989, pp. 1428 to 1430.

⁸ Sirju, A., and Shepson, P. B., "Laboratory and Field Evaluation of the DNPH Cartridge Technique for the Measurement of Atmospheric Carbonyl Compounds," *Environmental Science & Technology*, Vol 29, 1995, pp. 384-392.

⁹ Levin, J. O., and Lindahl, R., "Aldehyde Measuring Methods Using DNPH-coated Filters—Summary and Conclusions," *Proceedings of the Workshop "Sampling Project"*, Mol, Belgium, June 27-28, 1986.

¹⁰ Clark, W. L., Biller, W. F., Tejada, S. B., Siegl, W. O., Rosenhamer, D., Newkirk, M. S., and Crowley, R. J., "Round Robin Analysis of Alcohol and Carbonyl Synthetic Exhaust Samples," *SAE Technical Paper Series*, Paper 941944, 1994, pp. 71-87.