



Designation: D6902 – 04 (Reapproved 2023)

Standard Test Method for Laboratory Measurement of Formaldehyde Evolved During the Curing of Melamine-Formaldehyde-Based Coatings¹

This standard is issued under the fixed designation D6902; 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 is for the determination of formaldehyde evolved from melamine-formaldehyde-based coatings during the cure step. The results may be used to determine the “cure formaldehyde” evolved from a sample under controlled laboratory conditions.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 This test method is capable of measuring from 500 $\mu\text{g/g}$ to 22 000 μg formaldehyde/g dry coating under the test conditions specified (3 000 ml/min total flow, 50 ml/min DNPH tube flow). The ratio of total flow to DNPH tube flow could be adjusted to extend the range of the method.

1.4 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *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:*²

D362 Specification for Industrial Grade Toluene (Withdrawn 1989)³

¹ This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paints and Paint Materials.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on www.astm.org.

D1979 Test Method for Free Formaldehyde Content of Amino Resins (Withdrawn 2006)³

D6191 Test Method for Measurement of Evolved Formaldehyde from Water Reducible Air-Dry Coatings

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *cure formaldehyde, n*—the formaldehyde generated as the result of a chemical reaction during coating curing.

3.1.2 *free formaldehyde, n*—the residual formaldehyde in a coating due to the raw materials.

4. Summary of Test Method

4.1 Approximately 0.2 g of coating formulation is placed in an aluminum foil pan, dried in a vacuum oven at 40 °C (to remove free formaldehyde and solvents) and then baked at the optimum process cure temperature for 30 min. Formaldehyde emissions are collected from the cure chamber on a DNPH/Silica tube, which is then extracted and the extract analyzed by HPLC/UV. The amount of formaldehyde evolved from the coating during the cure step is calculated on both a wet-weight and dry-weight basis. The test is run in triplicate plus a blank and system standard.

5. Significance and Use

5.1 This test method measures the amount of formaldehyde that is evolved from a coating containing melamine-formaldehyde resin(s) during cure at elevated temperature. Cure formaldehyde results from a side-reaction during cross-linking of functionalized polymers with melamine-formaldehyde resins. Cure formaldehyde is evolved in the final bake or cure oven, when the coating temperature is high enough to initiate cross-linking. Formaldehyde can be released from a coating during application, solvent flash-off and cure. Free formaldehyde is primarily evolved during coating application and solvent flash-off. Test Method **D1979** measures “free formaldehyde” in amino resins and Test Method **D6191** measures formaldehyde evolved from coatings at ambient temperature. This method measures only the formaldehyde released during heat cure, which is primarily “cure formaldehyde.”

5.2 This test method is not intended to duplicate the evolved formaldehyde from an industrial process, but serves as a reproducible comparative laboratory evaluation.

5.3 This test method has not been evaluated with catalyzed coating systems that cure at or below 40 °C, such as those used by the wood-finishing industry, and would likely require special adaptation for this application.

6. Apparatus

6.1 *High Pressure Liquid Chromatograph (HPLC)*, either a gradient or isocratic system. A gradient system is preferred when other aldehydes or ketones are present.

NOTE 1—The system shall be equipped with a temperature-controlled column oven. A liquid autosampler is optional.

6.2 *Column*, a C₁₈ ODS packed with 5 μm pellicular beads with the dimensions of approximately 4 mm by 75 mm or 150 mm. A 2 cm guard column packed with the same material is recommended to protect the analytical column.

6.3 *Detector*, UV/VIS detector capable of measuring absorbance at 360 nm.

6.4 *Integrator*, peak integration system.

6.5 *Air Sampling Pump*, an air sampling pump with the capability of maintaining a constant flow rate between 3 L/min and 4 L/min. Both an inlet and outlet port must be available for measuring flow. An SKC AirCheck Sampler Model 224-PCXR8 has been found suitable.

6.6 *Flow Meters*—An in-line mass flow meter or flow sensor capable of measuring 30 mL/min to 120 mL/min with at least 3 % accuracy. A flow meter or bubble meter capable of measuring 3 L/min to 4 L/min with at least 5 % accuracy.

6.7 *Glass Purge Chamber*—A glass purge chamber with a mouth at least 60 mm wide and a lid with an air-tight gasket seal. One liter reaction flask, reaction flask head with two threads, two 5029 tetrafluorethylene polymer bushings and FETFE O-Ring and 124 mm anodized 2 piece clamp, Ace Glass part numbers 6511-53, 6513-SP, and 6508-6.

6.8 *Valves*—Two metering valves to adjust split flow rate. One valve must be constructed of stainless steel. A Swagelok 506-1-316 has been found suitable.

6.9 *Aluminum Foil Dishes*, 58 mm in diameter by 18 mm high with a smooth (planar) bottom surface.

6.10 *Forced Draft Oven*, oven, capable of maintaining 160 °C (320 °F), of adequate size to accommodate one or more purge chambers.

6.11 *Vacuum Oven*, capable of maintaining 40 °C and a vacuum of 0.1 Barr to 0.2 Barr (~100 mm Hg).

6.12 *Volumetric Glassware*, various volumetric flasks and pipettes for preparation of calibration standards. Also, 5 mL volumetric flasks for sample elution.

6.13 *Analytical Balance*—Four-place analytical balance capable of measuring to ±0.1 mg (0.0001 g).

6.14 *Sherer Impinger Diffuser*, A 25 mm dia, 275 mL with impinger stopper, Ace Glass part number 7538-29 has been found suitable.

6.15 *Water Trap*, 1000 mL vacuum flask with stopper.

6.16 *Thermometer*, thermocouple with temperature readout calibrated in range of 50 °F to 400 °F.

7. Reagents and Materials

7.1 *Purity of Reagents*—Use reagent grade chemicals in all tests, unless otherwise specified. Other grades may be used, provided it is first ascertained that the reagent is sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Toluene*, technical grade, Specification **D362**.

7.3 *Tetrahydrofuran*, HPLC Grade.

7.4 *Water*, HPLC Grade.

7.5 *Acetonitrile*, HPLC Grade.

7.6 *DNPH-Silica Cartridge*, Waters Sep-Pak Cartridges, Part # WAT037500.

7.7 *Formaldehyde/2,4-dinitrophenylhydrazine (DNPH) Complex*, may be purchased or prepared in the laboratory.

7.8 *Calcium Nitrate Tetrahydrate*, reagent grade.

7.9 *Paraformaldehyde*, reagent grade.

8. Hazards

8.1 Check the supplier's Safety Data Sheet (SDS) on all chemicals before use.

9. Preparation of Apparatus

9.1 Install the column in the chromatograph following the manufacturer's directions and establish the operating conditions required to give the desired separation (see **Table 1**). Allow sufficient time for the instrument to reach equilibrium as indicated by a stable baseline.

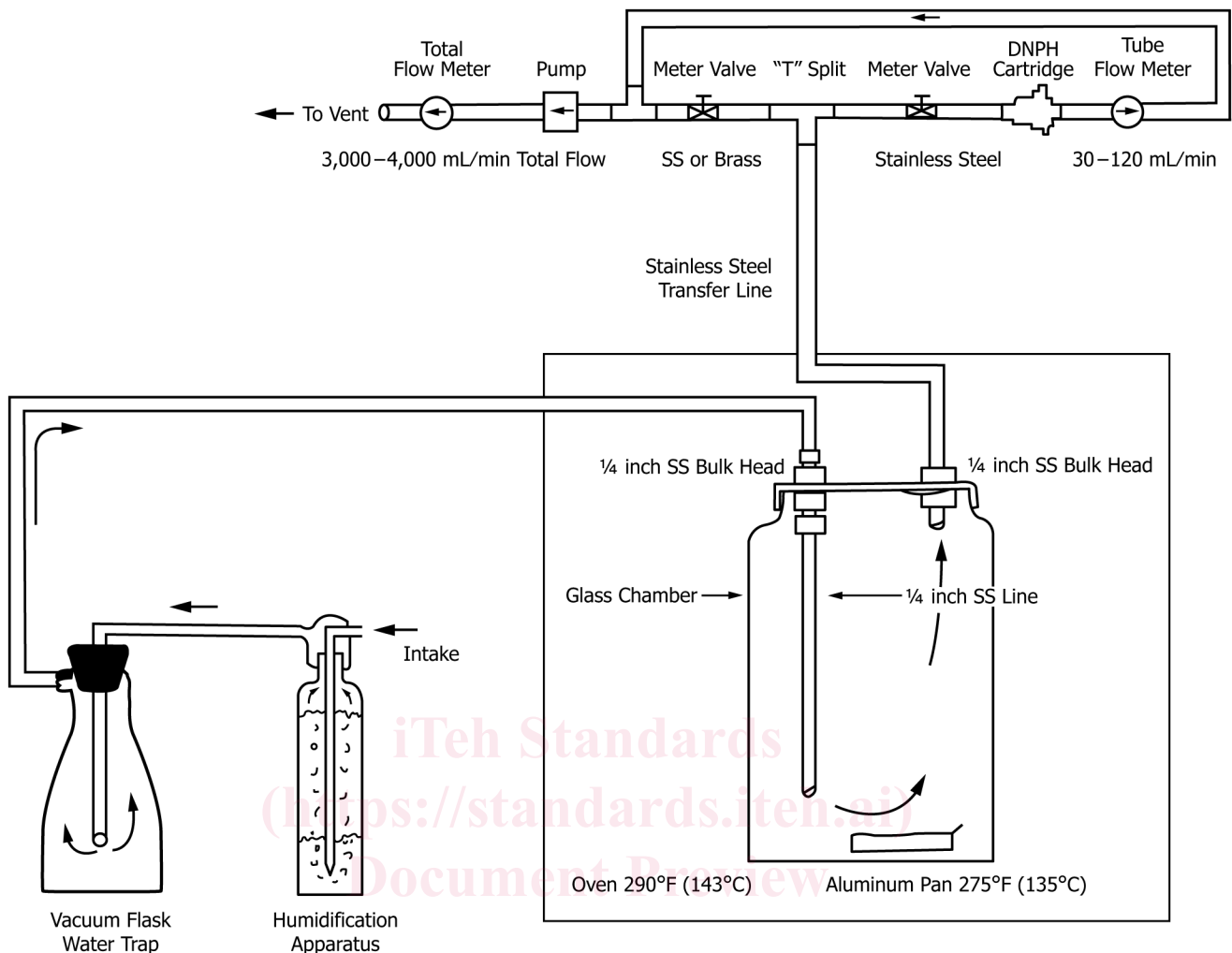
9.2 *Purge Chamber Set Up:*

9.2.1 Assemble apparatus (empty purge chamber, impinger, pump, flow meters and valving) as shown in **Fig. 1** with a DNPH cartridge in line (use two DNPH cartridges for water-borne coatings and paraformaldehyde calibration check).

9.2.2 Add 500 g of calcium nitrate tetrahydrate to 250 mL of reagent grade water to form a near saturated solution. Place this mixture in the constant humidity Insert the Sherer Impinger so

TABLE 1 Instrument Conditions

Detector	UV/VIS Absorbance 360 nm
Column (Isocratic)	C ₁₈ ODS 4 mm by 75 mm
Mobile Phase (Isocratic)	Water/Acetonitrile/Tetrahydrofuran 65/30/5 volume/volume
Column (Gradient)	C ₁₈ ODS 4 mm by 150 mm
Mobile Phase (Gradient)	Water/Acetonitrile/Tetrahydrofuran A: 65/30/10 volume/volume B: 40/60/0 volume/volume 100 % A for 1 min then linear gradient to 100 % B in 10 min
Flow Rate	1.5 mL/min
Column Temperature	40 °C
Run Time (Isocratic)	10 min
Run Time (Gradient)	15 min
Injection Volume	10 μL to 20 μL



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FIG. 1 Page Chamber Set-Up

<https://standards.iteh.ai/catalog/standards/sist/82e8e4b3-4261-4e27-bccb-f797c575e376/astm-d6902-042023>

that the solution is 8 in. above the bottom of the impinger tip. Mark the solution level on the impinger.

NOTE 2—This calcium nitrate tetrahydrate solution ensures a constant humidity of 55 %. Add water when the solution level falls below the mark.

9.2.3 Adjust the forced draft oven so that the pan temperature is set at the coating manufacturers recommended optimum process cure temperature ± 2 °F (usually with the range of 260 °F to 310 °F for automotive coatings). Use a thermocouple taped to the bottom of the pan to measure pan temperature.

9.2.4 Adjust pump flow rate to 3.0 L/min to 3.5 L/min.

9.2.5 Adjust valves A and B until the DNPB Cartridge has a flow of 50 mL/min.

9.2.6 Check pump flow rate to ensure it is still in the proper range. Recommended starting flows; Pump 3.0 L/min, DNPB Cartridge 50 mL/min (1:60 split).

10. Calibration

10.1 Use the information in Table 1 as a guide to select the conditions that give the necessary resolution of formaldehyde-DNPB derivative from interferences in the samples.

10.2 *Determination of Relative Response Factors*—The response factor relative to the standard is determined by means of

the following procedure. It is good practice to determine the relative retention time daily or with each series of determinations.

10.2.1 Prepare a minimum four-point standard curve of Formaldehyde-DNPB derivative in acetonitrile, ranging from 0.1 $\mu\text{g/mL}$ to 10 $\mu\text{g/mL}$ as formaldehyde. Recommended curve 0.1 $\mu\text{g/mL}$, 1.0 $\mu\text{g/mL}$, 5.0 $\mu\text{g/mL}$ and 10 $\mu\text{g/mL}$.

10.2.2 Inject a 10 μL to 20 μL aliquot of the standard mixture into the HPLC. At the end of the chromatographic run, calibrate the integrator by following the manufacturer's procedure for external standard calibration. If this capability is not available, refer to the following calculations. See Figs. 2 and 3 for typical chromatograms using the three listed columns.

10.2.3 The response factor of each analyte is calculated as follows:

$$R_{\text{analyte}} = \frac{A_{\text{analyte}}}{C_{\text{analyte}}} \quad (1)$$

where:

- R_{analyte} = response factor for the analyte being calibrated,
- C_{analyte} = concentration of formaldehyde in mg/mL, and
- A_{analyte} = peak area for the analyte being calibrated.

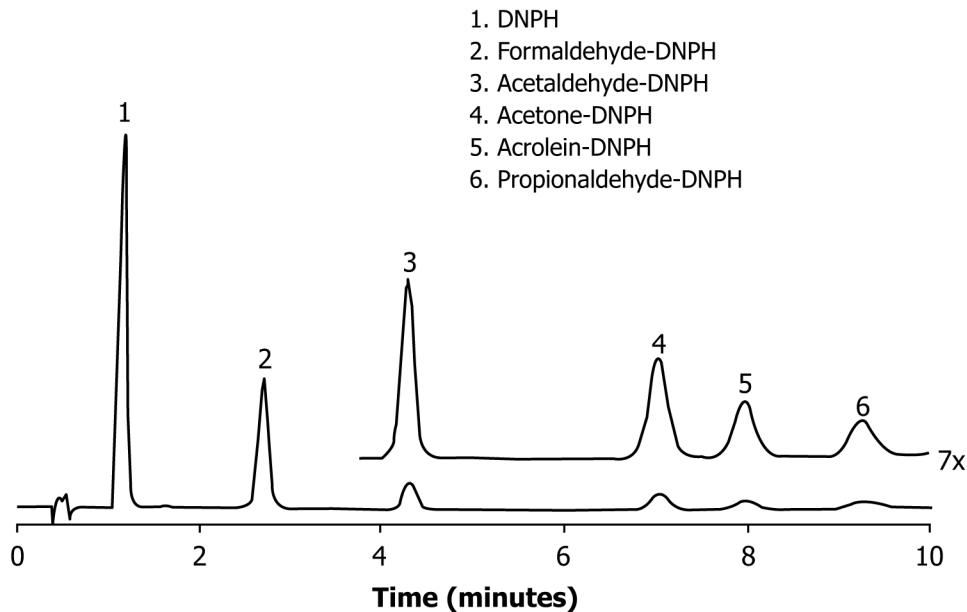


FIG. 2 Isocratic Separation of C₁-C₃ Aldehyde and Ketone Derivatives

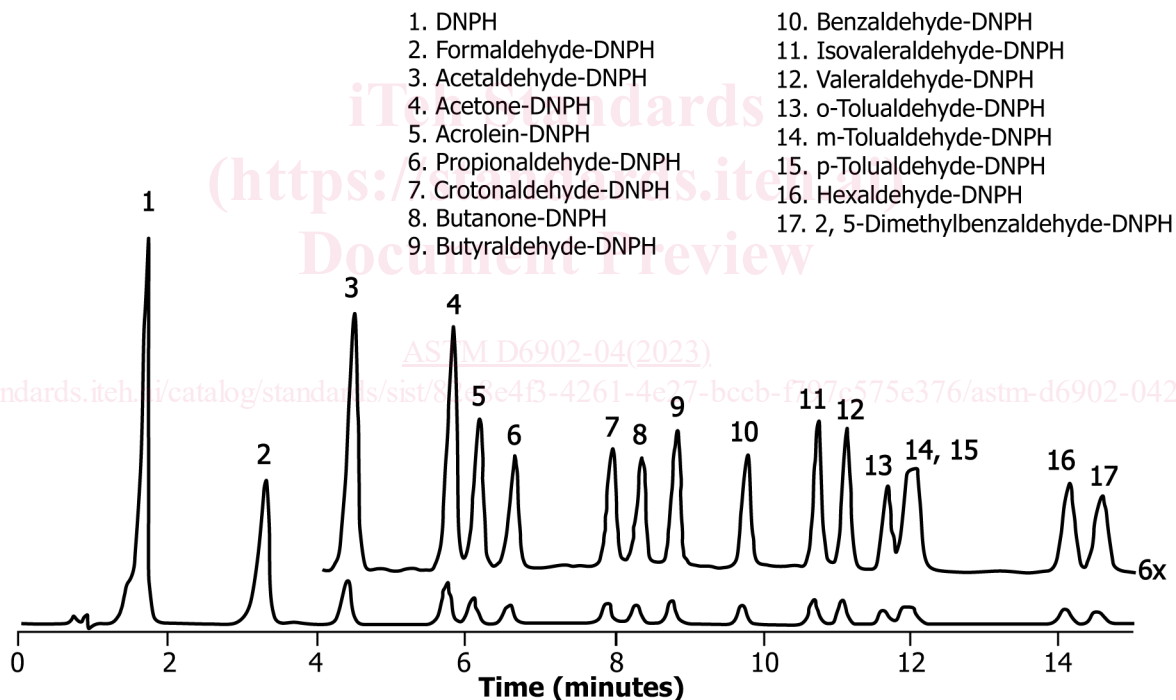


FIG. 3 Gradient Separation of C₁-C₉ Aldehyde and Ketone Derivatives

10.2.4 Calculate the average response factor for all concentrations and the correlation coefficient for calibration curve. If the correlation coefficient is not 0.9999 or greater, repeat calibration process.

10.3 System Integrity:

10.3.1 System Blank—Follow procedure (Section 11) below only using a blank aluminum foil dish. Result should be below detection for formaldehyde.

10.3.2 System Standard—Follow procedure beginning at 10.2, using two DNPH cartridges and an oven temperature of 150 °C. Add 4.0 mg ± 0.5 mg of paraformaldehyde to a cool empty pan and record weight to nearest 0.1 mg. Total formaldehyde measured should be equal to the amount of paraformaldehyde used ±5 %, with less than a 1 % breakthrough to the second cartridge. Analyze system standard on a minimum daily basis.