ASTM INTERNATIONAL

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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. This test method is most specific for formaldehyde but, with modification, at least 13 other carbonyl compounds can be detected and quantified.

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-11 (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, as a DNPH derivative, is similar to that of U.S. EPA Method TO-11 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 13. 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.

1.5 This test method instructs the user on how to prepare sampling cartridges from commercially available chromatographic grade silica gel cartridges[2] 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 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:*
D 1193 Specification for Reagent Water[4]
D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[5]
D 3195 Practice for Rotameter Calibration[5]
D 3631 Test Methods for Measuring Surface Atmospheric Pressure[5]

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[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] *Annual Book of ASTM Standards*, Vol 11.01.

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

Carbonyl Compound
(Aldehyde or Ketone)   **2,4-Dinitrophenylhydrazine**
                            (DNPH)
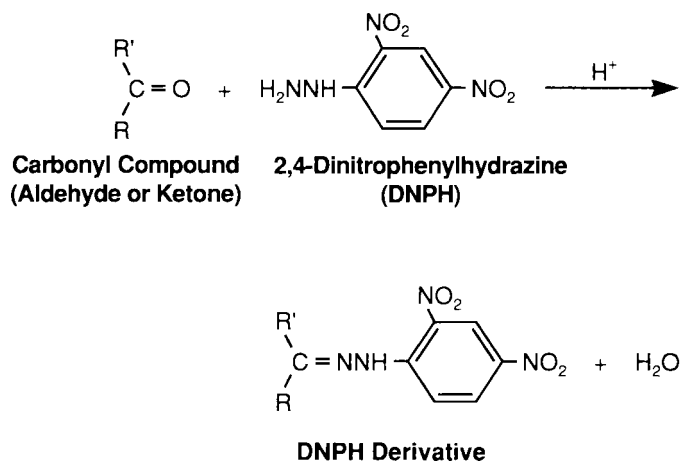
DNPH Derivative
FIG. 1 Reaction of Carbonyl Compounds

D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)[5]

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[6]

E 682 Practice for Liquid Chromatography Terms and Relationships[7]

2.2 *EPA Methods:*

Method TO-11, EPA-600/4-89-017, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1988 (PB90-116 989/AS)[8]

EPA-600/4-77-027a, Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II—Ambient Air Specific Methods, U.S. Environmental Protection Agency, Research Triangle Park, NC, July 1979[8]

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)[8]

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-formaldehyde derivative is determined using isocratic reverse phase HPLC, equipped with 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 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 formaldehyde. Interferences in this test method are certain isomeric aldehydes or ketones that may be unresolved by the HPLC system when analyzing for other aldehydes and ketones. Organic compounds that have the same retention time and significant absorbance at 360 nm as the DNPH derivative of formaldehyde 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.

6.3 Exposure of the DNPH-coated sampling cartridges to direct sunlight may produce artifacts and should be avoided.[9]

6.4 Ozone at high concentrations has been shown to interfere negatively by reacting with both the DNPH and its

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[6] *Annual Book of ASTM Standards*, Vol 14.02.

[7] *Annual Book of ASTM Standards*, Vol 14.01.

[8] Available from the U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Rd., Springfield, VA 22161.

[9] 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.

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carbonyl derivatives (hydrazones) in the cartridge.[10] The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds and the duration of sampling. Significant negative interference from ozone was observed even at concentrations of formaldehyde and ozone typical of clean ambient air (2 and 40 ppbv, respectively).[11]

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.
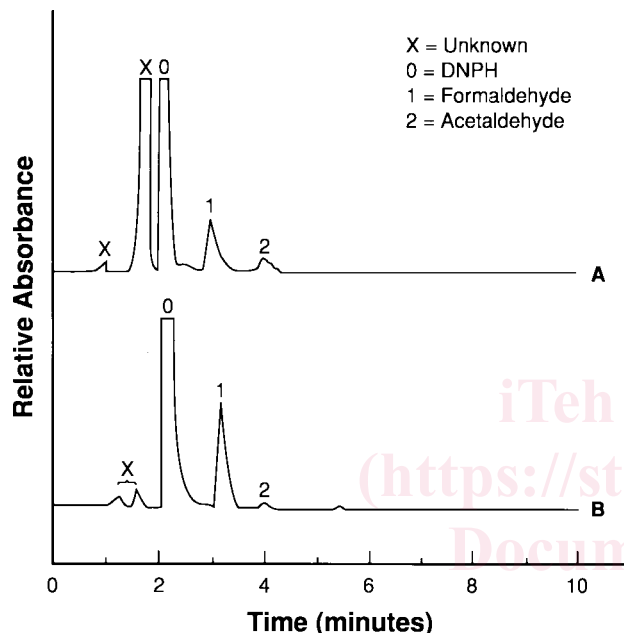

FIG. 2 Cartridge Samples of Formaldehyde in an Air Stream with (*A*) and without (*B*) Ozone

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 This test method is not intended to be used for accurate quantitation of acrolein in air. Inaccurate results for acrolein may result from the formation of multiple derivative peaks, the instability of the peak ratios, or interferences from acetone and acetaldehyde, or combination thereof.[12]

7. Apparatus

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

NOTE 2—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 a mobile phase reservoir; a high-pressure pump; an injection valve (automatic sampler with a 25-µL or other convenient loop volume (10 µL, 20 µL)); 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.

NOTE 3—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).

7.7 *Suction Filtration Apparatus*, for filtering HPLC mobile phase.

7.8 *Volumetric Flasks*, various sizes, 5 to 2000 mL.

7.9 *Pipets*, various sizes, 1 to 50 mL.

7.10 *Helium Purge Line*, for degassing HPLC mobile phase (optional).

7.11 *Erlenmeyer Flask*, 1 L, for preparing HPLC mobile phase.

7.12 *Graduated Cylinder*, 1 L, for preparing HPLC mobile phase.

7.13 *Syringes*, for HPLC injection, with capacity at least four times the loop volume (see 7.2).

7.14 *Sample Vials*.

7.15 *Melting Point Apparatus*, (optional).

7.16 *Rotameters*, (Refer to Practice D 3195), *Soap Bubble Meter*, or *Wet Test Meter*.

7.17 *Graduated Syringes*.

7.18 *Mass Flowmeters, Mass Flow Controllers, or Other Suitable Device* for metering/setting air flow rate of 0.50 to 1.20 L/min through sample cartridge.

7.19 *Positive Displacement, Repetitive Dispensing Pipets*, 0 to 10-mL range.

7.20 *Cartridge Drying Manifold*, with multiple standard male syringe connectors (see Fig. 3).

[10] 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.

[11] 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.

[12] 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.
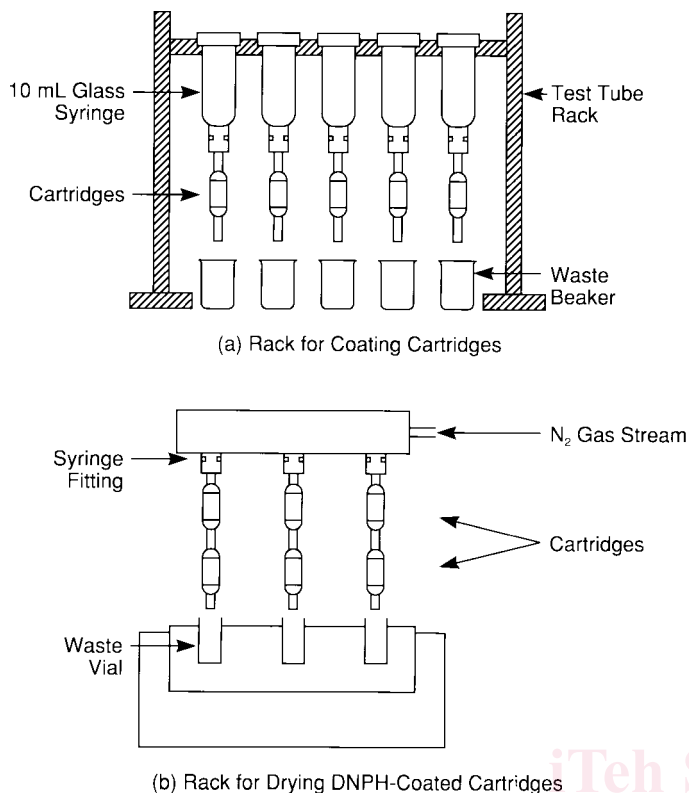
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(a) Rack for Coating Cartridges

(b) Rack for Drying DNPH-Coated Cartridges

FIG. 3 Syringe Rack for Coating and Drying Sample Cartridges

7.21 *Liquid Syringes*, (polypropylene syringes are adequate) 10 mL, used to prepare DNPH-coated cartridges.

7.22 *Syringe Rack*, made from an aluminum plate (0.16 by 36 by 53-cm) with adjustable legs on four corners. A matrix (5 by 9) of circular holes of diameter slightly larger than the diameter of the 10-mL syringes, symmetrically drilled from the center of the plate, to enable batch processing of 45 cartridges for cleaning, coating, or sample elution, or combination thereof (see Fig. 3).

7.23 *Syringe Fittings/Plugs*, to connect cartridges to the sampling system and to cap prepared cartridges.

7.24 *Hot Plates, Beakers, Flasks, Measuring and Disposable Pipets, Volumetric Flasks*, and so forth, used in the purification of DNPH.

7.25 *Borosilicate Glass Culture Tubes*, (20 by 125 mm) with polypropylene screw caps or other suitable container to transport coated cartridges.

7.26 *Heated Probe*, necessary for when the temperature of sampled air is below 15°C.

7.27 *Cartridge Sampler*, prepacked with silica gel and coated with DNPH in accordance with Section 9, or as commercially available.

7.28 *Polyethylene Gloves*, used to handle silica gel cartridges.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where

such specifications are available.[13]

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

8.3 *2,4-Dinitrophenylhydrazine (DNPH)*, recrystallized at least twice with UV-grade acetonitrile before use.

8.4 *Acetonitrile*, UV-grade.

8.5 *Perchloric Acid*, 60 %, specific gravity 1.51.

8.6 *Hydrochloric Acid*, 36.5–38 %, specific gravity 1.19.

8.7 *Formaldehyde*, 37 % solution (w/w).

8.8 *Aldehydes and Ketones*, used for preparation of DNPH derivative standards (optional).

8.9 *Ethanol or Methanol*.

8.10 *Silica Gel Solid-Phase Extraction Cartridges*.

8.11 *Nitrogen*, high-purity grade (best source).

8.12 *Charcoal*, granular (best source).

8.13 *Helium*, high-purity grade (best source).

9. Preparation of Reagents and Cartridges

9.1 *Purification of 2,4-Dinitrophenylhydrazine (DNPH)*:

NOTE 4—**Warning:** This procedure should be performed under a properly ventilated hood, as inhalation of acetonitrile can result in nose and throat irritation (brief exposure at 500 ppm) or more serious effects at higher concentrations/longer exposures (see MSDS for more details).

9.1.1 Prepare a supersaturated solution of DNPH by boiling excess DNPH in 200 mL of acetonitrile for approximately 1 h.

9.1.2 After 1 h, remove and transfer the supernatant to a covered beaker on a hot plate and allow gradual cooling to 40 to 60°C.

9.1.3 Maintain the solution at this temperature (40°C) until 95 % of solvent has evaporated.

9.1.4 Decant the solution to waste, and rinse the remaining crystals twice with three times their apparent volume of acetonitrile.

9.1.5 Transfer the crystals to another clean beaker, add 200 mL of acetonitrile, heat to boiling, and again let crystals grow slowly at 40 to 60°C until 95 % of the solvent has evaporated.

9.1.6 Repeat rinsing process as described in 9.1.4.

9.1.7 Take an aliquot of the second rinse, dilute ten times with acetonitrile, acidify with 1 mL of 3.8 *M* perchloric acid per 100 mL of DNPH solution, and analyze by HPLC, in accordance with 10.2.

NOTE 5—An acid is necessary to catalyze the reaction of the carbonyls with DNPH. Most strong inorganic acids such as hydrochloric, sulfuric, phosphoric or perchloric acids will perform satisfactorily. Perchloric acid was the preferred catalyst for impinger sampling when using acetonitrile solution of DNPH as the absorbing solution. The DNPH derivatives do not precipitate from solution as readily as when hydrochloric acid is used as the catalyst. This is an ideal situation for an HPLC analytical finish as this minimizes sample handling. For most ambient air sampling, precipitation is not a problem because the carbonyl concentration is generally in the parts per billion range.

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[13] Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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9.1.8 An acceptable impurity level is <0.025 µg/mL of formaldehyde in recrystallized DNPH reagent. If the impurity level is not acceptable for intended sampling application, repeat recrystallization.

9.1.9 Transfer the purified crystals to an all-glass reagent bottle, add 200 mL of acetonitrile, stopper, shake gently, and let stand overnight. Analyze the supernatant by HPLC in accordance with Section 11.

9.1.10 If the impurity level is not satisfactory, pipet the solution to waste, then add 25 mL of acetonitrile to the purified crystals. Repeat rinsing with 20-mL portions of acetonitrile until a satisfactorily low impurity level in the supernatant is confirmed by HPLC analysis.

9.1.11 If the impurity level is satisfactory, add another 25 mL of acetonitrile, stopper, and shake the reagent bottle, then set aside. The saturated solution above the purified crystals is the stock DNPH reagent.

9.1.12 Maintain only a minimum volume of saturated solution adequate for day-to-day operation. This will minimize waste of purified reagent, should it be necessary to rerinse the crystals to decrease the level of impurity for applications requiring more stringent purity specifications.

9.1.13 Use clean pipets when removing saturated DNPH stock solution for any analytical applications. Do not pour the stock solution from the reagent bottle.

9.2 *Preparation of DNPH-Formaldehyde Derivative*:

9.2.1 To a portion of the recrystallized DNPH add sufficient 2 N HCl to obtain an approximately saturated solution. Add to this solution formaldehyde in molar excess of the DNPH. Filter the DNPH-formaldehyde precipitate, wash it with 2 N HCl and water, and allow it to dry in air.

9.2.2 Check the purity of the DNPH-formaldehyde derivative by melting point determination or HPLC analysis. If the impurity level is not acceptable, recrystallize the derivative in ethanol. Repeat the purity check and recrystallization as necessary until an acceptable level of purity (for example, 99 %) is achieved.

9.2.3 The DNPH derivatives of formaldehyde and other carbonyl compounds suitable for use as standards are commercially available both in the form of pure crystals and as individual or mixed stock solutions in acetonitrile.

9.3 *Preparation of DNPH-Formaldehyde Standards*:

9.3.1 Prepare a standard stock solution of the DNPHformaldehyde derivative by dissolving accurately weighed amounts in acetonitrile.

9.3.2 Prepare a working calibration standard mix from the standard stock solution. The concentration of the DNPHformaldehyde derivative in the standard mix solutions should be adjusted to reflect the range of concentrations expected in real samples.

Note 6—Individual stock solutions of approximately 100 mg/L are prepared by dissolving 10 mg of the solid derivative in 100 mL of acetonitrile. The individual solution is used to prepare calibration standards containing the derivative of interest at concentrations of 0.5 to 20 µg/mL, that spans the concentration of interest.

9.3.3 Store all standard solutions in tightly capped containers in a refrigerator. They should be stable for several months.

9.4 *Preparation of DNPH-Coated Cartridges*:

Note 7—This procedure must be performed in an atmosphere with a very low aldehyde background. All glassware and plasticware must be scrupulously cleaned and rinsed with deionized water and aldehyde-free acetonitrile. Contact of reagents with laboratory air must be minimized. Polyethylene gloves must be worn when handling the cartridges.

9.4.1 *DNPH Coating Solution*:

9.4.1.1 Pipet 30 mL of saturated DNPH stock solution into a 1000-mL volumetric flask, then add 500 mL acetonitrile.

9.4.1.2 Acidify with 1.0 mL of concentrated HCl.

Note 8—The atmosphere above the acidified solution should preferably be filtered through a DNPH-coated silica gel cartridge, to minimize contamination from laboratory air. Shake the solution, then make up to volume with acetonitrile. Stopper the flask, invert, and shake several times until the solution is homogeneous. Transfer the acidified solution to a reagent bottle equipped with a 0 to 10-mL range positive displacement dispenser.

9.4.1.3 Prime the dispenser and slowly dispense 10 to 20 mL to waste.

9.4.1.4 Dispense an aliquot solution to a sample vial, and check the impurity level of the acidified solution by HPLC in accordance with 9.1.

9.4.1.5 The impurity level should be <0.025 µg/mL formaldehyde, similar to that in the DNPH stock solution.

9.4.2 *Coating of Silica Gel Cartridges*:

9.4.2.1 Open the cartridge package, connect the short end to a 10-mL syringe, and place it in the syringe rack. The syringe rack for coating and drying the sample cartridges is illustrated in Fig. 3(*a*) and 3(*b*).

9.4.2.2 Using a positive displacement, repetitive pipet, add 10 mL of acetonitrile to each of the syringes.

9.4.2.3 Let liquid drain to waste by gravity.

Note 9—Remove any air bubbles that may be trapped between the syringe and the silica cartridge by displacing them with the acetonitrile in the syringe.

9.4.2.4 Set the repetitive dispenser containing the acidified DNPH coating solution to dispense 7 mL into the cartridges.

9.4.2.5 Once the effluent flow at the outlet of the cartridge has stopped, dispense 7 mL of the coating reagent into each of the syringes.

9.4.2.6 Let the coating reagent drain by gravity through the cartridge until flow at the other end of the cartridge stops.

9.4.2.7 Wipe the excess liquid at the outlet of each of the cartridges with clean tissue paper.

9.4.2.8 Assemble a drying manifold as shown in Fig. 3(*b*). This contains a previously prepared, DNPH-coated cartridge at each of the exit ports (for example, these scrubber or "guard cartridges" can be prepared by drying a few of the newly coated cartridges in accordance with 9.4.2.9-9.4.2.15 and "sacrificing" these few to ensure the purity of the rest). The "guard cartridges" serve to remove traces of formaldehyde that may be present in the nitrogen gas supply.

9.4.2.9 Insert cartridge connectors (flared at both ends, 0.64 by 2.5-cm outside diameter TFE-fluorocarbon FEP tubing with inside diameter slightly smaller than the outside diameter of the cartridge port) onto the long end of the scrubber cartridges.

9.4.2.10 Remove the cartridges from the syringes and connect the short ends of the cartridges to the open end of the cartridge connectors already attached to the scrubber cartridges.

9.4.2.11 Pass nitrogen through each of the cartridges at about 300 to 400 mL/min.

9.4.2.12 Rinse the exterior surfaces and outlet end of the cartridges with acetonitrile using a Pasteur pipet.

9.4.2.13 After 15 min, stop the flow of nitrogen, wipe the cartridge exterior free of rinse acetonitrile, and remove the dried cartridges.

9.4.2.14 Plug both ends of the coated cartridge with standard polypropylene male syringe plugs and place the plugged cartridge in a borosilicate glass culture tube with polypropylene screw caps.

9.4.2.15 Put a serial number and a lot number label on each of the individual cartridge glass storage containers and refrigerate the prepared lot until use.

10. Procedure

10.1 *Sample Collection*:

10.1.1 Assemble the sampling system, and ensure that the pump is capable of constant flow rate throughout the sampling period. The coated cartridges can be used as direct probes and traps for sampling indoor air when the temperature is above 15°C (see 7.26). Add an ozone denuder (see 6.3) if required.

10.1.2 Before sample collection, check the system for leaks. Plug the inlet (short end) of the cartridge so no flow is indicated at the outlet end of the pump. The mass flowmeter should not indicate any air flow through the sampling apparatus.

NOTE 10—The silica gel is held in the cartridge between two fineporosity filter frits. Air flow during sampling could change as airborne particulates deposit on the front frit. The flow change could be significant when sampling particulate-laden atmospheres. For unattended or extended sampling periods, a mass flow controller or, as appropriate, a compensated personal sampling pump is highly recommended to maintain constant flow. The mass flow controller should be set at least 20 % below the maximum air flow through the cartridge.

10.1.3 Install the entire assembly (including a "dummy" sampling cartridge) and check the flow rate at a value near the desired rate. In general, flow rates of 0.5 to 1.2 L/min should be employed. The total moles of carbonyl in the volume of air sampled should not exceed that of the DNPH (2 mg or 0.01 mol/cartridge, 1 to 2 mg/cartridge for commercially available pre-coated cartridges). In general, a safe estimate of the sample size should be approximately 75 % of the DNPH loading of the cartridge (100 to 200 µg as HCHO). Generally, calibration is accomplished using a soap bubble flowmeter or calibrated wet test meter connected to the flow exit, assuming the system is sealed.

NOTE 11—Test Method D 3686 describes an appropriate calibration scheme that does not require a sealed flow system downstream of the pump.

10.1.4 The operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If the sampling period exceeds 2 h, the flow rate should be measured at intermediate points during the sampling period. Include a rotameter to allow observation of the flow rate without interruption of the sampling process. Alternatively, a sampling pump which directly measures and continuously records the flow can be used.

10.1.5 Before sampling, remove the glass culture tube from the friction-top metal can or other suitable container. Let the cartridge warm to room temperature in the glass tube before connecting it to the sample train.

NOTE 12—With a commercial pre-coated DNPH cartridge, let the cartridge warm to room temperature before connecting to the sampling train.

10.1.6 Using polyethylene gloves, remove the coated cartridge from the glass tube, remove the syringe plugs, and connect the cartridge to the sampling system with a syringe adapter fitting. Seal the glass tube for later use, and connect the cartridge to the sampling train so that the short end becomes the sample inlet.

NOTE 13—With commercial pre-coated cartridges, follow the manufacturer's instructions. Some cartridges may be constructed from sealed-glass tubes. For these, break the ends of the cartridge with a tube breaker. Connect the cartridge by inserting the end with the smaller quantity of sorbent to the sampling train so that the larger quantity of sorbent is at the air inlet end. Use care when handling the broken ends.

10.1.7 Turn the sampler on and adjust the flow to the desired rate. A typical flow rate through one cartridge is 1.0 and 0.8 L/min for two cartridges in tandem.

10.1.8 Operate the sampler for the desired period, with periodic recording of the sampling variables.

10.1.9 If the ambient air temperature during sampling is below 15°C, a heated inlet probe is recommended. No pronounced differences have been observed for sampling under various weather conditions—cold, wet, and dry winter months and hot and humid summer months. However, low results may be obtained for formaldehyde and other aldehydes in very dry air (<10 % RH).[14]

10.1.10 At the end of the sampling period, stop the flow. The flow rate must be checked just before stopping the flow. If the flow rates at the beginning and end of the sampling period differ by more than 15 %, the sample should be marked as suspect.

10.1.11 Immediately after sampling, remove the cartridge (using polyethylene gloves) from the sampling system, cap with the original end plugs, and place it back in the original labeled glass culture tube. Cap the culture tube, seal it with TFE-fluorocarbon tape, and place it in a friction-top can containing 2 to 5 cm of granular charcoal or styrofoam box with appropriate padding. If appropriate, a heat-sealable foil-lined plastic pouch may be used instead of the glass culture tube for storing the exposed cartridge. Refrigerate the culture tube or pouch containing the exposed sample cartridge until analysis. The refrigeration period prior to analysis should not exceed 30 days.

NOTE 14—If samples are to be shipped to a central laboratory for analysis, the duration of the non-refrigerated period should be kept to a minimum, preferably less than two days.

10.1.12 The average sample flow rate must be calculated from the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \ldots + Q_n}{n} \tag{1}$$

[14] Grosjean, E. and Grosjean, D., Carbonyl Collection Efficiency of the DNPH-Coated C18 Cartridge in Dry and in Humid Air," *Environmental Science & Technology*, Vol 30, 1996, pp. 859–863.