Designation: D5197 – 16

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 D5197; 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 presents a procedure for the determination of formaldehyde (HCHO) and other carbonyl compounds (aldehydes and ketones) in air. Other carbonyl compounds that have been successfully quantified by this method include acetaldehyde, acetone, propanal (propionaldehyde), 2-butanone (methyl ethyl ketone), butyraldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, o-tolualdehyde, m-tolualdehyde, p-tolualdehyde, hexanal, and 2,5-dimethylbenzaldehyde.

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 either, or both 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 applicability of this test method is extended beyond the stated applicability of TO-11A to include other carbonyl compounds that can be determined as stated in 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). Lower concentrations may be determined with careful control of contamination, appropriate selection of flow rate and sampling duration.

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. Shorter sampling times or low flow rates will result in higher detection limits and may result in greater variation in co-located sampler results. Tests should be performed over a duration and a flow rate that allows the data quality objective of the project to be achieved. Sample times for other carbonyls, such as acetaldehyde, may be limited to short term (**1**).[2] The data provides total concentrations of carbonyl compounds from which time weighted average concentrations can be calculated.

1.5 This test method instructs the user on how to prepare sampling cartridges from commercially available chromatographic grade silica gel cartridges[3] 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 for formaldehyde. 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 (**2**). 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 standard. No other units of measurement are included in this standard.

1.9 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the*

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

[3] The cartridge used in the development and performance evaluation of this test method was the Sep-Pak Plus Silica cartridge. Other manufactures make similar products.

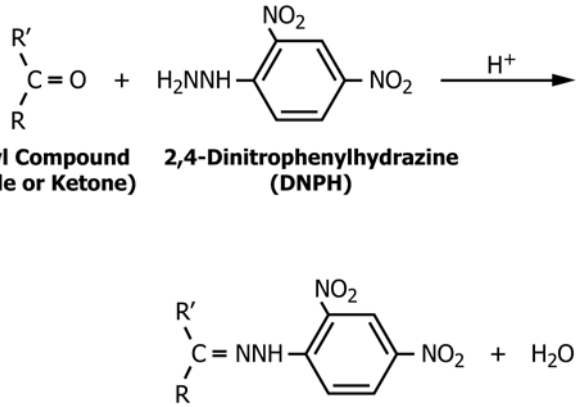

FIG. 1 Reaction of Carbonyl Compounds

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]

D1193 Specification for Reagent Water

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D3195 Practice for Rotameter Calibration

D3631 Test Methods for Measuring Surface Atmospheric Pressure

D3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)

E682 Practice for Liquid Chromatography Terms and Relationships

2.2 *EPA Methods:*[5]

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 1999

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D1356 and Practice E682.

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 air is drawn through a prepacked silica gel cartridge coated with acidified DNPH, at a sampling rate of 0.5 to 1.5 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. Charcoal may only be useful if sampling chemicals other than formaldehyde and acetaldehyde. The cartridges are stored at <4°C until analysis. Alternatively, the cartridges may be desorbed, diluted to a known volume, and refrigerated at <4°C until analysis.

NOTE 1—A re-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 C18 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, workplace, outdoor air or for emission testing.

6. Interferences

6.1 There are a number of known interferences and factors potentially impacting sampling and quantification of carbonyl compounds using DNPH impregnated cartridges. These interferences and other factors are summarized in Table 1.

6.2 Ozone (~50 ppbv and above) has been shown to interfere negatively by reacting with both the DNPH and its carbonyl derivatives (hydrazones) in the cartridge (**4-7**). The extent of interference depends on the temporal variations of both 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 ppbv 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 6.2.2 and 6.2.4 before the sample reaches the cartridge (**4**).

6.2.1 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.

[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.

[5] Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

TABLE 1 Interferences and Other Factors Impacting Sampling and Analysis of Carbonyls Using DNPH Impregnated Cartridges (Adapted From et al. (3))

Section	Agent or Parameter	Influenced Species	Interferences	Remedy
6.2	Ozone	All Carbonyls	Positive and negative artifacts on carbonyl derivatives; baseline and retention time shifts	Sample with upstream ozone scrubber
6.3	Nitrogen Dioxide and Nitric Oxide	Formaldehyde and Acetaldehyde	Nitrogen dioxide and nitric oxide react with DNPH forming side products which may co-elute with formaldehyde and acetaldehyde derivative peaks	Better chromatographic separation
6.4	Relative Humidity (RH)	Ketones, Carbonyls at extremes	Poor ketone collection efficiencies at nominal sampling flow rates, leading to large underestimation of ketone concentrations; relative humidity below 10 % and above 75 % can result in low carbonyl collection efficiencies	Use alternative derivation agent for ketones
6.5	Polymerization	Unsaturated Carbonyls	Derivatives undergo polymerization	Use alternate quantification method for acrolein, methacrolein, and crotonaldehyde
6.6	DNPH Reagent Contamination	Formaldehyde and Other Carbonyls	Formaldehyde and other carbonyls present in DNPH reagent	Purify DNPH by recrystallization
6.7	Co-elution	All Carbonyls	Isomeric aldehydes or ketones may co-elute with DNPH derivatives of carbonyls in sample	Better chromatographic separation
6.8	Sunlight	All Carbonyls	Artifacts may be created	Store cartridges in opaque containers. Shield outdoor samples
6.9	Temperature	All Carbonyls	High temperatures can cause disassociation of carbonyl-DNPH derivatives with loss of the carbonyl	Store cartridges at <4°C
6.10	Particles	All Carbonyls	Particulates collected on the surface of the cartridge packing may cause cartridge clogging and baseline disturbance	Filter any acetonitrile extract with visible particles prior to analysis to prevent clogging of HPLC
6.11	Sample Duration	Acetaldehyde	Low collection efficiencies can occur at sample durations greater than two hours	Only report acetaldehyde concentrations for sampling times less than two hours

6.2.2 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. Typically, denuders and scrubbers utilize potassium iodide (KI). Manganese oxide scrubbers have also been used (**8**). At least some air moisture (relative humidity >10 % at 25°C) is required for effective ozone removal when using KI (**9**). A denuder may be constructed by filling a 1-m section of 0.64-cm outside diameter by 0.46-cm inside diameter copper tubing with a saturated solution of KI in water, allowing the solution to stand for a few minutes (~5), draining the solution and drying the tubing with a stream of clean air or nitrogen for about 1 h. The capacity of the ozone denuder as described is about 100 ppmv-hour of ozone. Test aldehydes (formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde, and p-tolualdehyde) that were dynamically spiked into an ambient sample air stream passed through the denuder. Scrubbers may be constructed by impregnating 37-mm cellulose fiber filters with 0.6M KI solution.

6.2.3 Ozone scrubbers (cartridges filled with granular KI) are also commercially available from suppliers of pre-coated DNPH cartridges. However, in high humidity environments these scrubbers can become saturated with water, reducing the sample flow through the cartridge. To overcome the moisture issue in high humidity environments, the ozone scrubbers

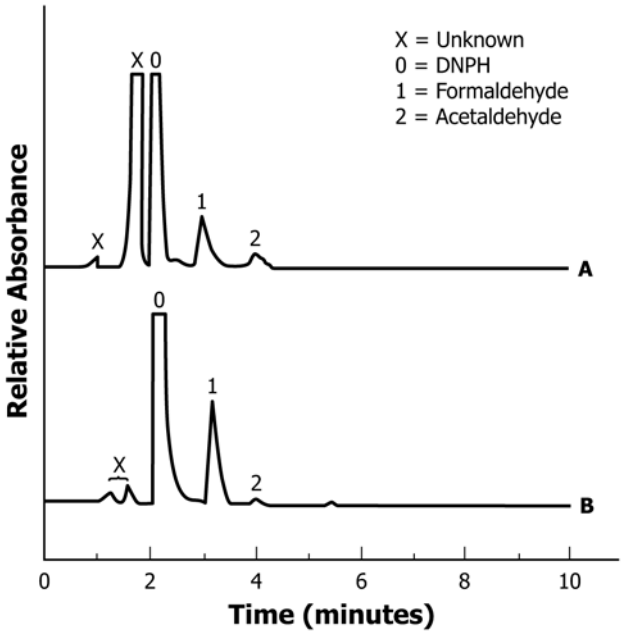

FIG. 2 Cartridge Samples of Formaldehyde in an Air Stream with (*A*) and without (*B*) Ozone

should be maintained at a temperature of 90°C and consistent sample flow should be verified at the end of the sampling period.

6.2.4 Using KI denuders and scrubbers under high humidity conditions can cause interferences. Moist KI can trap carbonyls prior to the DNPH cartridge. Wet KI can form iodine and the hydroxyl radical which can migrate to the DNPH cartridge and degrade the DNPH and the carbonyl-DNP-hydrazone derivatives (**6**). This reaction can be avoided by keeping the ozone scrubbers at a temperature of 90°C. Alternatively, the hydroxyl radical can be neutralized by placing an acid permeated filter between the ozone denuder/scrubber and the DNPH cartridge, thus, increasing the collection efficiency in the presence of ozone and elevated relative humidity (**10**).

6.3 Nitrogen dioxide and nitric oxide can react with DNPH forming side products which may co-elute or overlap with the formaldehyde and acetaldehyde derivative peaks (**11, 12**). Better chromatographic separation can be achieved by altering the separation conditions, for example, by using alternative HPLC columns or mobile phase compositions.

6.4 Low collection efficiencies may occur for formaldehyde and other carbonyls in both very dry air (<10 % RH) (**13**) and very moist air (>75% RH) (**10**). Ketones are less reactive than aldehydes and are more readily impacted by the sampling conditions. Collection efficiencies of acetone and 2-butanone in atmospheres with relative humidity above 50 % can be as low as 20 % (**3**). Air temperature also may impact collection efficiency. If the ambient air temperature during sampling is below 15°C, a heated inlet probe is recommended.

6.5 Acrolein, methacrolein and crotonaldehyde should not be quantified using the analytical procedure described in 10.2 due to the formation of multiple derivative peaks (**14-16**). In an acidic environment in the presence of excess DNPH, the DNPH derivatives of acrolein, methacrolein and crotonaldehyde have been shown to partially transform into several compounds that have UV spectra suggesting the presence of the DNPH chromophore. The sequential conversion of the carbonyl-DNP-hydrazone (monomer) to carbonyl-DNP-hydrazone-DNPH (dimer), and finally 2(carbonyl-DNP-hydrazone)-DNPH (trimer) has been demonstrated (**14**). The chromatic response areas of the dimers and trimers have been summed in the past to estimate the concentration of acrolein. However, this process does not account for the variations in carbonyl in the trimer, the varying response factors for the dimer and trimer, and the potential for co-elution of other hydrazine products (for example, from crotonaldehyde) that complicate quantification. Hence, the summing of the dimer and trimers to estimate acrolein concentration is not a reliable quantitative procedure (**15**).

6.6 Contamination of DNPH reagent with formaldehyde and other carbonyls such as acetone 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 and in commercial coated DNPH cartridges are determined prior to use by HPLC and, at a minimum, should be less than 0.15 µg per cartridge. Acceptable blanks are dictated by the application, that is, the compounds that are being measured, their expected concentrations and the desired detection level.

6.7 The solid sorbent sampling procedure is for the sampling and analysis of specific carbonyl compounds that are identified based on their chromatographic retention times. Certain isomeric aldehydes or ketones may be chromatographically unresolved by the HPLC system and may co-elute with DNPH derivatives of the target carbonyl compounds in the sample. Organic compounds that are retained by the sample and that have UV absorbance at 360 nm may also cause interferences. Such interferences can often be identified and overcome by altering the chromatographic separation conditions.

6.8 Exposure of the DNPH-coated sampling cartridges to direct sunlight may produce artifacts and should be avoided by storing cartridges in opaque containers such as foil-lined pouches (**17**). When sampling outdoors, samplers should be shielded from direct exposure to sunlight.

6.9 High temperatures can cause disassociation of carbonyl-DNPH derivatives with loss of the carbonyl as the carbonyl-DNPH reaction is an equilibrium reaction. Formaldehyde-DNPH derivatives are particularly sensitive to temperature. Cartridges should be chilled at <4°C prior to sampling, as soon as possible after sampling, and extracts should also be stored at <4°C prior to analysis (**18**).

6.10 Particulates collected on the surface of the cartridge packing may cause cartridge clogging and create back-pressure during analysis. If these particulates are insoluble in acetonitrile (for example: α-pinene aerosol) they may create significant baseline disturbance during analysis. To prevent clogging

of HPLC components, remove insoluble acetonitrile particles by filtration prior to analysis (**19**).

6.11 Sample collection efficiency was shown to be between 1–62 % for 24-hour sampling of acetaldehyde. Collection efficiencies of 100 % were reported for samples of less than 2 hours (**1**). It is recommended that reporting of acetaldehyde concentrations should be from samples of 2 hours or less.

7. Apparatus

7.1 *Sampling System,* capable of accurately and precisely sampling 0.5 to 1.50 L/min to the nearest 0.01 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 0.5 to 1.5 L/min.

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,* an example HPLC system used for this analysis consists 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 fixed-volume sampling loop (for example, 10 L, 20 L)); a C18 reverse phase (RP) column (for example, 25-cm by 4.6-mm inside diameter); a UV detector operating at 360 nm; and a data system. 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 D3631).

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

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) (optional).

7.14 *Sample Vials.*

7.15 *Melting Point Apparatus,* (optional).

7.16 *Rotameters* (refer to Practice D3195), *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 0.5 to 1.5 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. 5).

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 or other suitable material (0.16 by 36 by 53-cm) with adjustable legs on four corners. A matrix (5 by 9) of circular holes of diameter

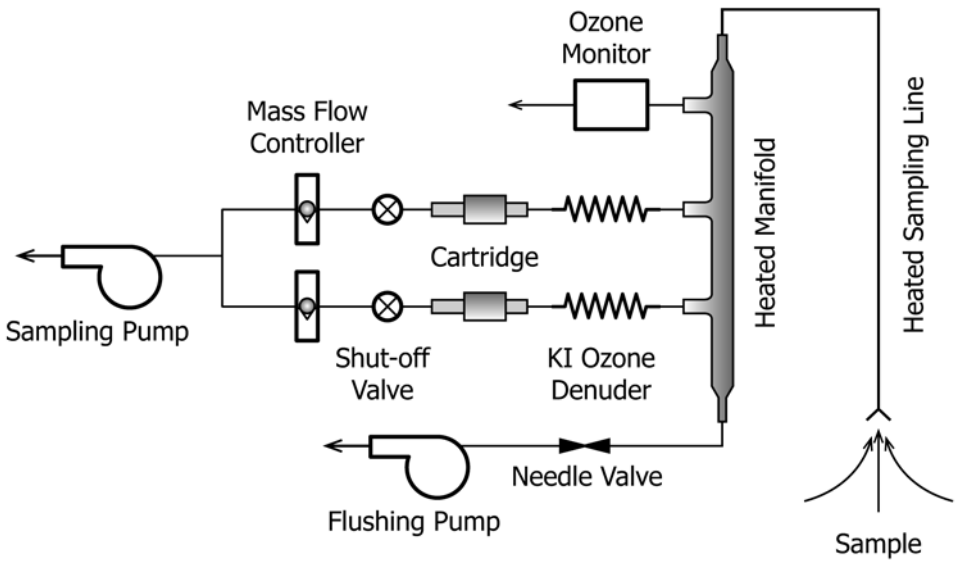

FIG. 3 A Dual-Cartridge Sampling System with Heated Manifold for Carbonyl Compounds in Ambient Air

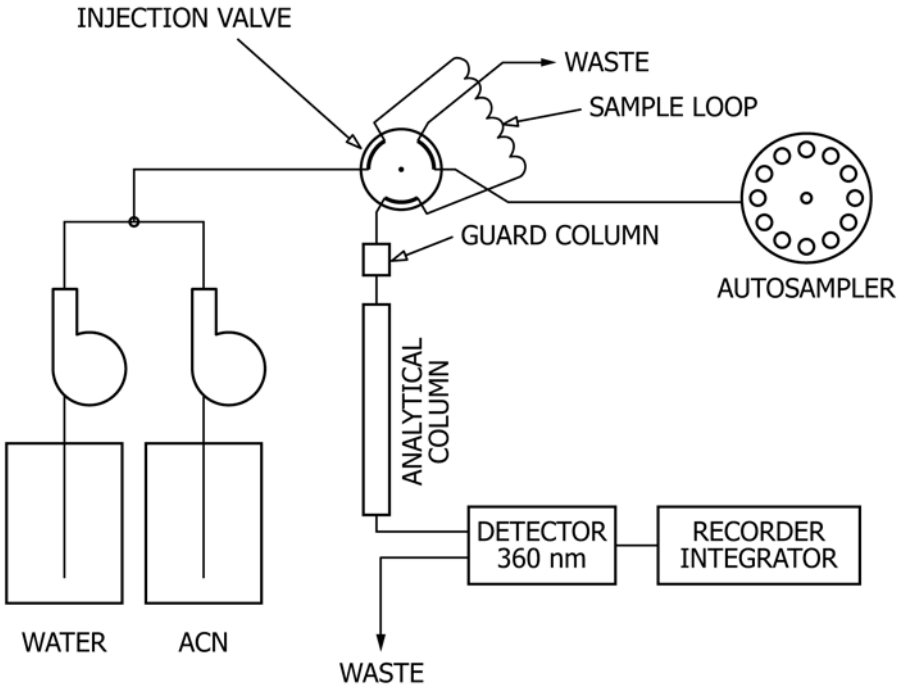

FIG. 4 A Typical Gradient HPLC System Configuration for Determination of Carbonyl Compounds Collected on DNPH Cartridges

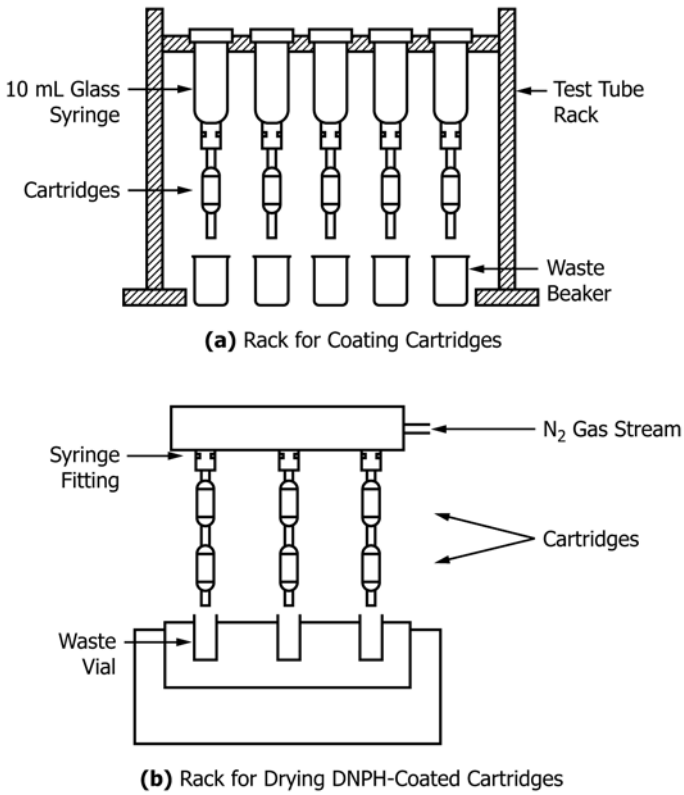

FIG. 5 Syringe Rack for Coating and Drying Sample Cartridges

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. 5).

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.[6]

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 D1193.

[6] 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.

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

NOTE 5—This section is intended for users who desire to prepare their own sampling cartridges by coating prepacked silica gel cartridges with acidified DNPH. Users who intend to purchase DNPH-coated cartridges and DNPH derivative standards from commercial sources may skip any or all portions of this section. Users are cautioned to check that the carbonyl background of the purchased cartridges meet the quality control and accuracy required for their intended applications.

9.1 *Purification of 2,4-Dinitrophenylhydrazine (DNPH):* **Warning—**This procedure should be performed under a properly ventilated hood and behind a protective shield, as there is an explosion potential from perchloric acid and 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 the Safety Data Sheet (SDS) 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 10.2.4.

NOTE 6—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.

9.1.8 An acceptable impurity level in 9.1.7 is <0.025 µg/mL of formaldehyde DNPH reagent derivative. 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 as in 9.1.7 by HPLC in accordance with 10.2.3.

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 (166°C) 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 DNPH formaldehyde 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 DNPH formaldehyde derivative in the standard mix solutions should be adjusted to reflect the range of concentrations expected in real samples.

NOTE 7—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 at <4°C in a refrigerator. They should be stable for several months.

9.4 *Preparation of DNPH-Coated Cartridges:*

NOTE 8—This procedure must be performed in an atmosphere with a very low aldehyde background. All glassware and plastic ware 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 9—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 as the DNPH derivative, 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. 5(*a*) and Fig. 5(*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 10—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. 5(*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 air when the temperature is above 15°C (see 7.26). Add an ozone denuder or scrubber (see 6.2) 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 11—The silica gel is held in the cartridge between two fine porosity 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 its maximum airflow rate.

10.1.3 Install the entire assembly, an example is shown in Fig. 3, (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 1.5 L/min should be employed. The total moles of carbonyl in the volume of air sampled should not exceed that of the DNPH (0.005 to 0.01 mmol/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 g as HCHO). Generally, flow calibration is accomplished using a soap bubble flowmeter or calibrated wet test meter connected to the flow exit, assuming the system is sealed. If the system is not sealed a sacrificial cartridge can be temporarily replace the sample cartridge allowing the flow calibration to be measured at the inlet to the sacrificial cartridge.

NOTE 12—Test Method D3686 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. 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. 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 is 1.0 L/min through one cartridge and 0.8 L/min for two cartridges in series.

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 to minimize the liquid water interferences in the DNPH cartridge and to increase reaction rates.

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. If appropriate, a re-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 at < 4 °C until analysis. The refrigeration period prior to analysis should not exceed 14 days.

NOTE 13—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 is calculated from the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \ldots + Q_n}{n} \quad (1)$$

where:

Q_A = average flow rate, mL/min,
$Q_1, Q_2, \ldots Q_n$ = flow rates determined at beginning, end, and intermediate points during sampling, and
n = number of points averaged.

10.1.13 The total flow volume is then calculated using the following equation:

$$V_m = \frac{(T_2 - T_1) \times Q_A}{1000} \quad (2)$$

where:

V_m = total volume, L, sampled at the measured temperature and pressure,
T_2 = stop time, min,
T_1 = start time, min,
$T_2 - T_1$ = total sampling time, min, and
Q_A = average flow rate, mL/min.

10.1.14 The total volume (V_m) at standard conditions, 25°C and 101.3 kPa, is calculated from the following equation:

$$V_s = V_m \times \frac{P_A}{101.3} \times \frac{298}{273 + t_A} \quad (3)$$

where:

V_s = total sample volume, L, at 25°C and 101.3-kPa pressure,
V_m = total sample volume, L, at measured temperature and pressure,
P_A = average pressure, kPa, and
t_A = average temperature, °C.

10.2 *Sample Analysis:*

10.2.1 *Sample Storage*—The samples are returned to the laboratory in an insulated box with appropriate padding and stored in a refrigerator at <4°C until analysis. Alternatively, the samples may also be stored alone in a refrigerator at <4°C in their individual glass containers or pouches. The time between sampling and analysis should not exceed 14 days.

10.2.2 *Sample Desorption:*

NOTE 14—Sample desorption can be automated provided quantitative recovery during extraction is demonstrated, for example, by performance testing.

10.2.2.1 Connect the sample cartridge (inlet or short end during sampling) to a clean syringe.

NOTE 15—The liquid flow during desorption should be in the same direction as the air flow during sampling to prevent insoluble particulates from getting into the eluate. Reverse desorption may be performed if the eluate is filtered prior to HPLC analysis. A filtered blank extract must be analyzed to confirm that no contamination is being introduced by the LC filter.

10.2.2.2 Place the cartridge/syringe in the syringe rack.

10.2.2.3 Extract the DNPH derivatives of the carbonyls and the unreacted DNPH from the cartridge (gravity feed) by passing 6 mL of acetonitrile from the syringe through the cartridge to a graduated test tube or to a 5-mL volumetric flask.

NOTE 16—A dry cartridge typically has an acetonitrile holdup volume slightly greater than 1 mL. The eluate flow may stop before the acetonitrile in the syringe is completely drained into the cartridge because of air trapped between the cartridge filter and the syringe adapter tip. If this

happens, displace the trapped air with the acetonitrile in the syringe using a long-tip disposable Pasteur pipet.

10.2.2.4 Dilute to the 5-mL mark with acetonitrile. Label the flask with sample identification. Pipet two aliquots into sample vials having TFE-fluorocarbon-lined septa. Analyze the first aliquot for the carbonyl derivatives by HPLC. Store the second aliquot in the refrigerator until the results of the analysis of the first aliquot are complete and validated. The second aliquot can be used for confirmatory analysis, if necessary.

NOTE 17—With commercial pre-coated sampling cartridges, follow the manufacturer's instructions. For glass-sealed DNPH sampling tubes that contain two sorbent beds, uncap the inlet end of the tube, then carefully remove the spring (or other retaining device) and plug of glass wool holding the sorbent layer in place. Empty the sorbent into a clean 4-mL glass vial with TFE-fluorocarbon-lined septum or cap. Mark this as the *primary* sampling section. Carefully remove the next plug of glass wool and empty the remaining sorbent into another 4-mL vial. Mark this as the *back-up* sampling section. Carefully pipette 3 mL acetonitrile into each vial, cap the vials, and let stand for 30 min with occasional agitation.

10.2.3 *HPLC Analysis:*

10.2.3.1 An example HPLC system configuration is shown in Fig. 4. This section lists suggested procedures for operating the HPLC. Operate the HPLC and the analytical column in accordance with the manufacturers' instructions. Calibrate the HPLC as described in 10.2.4.

10.2.3.2 Operate the HPLC in the isocratic mode if the analytes of interest are limited to the derivatives formaldehyde, acetaldehyde, acetone and propionaldehyde; otherwise, operate the system in the gradient mode. For isocratic separation of formaldehyde, the parameters in Table 2 can be used.

Before each analysis, check the detector baseline to ensure stable conditions.

10.2.3.3 The operating parameters found adequate for the separation of the 17 carbonyls within the scope of this test method are shown in Table 3.

10.2.3.4 The gradient program in 10.2.3.3 adequately separates DNPH derivatives of formaldehyde and acetaldehyde; acrolein and its principal transformation product from the derivatives of acetone and propionaldehyde; the derivative of crotonaldehyde from its principal transformation product; the derivative of methacrolein from the derivatives of 2-butanone and butyraldehyde; the derivatives of isovaleraldehyde, valeraldehyde, hexanal, 2,5-dimethylbenzaldehyde; and the isomers of the tolualdehyde derivatives. Due to transformations (6.5) acrolein, methacrolein and crotonaldehyde should not be quantified with this method.

TABLE 2 Parameters for Isocratic Separation of Formaldehyde

Column	C18 (4.6-mm inside diameter by 25 cm, or equivalent)
Mobile Phase	60 % acetonitrile/40 % water, isocratic
Detector	ultraviolet, operating at 360 nm
Flow Rate	1.0 mL/min
Retention Time	7 min for formaldehyde with one C18 column. Thirteen min for formaldehyde with two C18 columns
Sample Injection Volume	25 µL

TABLE 3 Operating Parameters

Column	C18 (4.6-mm inside diameter by 25 cm, or equivalent)		
Column Temperature	25°C		
Mobile Phase	Acetonitrile, Water		
	Linear Gradient Program		
	Time (minutes)	% Acetonitrile	% Water
	0	60	40
	36	75	25
	56	100	0
	57	60	40
	72	60	40
Detector	ultraviolet, operating at 360 nm		
Flow Rate	1.0 mL/min		
Retention Time	~10 min for formaldehyde with two C18 columns in series.		
Sample Injection Volume	25 µL		

10.2.3.5 Chromatographic parameters that have been used in round robin analysis of the carbonyl derivatives participated in by several laboratories have been described in the literature (**20**).

NOTE 18—Column manufacturers as well as suppliers of pre-coated DNPH cartridges usually recommend optimal conditions for the separation of DNPH derivatives in reverse-phase columns. These recommendations may eliminate the need for dual columns without compromising resolution of the other carbonyl compounds.

10.2.3.6 Mobile phase solvents should be HPLC-UV grade and should be filtered through a 0.2-µm TFE-fluorocarbon membrane filter in an all-glass and TFE-fluorocarbon suction filtration apparatus. Degas the filtered mobile phase by purging with helium for 10 to 15 min (100 mL/min) or by heating to 60°C for 5 to 10 min in an Erlenmeyer flask covered with a watchglass. An effective degassing alternative is to partially immerse the liquid reservoir in an ultrasonic bath and apply vacuum above the liquid surface.

10.2.3.7 In-line vacuum degassers placed before the HPLC pump are commercially available. These operate by passing the mobile phase through a solvent-inert, semi-permeable membrane coil that allows air to pass through and not the solvent. Air is removed by applying vacuum above the membrane.

10.2.3.8 For HPLC systems not equipped with an inline degasser, a constant back pressure restrictor (350 kPa) or short length (15 to 30 cm) of 0.25-mm inside diameter TFE-fluorocarbon tubing should be placed after the detector to eliminate further mobile phase outgassing.

10.2.3.9 Place the mobile phase(s) in the HPLC solvent reservoir(s) and set the pump at a flow rate of 1.0 mL/min. For isocratic separation, allow it to pump for 20 to 30 min to condition the column before the first analysis. For gradient separation, let the pump run through at least a full gradient

program cycle to condition the column. The detector should be on and warmed for at least 30 minutes before the column conditioning begins.

10.2.3.10 Using an autosampler, inject the sample into

10.2.3.11 After elution of the last DNPH-carbonyl derivative (see Fig. 6), terminate data acquisition and calculate the component concentrations as described in Section 11. A cleanup program may be run to remove contaminants.

10.2.3.12 The carbonyl compounds in the sample are identified and quantified by comparing their retention times and area counts with those of standard DNPH derivatives. Formaldehyde, acetaldehyde, acetone, propionaldehyde, benzaldehyde. isovaleraldehyde, valeraldehyde, and o-, m-, p-tolualdehydes, hexanal and 2,5-dimethylbenzaldehyde can be identified with a high degree of confidence. The identification of butyraldehyde is less certain, because it co-elutes with isobutyraldehyde and not sufficiently resolved from 2-butanone (methyl ethyl ketone) under the stated chromatographic conditions. Fig. 6 illustrates a typical chromatogram obtained with the gradient HPLC system.

NOTE 19—After several cartridge analyses, buildup on the column (if indicated, as by increasing pressure from run to run at a given flow and solvent composition) may be removed by flushing with several column volumes of 100 % acetonitrile or other appropriate solvent.

10.2.3.13 The concentrations of individual carbonyl compounds are determined as outlined in Section 11.

10.2.3.14 After a stable baseline is achieved, the system can be used for another sample injection as previously described.

10.2.3.15 If the concentration of analyte exceeds the linear range of the instrument, the sample should be diluted with mobile phase, or a smaller volume can be injected into the HPLC.

10.2.3.16 If the retention time found in earlier runs is not duplicated (±10 %), the acetonitrile/water ratio may be increased or decreased to obtain the correct elution time. If the elution time is too long, increase the ratio; if it is too short, decrease the ratio. If a solvent change is necessary, always recalibrate (see 10.2.4) before running samples.

NOTE 20—The chromatographic conditions described here have been optimized for the detection of formaldehyde and other carbonyls within the scope of this test method. Users are advised to experiment with their HPLC system to optimize chromatographic conditions for their particular analytical needs.

10.2.4 *HPLC Calibration:*

10.2.4.1 Prepare a calibration standard stock solution of each individual DNPH-carbonyl standard by dissolving accurately weighed amounts (for example, 10 mg) with acetonitrile in a 100 mL volumetric flask. These individual solutions are used to prepare calibration standards at concentrations spanning the range of interest.

NOTE 21—Purified crystals or solutions of DNPH derivatives of

Peak Identification

Number	DNPH Derivative	Concentration µg/mL
1	Formaldehyde	7.32
2	Acetaldehyde	1.94
3	Acrolein	1.06
4	Acetone	1.75
5	Propionaldehyde	0.85
6	Crotonaldehyde	0.85
7	Methacrolein	0.63
8	2-Butanone	0.87
9	Butyraldehyde	0.77
10	Benzaldehyde	0.84
11	Isovaleraldehyde	1.02
12	Valeraldehyde	1.03
13	o-Tolualdehyde	0.75
14	m-Tolualdehyde	0.25
15	p-Tolualdehyde	0.94
16	Hexanal	1.00
17	2,5-Dimethylbenzaldehyde	1.07

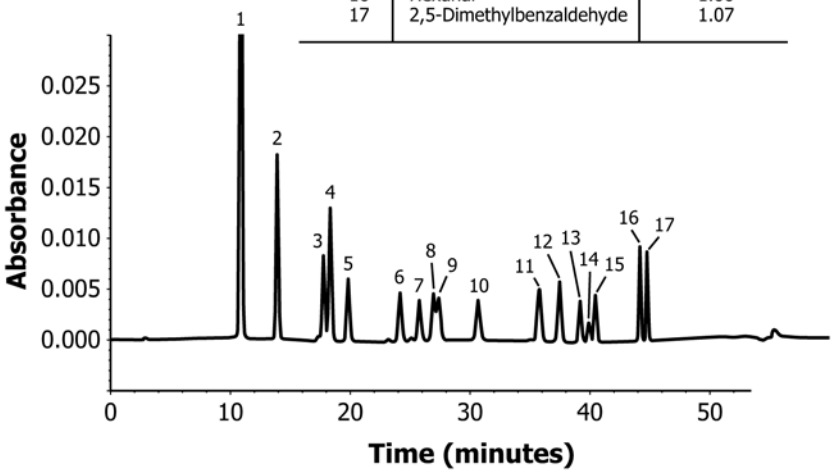

FIG. 6 Typical Chromatographic Separation of DNPH Derivatives of 17 Carbonyl Standards

carbonyls are available from commercial sources.

10.2.4.2 Analyze each calibration standard (at least five levels) and tabulate area response against mass injected (or, more conveniently, versus the concentration of the DNPH-carbonyl injected, for a fixed loop volume). An example of a multicomponent, six level calibration chromatogram is shown in Fig. 7. Perform all calibration runs as described for sample analyses in 10.2.3. Using the UV detector, a linear response range from approximately 0.5 to 20 µg/mL should be achieved for 25-µL injection volumes. The results may be used to prepare a calibration curve, as illustrated in Fig. 8 for formaldehyde. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of the data (concentration versus area response) is obtained. The retention times for each analyte should agree within 2 %.

10.2.4.3 Once linear response has been documented, an intermediate concentration standard near the anticipated levels of each component, but at least ten times the detection limit, should be chosen for daily calibration verification. Calibration verification standards should be analyzed periodically, for example, one standard for each ten injections. The day to day response for the various components should be within 10 % for analyte concentrations of 1 g/mL or greater and within 15 to 20 % for analyte concentrations near 0.5 g/mL. A higher value, for example 20 %, may be used as a practical limit for runs containing more than two target compounds. If these requirements are not meet, a new full calibration shall be performed. When the instrument performance begins to degrade from its normal range, investigate and perform corrective action which may include generation of a new calibration curve prepared from fresh standards.

11. Calculation

11.1 The total mass of analyte (DNPH-formaldehyde) is calculated for each sample using the following equation:

$$W_d = W_s - W_b \quad (4)$$

where:

W_d = corrected quantity, µg, of DNPH derivative extracted from the cartridge,
W_s = uncorrected analyte mass, µg, on the sample cartridge
= $A_s \times (C_{std}/A_{std}) \times v_s \times d_s$, and
W_b = analyte mass, µg, in the blank cartridge
= $A_b \times (C_{std}/A_{std}) \times v_b \times d_b$,

where:

A_s = area counts, eluate from sample cartridge,
A_b = area counts, eluate from blank cartridge,
A_{std} = area counts, standard,
C_{std} = concentration (µg/mL) of analyte in the daily calibration standard,
v_s = total volume (mL) of the sample cartridge eluate,
v_b = total volume (mL) of the blank cartridge eluate,
d_s = dilution factor for the sample cartridge eluate
= 1 if sample was not rediluted
= v_d/v_a if sample was rediluted to bring the detector response within linear range,
v_d = redilution volume (mL),
v_a = aliquot used for redilution (mL), and
d_b = dilution factor for the blank cartridge eluate = 1.

11.2 The concentration of carbonyl compound in the original sample is calculated from the following equation:

$$C_A = W_d \times (MW_c/MW_{der}) \times 1000/V_m \,(or\ V_s) \quad (5)$$

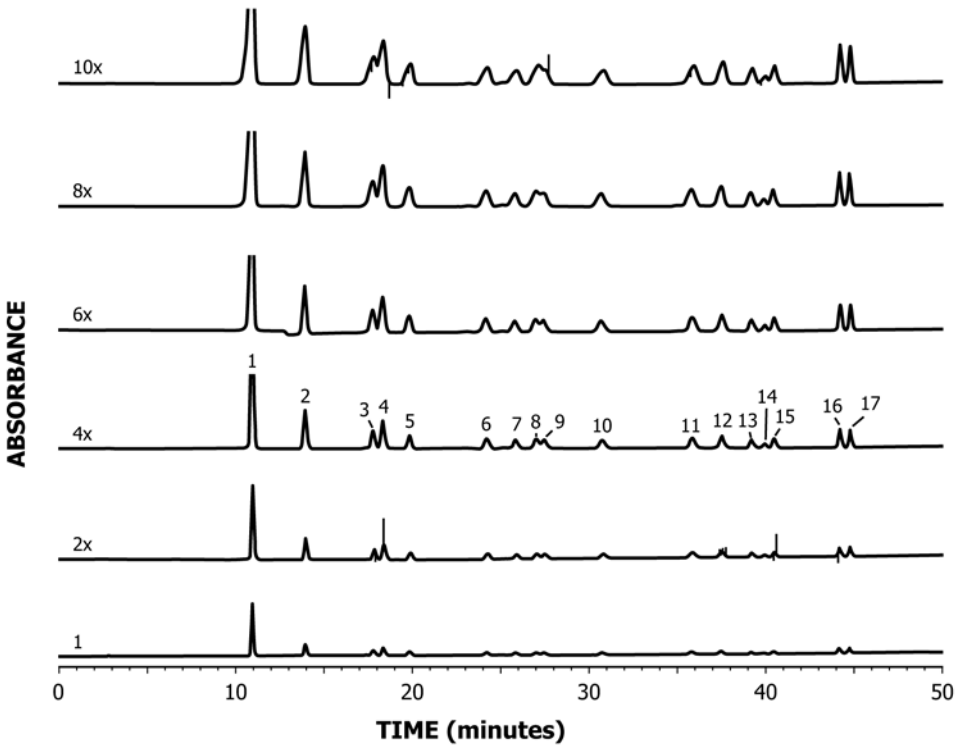

FIG. 7 Typical Six-Level Multiple-Component Standard Calibration Chromatogram

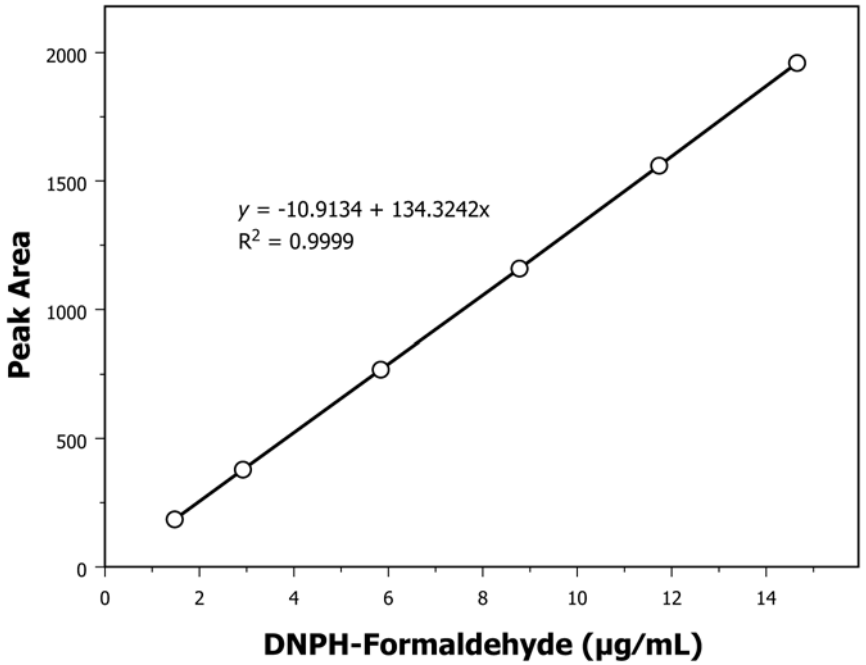

FIG. 8 Example Calibration Curve for Formaldehyde

where:

C_A = concentration (ng/L) of carbonyl compound in the original sample,
V_m = total air sample volume (L) under the sampling conditions, from 10.1.13,
V_s = standard air sample volume (L) at 25°C and 101.3 kPa, from 10.1.13,
MW_c = molecular weight of the carbonyl compound, and
MW_{der} = molecular weight of the DNPH derivative of the carbonyl compound.

The carbonyl compound concentrations can be converted to ppbv using the following equation:

$$C_A(ppbv) = C_{As}(\text{ng/L}) \times 24.4/MW_c \quad (6)$$

where:

$C_A(ppbv)$ = concentration of carbonyl compound in parts per billion by volume,
C_{As} = concentration (ng/L) of carbonyl compound in the original sample, calculated using V_s, and
24.4 = ideal gas volume nL/nmole, corrected to 25°C.

12. Performance Criteria and Quality Assurance

12.1 This section summarizes required quality assurance measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

12.1.1 *Standard Operating Procedures (SOPs):*

12.1.1.1 Users should generate SOPs describing the following activities in their laboratory: assembly, calibration, and operation of the sampling system, with make and model of equipment used; preparation, purification, storage, and handling of sampling reagent and samples; assembly, calibration, and operation of the HPLC system, with make and model of equipment used; and all aspects of data recording and processing, including lists of computer hardware and software used.

12.1.1.2 The SOPs should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

12.1.2 *HPLC System Performance:*

12.1.2.1 A column efficiency of >5000 theoretical plates should be obtained. The HPLC system efficiency[7] is calculated according to the following equation:

$$n = 5.54\,(t_r/W_{1/2})^2 \quad (7)$$

where:

n = column efficiency (theoretical plates),
t_r = retention time of analyte, and
$W_{1/2}$ = width of component peak at half height.

12.1.2.2 Precision or response for replicate HPLC injections should be ±10 % or less, day to day, for analyte calibration standards at 1µ g/mL or greater levels. At the 0.5-µg/mL level and below, precision of replicate analyses may vary up to 25 %. Precision of retention times should be ±7 % on a given day.

12.1.3 *Blanks*—At least one field blank or a number of field blanks equal to 10 % of the field samples, whichever is larger, should be shipped and analyzed with each group of samples. The number of samples within a group or time frame, or both, should be recorded so that the specified percentage of blanks is obtained for a given number of air samples. The field blank is treated identically as the samples except that no air is drawn through the cartridge. The performance criteria described in 9.1 should be met for field blanks. It is desirable to analyze blank cartridges retained in the laboratory (method blanks) as well, to distinguish between possible field and laboratory contamination.

[7] See Practice E682 for definitions of terms used in this section.

12.1.4 Sample loss can occur when the capacity of the sorbent is exceeded, or when the sample volume exceeds the maximum for complete collection. This possibility can be guarded against by employing two sampling cartridges in series, and analyzing the contents of each, or by analyzing both sections of a two-bed sorbent cartridge. Should the quantity of collected analyte in the backup section exceed 15 to 25 % of the analyte collected by the primary sampling section, breakthrough may be assumed to have occurred. The absence of the collected analyte on the second cartridge does not automatically indicate 100 % collection efficiency (**1**). Collection efficiency is defined as the "ratio of the carbonyl concentration determined from the collection media, to the actual (known) concentration." Hence, collection efficiencies must be measured using generated test atmospheres. Test atmospheres are typically produced in laboratories using permeation tubes. If it is necessary to report data in cases where breakthrough is suspected, the results should be flagged and reported as equal to or greater than the value obtained from analysis of both cartridges or both sorbent beds.

12.1.5 Laboratories performing this analysis on a regular basis should participate in carbonyl analysis performance tests (PTs) or audits on a periodic basis.

13. Precision and Uncertainty[8]

13.1 The precision and uncertainty of this or any other measurement method for formaldehyde and other carbonyl compounds will be influenced by two parameters: the reproducibility of the method and the variation of the concentration of the analyte in air over time. It is reasonable to assume that the latter (temporal concentration change) will have a much larger effect on precision and uncertainty than the former.

13.2 This test method has been evaluated by round-robin testing using 55 to 105-µm silica gel cartridges coated by the U.S. Environmental Protection Agency and two of its contract laboratories. These cartridges have been used by two different laboratories to make over 1500 measurements of formaldehyde and other aldehydes in ambient air for the U.S. Urban Air Toxics Program (UATP), conducted in 14 cities throughout the United States.

13.3 The precision of 45 replicate HPLC injections of a stock solution of formaldehyde-DNPH derivative over a two-month period has been shown to be 0.85 % relative standard deviation (rsd).

13.4 Triplicate analyses of each of twelve identical samples of exposed DNPH cartridges provided formaldehyde measurements that agreed within 10.9 % rsd.

13.5 A total of 16 laboratories in the United States, Canada, and Europe participated in a round-robin test that included 250 blank DNPH-cartridges, three sets of 30 cartridges spiked at three levels with DNPH derivatives, and 13 sets of cartridges exposed to diluted automobile exhaust gas. These cartridges were coated by the U.S. EPA and were of the same type described in 4.1. All round-robin samples were randomly distributed to the participating laboratories. A summary of the round-robin results is shown in Table 4.

NOTE 22—There was no attempt to standardize the HPLC analysis in this round robin. The participants used HPLC procedures as practiced in their laboratories.

13.6 The absolute percent differences between collocated duplicate sample sets from the 1988 UATP program were 11.8 % for formaldehyde (n = 405), 14.5 % for acetaldehyde (n = 386), and 16.7 % for acetone (n = 346).

13.7 Collocated duplicate samples collected in the 1989 UATP program and analyzed by a different laboratory showed a mean relative standard deviation of 0.07, correlation coefficient of 0.98, and bias of –0.05 for formaldehyde. Corresponding values for acetaldehyde were 0.12, 0.95, and –0.50, and for acetone were 0.15, 0.95, and –0.54.

13.8 In the 1988 UATP program, single-laboratory analyses of spiked DNPH cartridges provided over the year showed an average bias of +6.2 % for formaldehyde (n = 14) and +13.8 % for acetaldehyde (n = 13).

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D22-1024. Contact ASTM Customer Service at service@astm.org.

TABLE 4 Round-Robin Test Results[A]

Sample Type	Formaldehyde	Acetaldehyde	Propionaldehyde	Benzaldehyde
Blank cartridges:				
µg aldehyde	0.13	0.18	0.12	0.06
(% rsd)	46	70	47	44
n	33	33	23	8
Spiked[B] cartridges:				
% recovery (% rsd)				
low	89.0 (6.02)	92.6 (13.8)	108.7 (32.6)	114.7 (36.1)
medium	97.2 (3.56)	97.8 (7.98)	100.9 (13.2)	123.5 (10.4)
high	97.5 (2.15)	102.2 (6.93)	100.1 (6.77)	120.0 (8.21)
n	12	13	12	14
Exhaust samples:				
µg aldehyde	5.92	7.99	0.522	0.288
% rsd	12.6	16.54	26.4	19.4
n	31	32	32	17

[A] Sixteen participating laboratories. Statistics shown after removal of outliers.
[B] Normal spiking levels were approximately 0.5, 5, and 10 µg of aldehyde, designated as low, medium, and high in this table.

13.9 Single-laboratory analyses of 30 spiked DNPH cartridges during the 1989 UATP program showed an average bias of +1.0 % (range from –49 to +28 %) for formaldehyde and +5.1 % (range from –38 % to +39 %) for acetaldehyde.

14. Keywords

14.1 active sampler; air; carbonyl compounds; DNPH cartridge; formaldehyde; HPLC analysis

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