Designation: ~~D5197 – 16~~ D5197 – 21

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 acidified DNPH reagent. The DNPH derivatives are analyzed for parent aldehydes and ketones ~~utilizing~~using high performance liquid chromatography ~~(HPLC).~~ (HPLC) or ultra-high performance liquid chromatography (UHPLC). UHPLC systems use higher pressures and smaller particle sizes in columns compared to HPLC systems. 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~~ uses HPLC or UHPLC for separation of carbonyl compounds followed by UV adsorption or photodiode array detection. This test method exceeds 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 airborne concentration range from approximately ~~1~~0.10 $ppb_{v/v}$ ~~ppb~~ (12 µg/m^3), requires sampling for 1 h at 1 L/min) to ~~1~~1 $ppm_{v/v}$ ~~ppm~~(1.2 mg/m^3 ~~(v/v).~~). Lower concentrations in air may be determined ~~with careful~~ using higher sampling volume and with 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] 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.

Current edition approved ~~Oct. 1, 2016~~Sept. 1, 2021. Published ~~November 2016~~May 2022. Originally approved in 1991. Last previous edition approved in ~~2009~~2016 as ~~D5197 – 09~~D5197 – 16.~~ε1~~. DOI: ~~10.1520/D5197-16.~~10.1520/D5197-22.

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

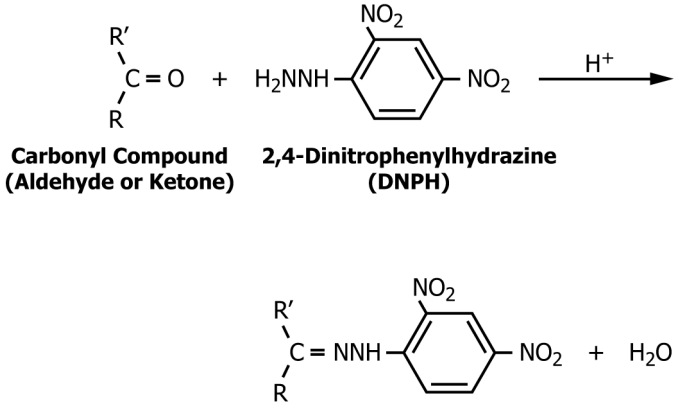


FIG. 1 Reaction of Carbonyl Compounds

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~~ meet blank and analyte trapping acceptance criteria (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 responsibility of the user of this standard to establish appropriate ~~safety~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

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

2. Referenced Documents

2.1 *ASTM Standards:*[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] 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.

[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.

2.3 *Other Documents:*
40 CFR Part 136 Appendix B, the MUR Definition and Procedure for the Determination of the Method Detection Limit – Revision 2[6]

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.~~ time based upon the intended use of the measurement. 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 which 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~~ <4 °C protected from light until analysis. Alternatively, the cartridges may be desorbed, diluted to a known volume, and refrigerated at ~~<4°C~~<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 or UHPLC system, equipped with a C18 reverse phase column and an ultraviolet (UV) absorption or photodiode array 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~~ambient 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 acidified 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] Available from U.S. Government Publishing Office (GPO), 732 N. Capitol St., NW, Washington, DC 20401, http://www.gpo.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; reaction with carbonyl compounds; 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~~
6.9	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

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

6.2.2 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~~use potassium iodide (KI). Manganese oxide scrubbers have also been used (**8**). At least some air moisture (relative humidity >10 % at ~~25°C)~~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

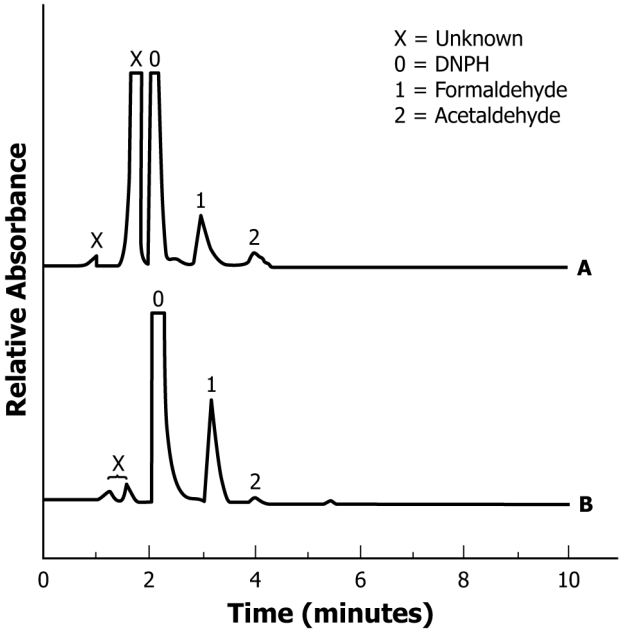


FIG. 2 Cartridge Samples of Formaldehyde in an Air Stream with (*A*) and without (*B*) Ozone

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 should be maintained at a temperature of ~~90°C~~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.~~ 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 chromatographically 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%~~(>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,~~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~~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.~~ encountered. The DNPH must be purified by multiple recrystallizations in UV-grade acetonitrile. Recrystallization is accomplished, at 40 to ~~60°C,~~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 or UHPLC 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. Alternatively, UHPLC systems can improve chromatographic resolution and overcome interferences and some coelution issues.

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~~<4 °C prior to sampling, as soon as possible after sampling, and extracts should also be stored at ~~<4°C~~<4 °C prior to analysis (**18**). Note, excessively low temperature (typically <10 °C) storage of commercially produced cartridges should be avoided to prevent mounting rings from falling off or cartridge bodies from cracking.

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.~~ acetaldehyde at a sample collection rate of 0.15 L/min. Collection efficiencies of 100 % were reported for ~~samples~~sampling 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. In some applications, it may be desirable or required that the sampling system flow is certified on a periodic basis against a NIST or equivalent reference standard.

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 or UHPLC 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.

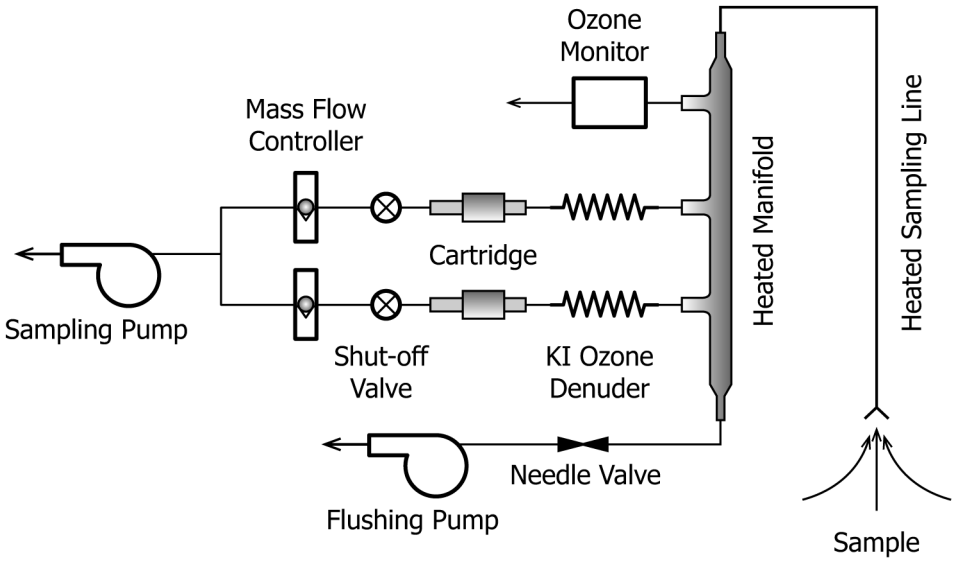


FIG. 3 A Dual-Cartridge Sampling System with Heated Manifold for Carbonyl Compounds in Ambient Air

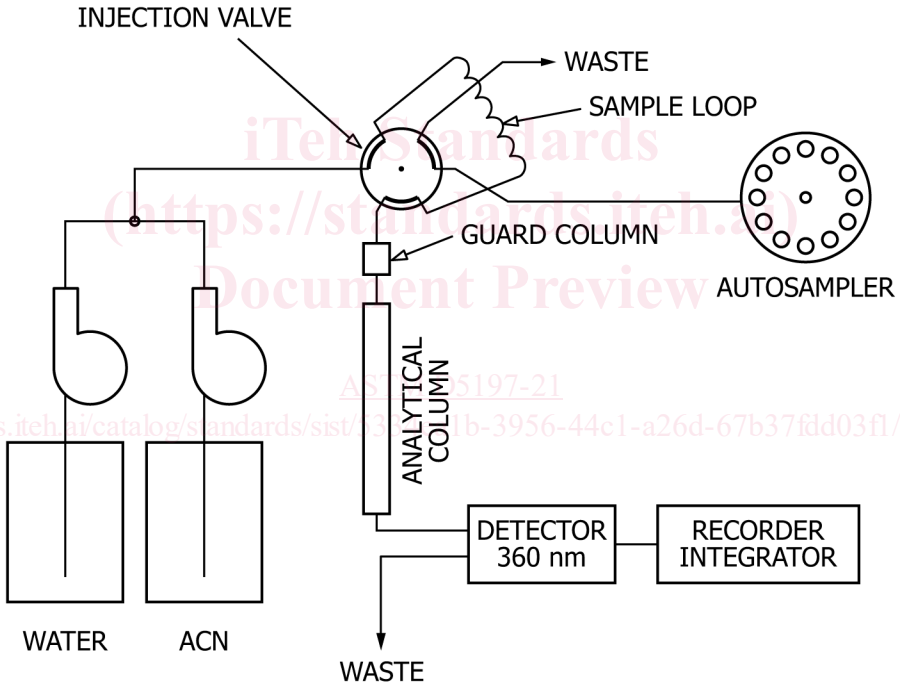


FIG. 4 A Typical Gradient HPLC System Configuration for Determination of Carbonyl Compounds Collected on DNPH Cartridges

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 acidified 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 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.

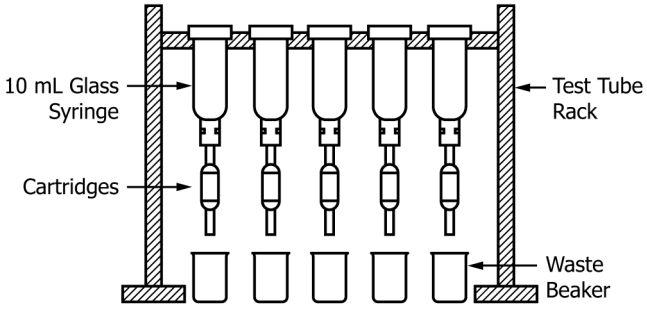
7.24 *Hot Plates, Beakers, Flasks, Measuring and Disposable Pipets, Volumetric Flasks,* and so forth, used in the purification of DNPH.

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

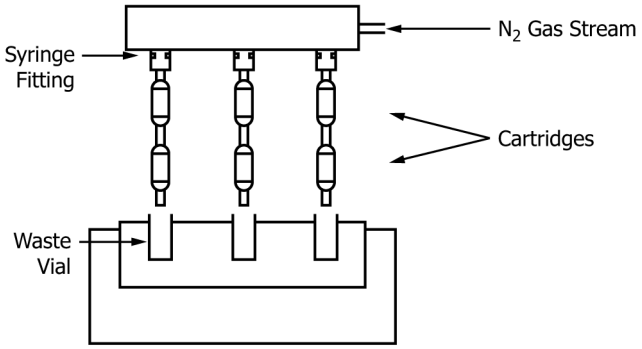
7.26 *Heated Probe,* necessary for when the temperature of sampled air is below ~~15°C.~~15 °C.

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.



(a) Rack for Coating Cartridges



(b) Rack for Drying DNPH-Coated Cartridges

FIG. 5 Syringe Rack for Coating and Drying Sample 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.[7]

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.

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.*

[7] ~~*Reagent Chemicals, American Chemical Society Specifications, American Chemical*~~ *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials,* 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.

8.10 *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.~~60 °C.

9.1.3 Maintain the solution at this temperature ~~(40°C)~~(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~~ 200 mL of acetonitrile, heat to boiling, and again let crystals grow slowly at 40 to ~~60°C~~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 typically <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~~ 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~~re-rinse 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)~~(166 °C) determination or ~~HPLC~~HPLC/UHPLC 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~~20 µg ~~µg/mL~~/mL that spans the concentration of interest.

9.3.3 Store all standard solutions in tightly capped containers at ~~<4°C~~<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~~ 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~~HPLC/UHPLC in accordance with 9.1.