Designation: D6902 – 04 (Reapproved 2011)

Standard Test Method for
Laboratory Measurement of Formaldehyde Evolved During the Curing of Melamine-Formaldehyde-Based Coatings[1]

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 µg/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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D362 Specification for Industrial Grade Toluene (Withdrawn 1989)[3]

D1979 Test Method for Free Formaldehyde Content of Amino Resins (Withdrawn 2006)[3]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

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[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.

Current edition approved June 1, 2011. Published June 2011. Originally approved in 2003. Last previous edition approved in 2004 as D6902 – $04^{\varepsilon 1}$. DOI: 10.1520/D6902-04R11.

[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.

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 C_{18} ODS packed with 5-µm pellicular beads with the dimensions of approximately 4 mm by 75 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 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 to 120 mL/min with at least 3 % accuracy. A flow meter or bubble meter capable of measuring 3 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 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 ±0.1mg (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-dinitrophenylhydrazone (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 Material Safety Data Sheet (MSDS) 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 waterborne 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 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.

TABLE 1 Instrument Conditions

Detector	UV/VIS Absorbance 360 nm
Column (Isocratic)	C_{18} ODS 4 by 75 mm
Mobile Phase (Isocratic)	Water/Acetonitrile/Tetrahydrofuran 65/30/5 volume/volume
Column (Gradient)	C_{18} ODS 4 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 to 20 µL

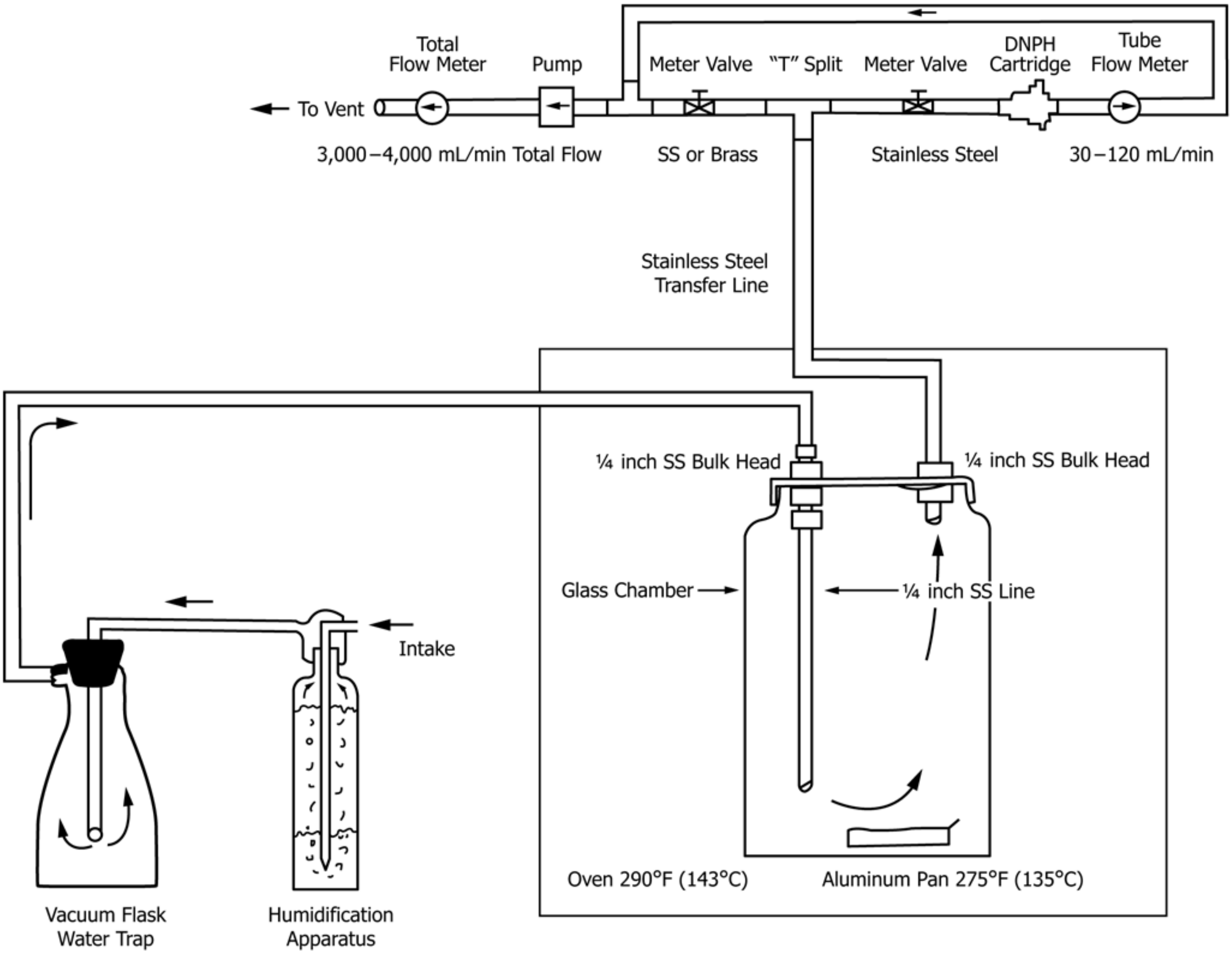


FIG. 1 Page Chamber Set-Up

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 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 to 3.5 L/min.

9.2.5 Adjust valves A and B until the DNPH 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, DNPH 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-DNPH 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-DNPH derivative in acetonitrile, ranging from 0.1 to 10 µg/mL as formaldehyde. Recommended curve 0.1, 1.0, 5.0 and 10 µg/mL.

10.2.2 Inject a 10 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:

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

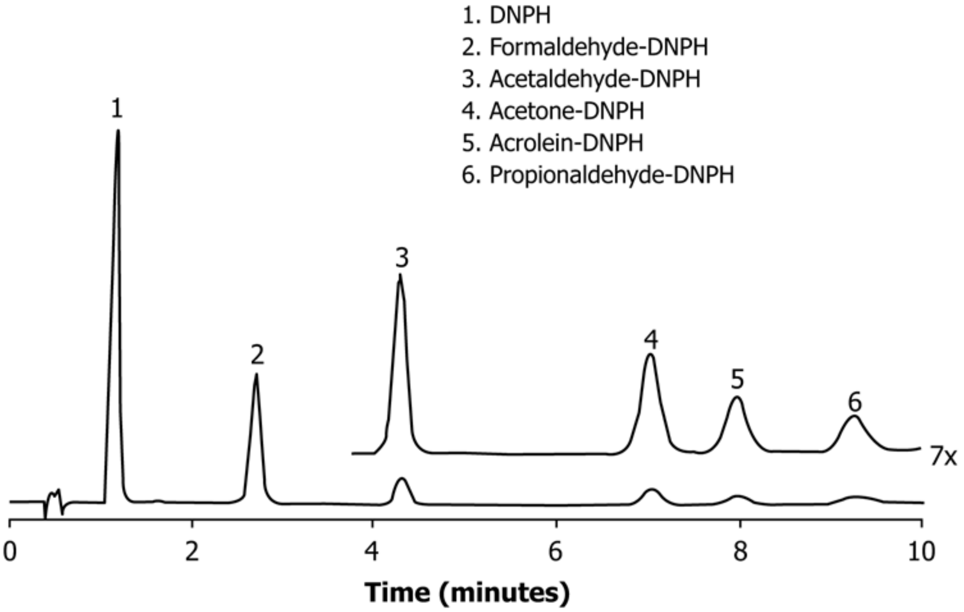


FIG. 2 Isocratic Separation of C_1-C_3 Aldehyde and Ketone Derivatives

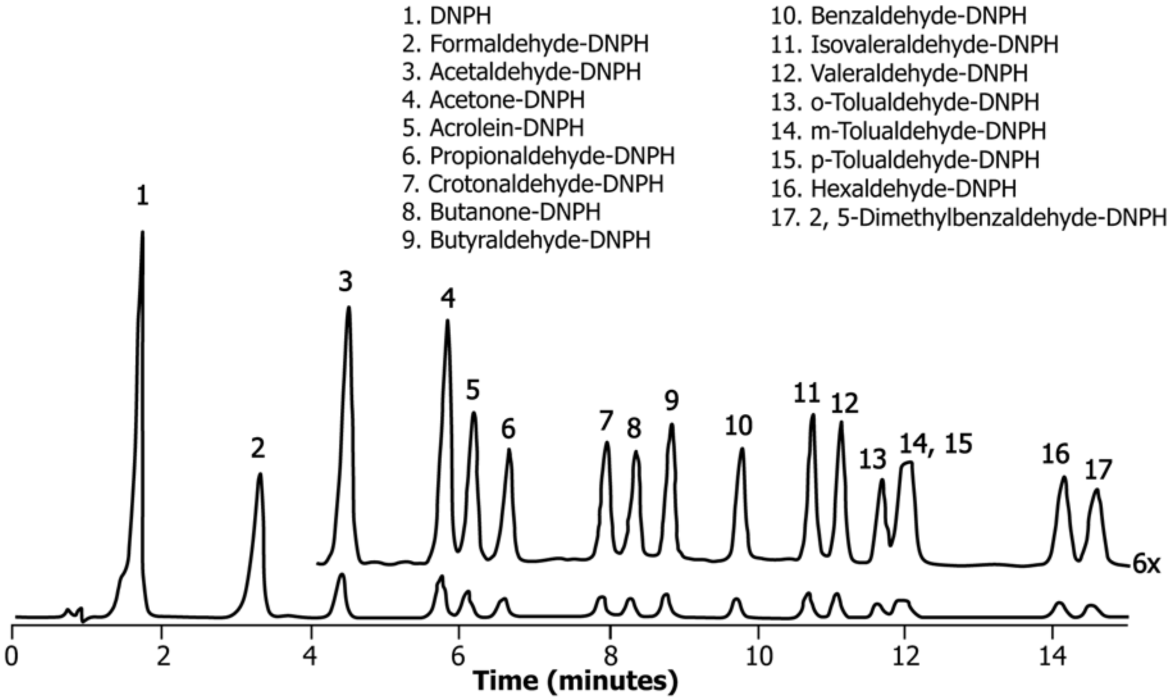


FIG. 3 Gradient Separation of C_1-C_9 Aldehyde and Ketone Derivatives

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.

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 ± 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.

11. Procedure

11.1 *Prepare Coating Specimens:*

11.1.1 Mix the coating sample, preferably on a mechanical shaker or roller for solventborne and by hand for waterborne coatings, until homogeneous. If air bubbles become entrapped, stir by hand until air has been removed.

11.1.2 Rinse aluminum foil dishes (6.9) with toluene, wipe dry with a lint-free cloth then bake at cure temperature and time. Place dishes in a desiccator to cool after baking.

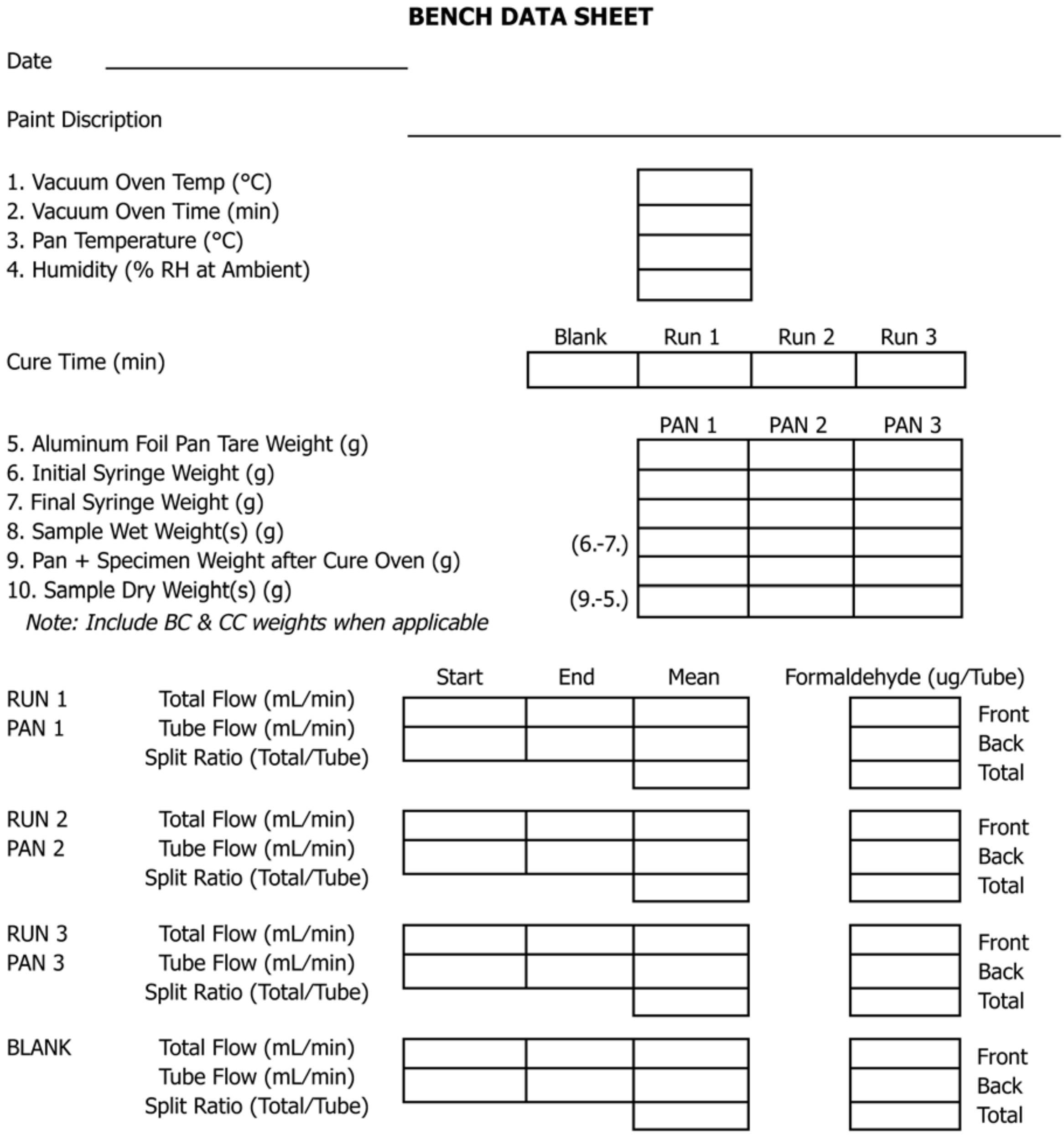
11.1.3 Record the weight of three dry aluminum foil dishes.

11.1.4 Measure 0.2 ± 0.05 g of coating formulation into a tared aluminum foil dish using a syringe by measuring the weight of the syringe before and after dispensing the coating. Record weight of the dispensed coating on Bench Data Sheet (Fig. 4).

11.1.4.1 For solventborne coatings add 1.5 mL of toluene to disperse the coating evenly on the bottom of the dish.

11.1.4.2 For waterborne coatings add one mL of distilled water, swirling pan until the coating formulation is fully wetted. Add one mL of ethanol again swirling the pan until the coating is fully dispersed.

11.1.5 Place dish immediately into a level vacuum oven set at 40°C.



BENCH DATA SHEET

Date ____________________

Paint Discription ____

1. Vacuum Oven Temp (°C)	
2. Vacuum Oven Time (min)	
3. Pan Temperature (°C)	
4. Humidity (% RH at Ambient)	

	Blank	Run 1	Run 2	Run 3
Cure Time (min)				

		PAN 1	PAN 2	PAN 3
5. Aluminum Foil Pan Tare Weight (g)				
6. Initial Syringe Weight (g)				
7. Final Syringe Weight (g)				
8. Sample Wet Weight(s) (g)	(6.-7.)			
9. Pan + Specimen Weight after Cure Oven (g)				
10. Sample Dry Weight(s) (g)	(9.-5.)			

Note: Include BC & CC weights when applicable

		Start	End	Mean	Formaldehyde (ug/Tube)	
RUN 1	Total Flow (mL/min)					Front
PAN 1	Tube Flow (mL/min)					Back
	Split Ratio (Total/Tube)					Total
RUN 2	Total Flow (mL/min)					Front
PAN 2	Tube Flow (mL/min)					Back
	Split Ratio (Total/Tube)					Total
RUN 3	Total Flow (mL/min)					Front
PAN 3	Tube Flow (mL/min)					Back
	Split Ratio (Total/Tube)					Total
BLANK	Total Flow (mL/min)					Front
	Tube Flow (mL/min)					Back
	Split Ratio (Total/Tube)					Total

FIG. 4 Bench Data Sheet

11.1.6 Repeat steps 11.1.3 – 11.1.5 two more times. Then evacuate the oven to 0.1 to 0.2 Barr (100 mm Hg).

11.1.7 Allow specimens to dry in vacuum oven for 1 h at 40°C.

11.1.8 Remove the dishes from the vacuum oven and place in a covered container at room temperature. Specimens should not stand for more than 72 h between solvent evaporation and curing.

NOTE 3—For applications where a clearcoat is applied on top of a basecoat, it is recommended that the procedure be followed through step 11.1.8 for the basecoat then return to step 11.1.4 and apply the clearcoat.

11.2 *Cure Coating Specimens:*

11.2.1 Assemble apparatus as described in 9.2 with a fresh DNPH Cartridge (two cartridges for waterborne coatings).

11.2.2 Place one dish containing specimen in a cool (room temp) purge chamber.

11.2.3 Replace hot empty purge chamber (using insulated gloves) with chamber containing specimen, attaching the cover as quickly as possible.

11.2.4 Record initial flows (Total Flow and Tube Flow) and start time on Bench Data Sheet.

11.2.5 Allow coating to cure for 30 min then record final flows (Total Flow and Tube Flow) and end time on Bench Data Sheet.

11.2.6 Disconnect, cap and label the DNPH Cartridge(s).

11.2.7 Remove purge chamber from oven (using insulated gloves), remove aluminum foil dish from purge chamber with tongs and place into a desiccator to cool.

11.2.8 Repeat steps 11.2.1 – 11.2.7 for other two replicates and one blank run with empty foil dish.

NOTE 4—An alternative to running a purge chamber blank would be to attach a DNPH cartridge at the inlet to the purge chamber (outside of the oven) and analyze this cartridge every 20 runs to demonstrate that formaldehyde has not broken through (<75 µg formaldehyde/cartridge).

11.2.9 After the cured aluminum foil dishes have cooled, record the weight of the dry coating on the Bench Data Sheet.

11.3 *Analysis of DNPH Cartridges:*

11.3.1 Store DNPH Cartridges in a refrigerator until analysis.

11.3.2 Elute DNPH Cartridge with 3 mL of acetornirile into a 5 mL volumetric flask over a 1-minute period.

NOTE 5—Flow rates greater than 3 mL/min can result in reduced recovery.

11.3.3 Bring the volume of the volumetric flask to 5 mL with acetonitrile, mix sample then transfer to vial.

11.3.4 Set up HPLC according to 9.1.

11.3.5 Analyze the eluent from each cartridge by injecting the same volume of sample as used for calibration standards (10 to 20 µL). Bracket every 10 samples with a mid-range calibration standard. Samples that contain formaldehyde greater than the highest calibration standard must be diluted.

12. Calculation

12.1 Using the standard calibration curve, calculate the amount of formaldehyde on each DNPH cartridge from data obtained from the sample run (see 11.3) as follows:

$$\text{Formaldehyde, } \mu\text{g/tube} = \frac{A_{analyte} \times 5 \text{ mL}}{R_{analyte}} \qquad (2)$$

where:

$A_{analyte}$ = area of the analyte peak, and
$R_{analyte}$ = average response factor for all standards in calibration curve (as determined in 10.2.4).

NOTE 6—Mid-range bracketing standards must fall within ±5 % of a calibration standard.

12.2 Record Formaldehyde concentrations (µg/tube) on Bench Data Sheets.

12.3 Calculate the split ratio for each replicate run and blank as follows:

$$\text{Run N Split Ratio} = \qquad (3)$$

$$\frac{(\text{Initial Total Flow} + \text{Final Total Flow}) \cdot 273 \cdot \text{Pressure}}{(\text{Initial Tube Flow} + \text{Final Tube Flow}) \cdot (273 + \text{Temperature}) \cdot 29.9}$$

where:

N= 1-3 and Blank
Flows in mL/min
Pressure at low flow meter in mmHg
Temperature at low flow meter in °C

12.4 Calculate the Total amount of formaldehyde for each replicate run as follows:

$$\text{Run N, } \mu\text{g Total} = \text{Run N Split Ratio} \times \text{Run N, } \mu\text{g/Tube} \qquad (4)$$

where:

N = 1-3 and Blank
Run N Split Ratio from 12.3
Run N, µg/Tube from 12.1

12.5 Calculate the Net amount of formaldehyde for each replicate run as follows:

$$\text{Run N, } \mu\text{g Net} = \text{Run N, } \mu\text{g Total} - \text{Blank, } \mu\text{g Total} \qquad (5)$$

where:

N = 1-3
Run N, µg Total from 12.4 for N = 1-3
Blank µg Total from 12.4 for Blank

12.6 Calculate the Wet Weight concentration of formaldehyde for each replicate run as follows:

$$\text{Run N, } \mu\text{g/g (Wet Wt.)} = \frac{\text{Run N, } \mu\text{gNet}}{\text{Pan, g Wet Wt.}} \qquad (6)$$

where:

N = 1-3
Run N, µg Net from 12.5
Pan N, g Wet Wt. from 11.1.4

12.7 Calculate the Dry Weight concentration of formaldehyde for each replicate run as follows:

$$\text{Run N, } \mu\text{g/g (Dry Wt.)} = \frac{\text{Run N } \mu\text{gNet}}{\text{Pan, g Dry Wt.}} \qquad (7)$$

where:

N = 1-3
Run N, µg Net from 12.5
Pan N, g Dry Wt. from 11.2.9

12.8 Calculate the Average Wet Weight concentration of formaldehyde for coating as follows:

$$\text{Ave, } \mu g/g \left(\text{Wet Wt.}\right) = \frac{\left(\text{Run1} + \text{Run2} + \text{Run3}\right)}{3} \tag{8}$$

where:
Wet Wt. (12.6) for Run 1, Run 2 and Run 3

12.9 Calculate the Average Dry Weight concentration of formaldehyde for coating as follows:

$$\text{Ave, } \mu g/g \left(\text{Dry Wt.}\right) = \frac{\left(\text{Run1} + \text{Run2} + \text{Run3}\right)}{3} \tag{9}$$

where:
Dry Wt. (12.7) for Run 1, Run 2 and Run 3

13. Precision and Bias[4]

13.1 *Interlaboratory Test Program*—An interlaboratory study of this test method was conducted in which operators in four laboratories measured the cure formaldehyde of seven automotive coatings. The coatings consisted of two solventborne primers, two solventborne basecoats, two solventborne basecoat/clearcoat combinations and one waterborne basecoat. All coatings were analyzed in triplicate (each result being the mean of triplicate determinations) and results analyzed in accordance with Practice E691. Results ranged from 5 700 µg/g (a solventborne primer) to 13 480 µg/g (solventborne basecoat). The minimum requirements for Practice E691 are six laboratories, four materials and two determinations or 45 degrees of freedom. This study had four laboratories, seven materials and three determinations or 81 degrees of freedom. One of the participating laboratories deviated slightly from the study procedure by having a total cure time of 45 min as opposed to 30 min. As a result this laboratory was not included in the calculation for reproducibility providing only 60 degrees of freedom for the precision estimates.

13.2 *Precision*—The precision information given below for cure formaldehyde in percent relative standard deviation (coefficient of variation) is for the comparison of two test results, each of which is the average of three test determinations.

13.2.1 *Repeatability:*

Coefficient of variation	11.81 %
Degrees of freedom	7
Factor (based on 95 % confidence level)	2.8
Precision	33.06 %

13.2.1.1 Two results, each the mean of triplicate determinations obtained by the same operator on different days should be considered suspect if they vary by more than 33 % relative.

13.2.2 *Reproducibility:*

Coefficient of variation	14.84 %
Degrees of freedom	6
Factor (based on 95 % confidence level	2.8
Precision	41.55 %

13.2.2.1 Two results, each the mean of triplicate determinations obtained by the same operator on different days should be considered suspect if they vary by more than 41 % relative.

13.3 *Bias*—Since there is no accepted reference material, method or laboratory for determining the bias for the procedure in this test method for measuring cure formaldehyde in coatings, no statement is being made.

14. Keywords

14.1 coating; cure; DNPH; formaldehyde; HPLC; melamine; VOC; volatiles

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1129. Contact ASTM Customer Service at service@astm.org.