METHOD 311

APPENDIX A

METHOD FOR THE MEASUREMENT OF CURE HAPS FROM PAINTS AND COATINGS

A1.0 Scope and Application.

A1.1 Analytes. This Appendix A of Method 311 includes procedures for measurement of methanol and formaldehyde, which are the most common cure volatiles that are also hazardous air pollutants (HAP's), although other volatile organic compounds are also collected and could be measured.

A1.2 Applicability. This method allows direct measurement of methanol and formaldehyde emitted from paints and coatings as they cure. The compounds may be present in the coating formulation or formed during the curing process or both. Derivatization of formaldehyde improves the sensitivity of the chromatographic detection procedure and increases holding time for samples. The method can also be used to measure other volatile HAP's emitted by coatings as they cure regardless of whether the compounds are present in the coating formulation or formed during curing.

A1.3 Data Quality Objectives.

A1.3.1 Accuracy. The DQO for accuracy, expressed as a percentage of measured value divided by known true value, is 100 ± 10%.

A1.3.2 Precision. The DQO for precision, defined as relative standard deviation, is $\leq$ 10%.

A2.0 Summary of Method

The proposed method involves purging volatiles from a weighed sample of coating with dry nitrogen at 110˚C (or the curing temperature recommended by the manufacturer); collecting cure volatiles with impingers using water and 1-butanol (or dimethylformamide) as collection solvents; determining formaldehyde and methanol concentrations in the impinger solutions by gas chromatography with flame ionization detection (GC-FID); and calculating weight percent of cure volatiles in the original coating.

A3.0 Definitions. [Reserved]

A4.0 Interferences.

A4.1 Coating samples may contain one of the compounds used as internal standards. This can be determined by analyzing two aliquots of the same impinger solution, with one aliquot spiked with the internal standard and the other aliquot not spiked. If necessary, a different internal standard may be used.

A4.2 Coating samples may contain other VOC's that coelute with either a target analyte or one of the internal standards. If there is any doubt about the identification or resolution of any GC peak, it may be necessary to analyze the sample using a different GC column or different GC operating conditions.

A4.3 Care must be taken to avoid cross-contamination due to contaminated glassware and other items that come into contact with samples before or during analysis.

A5.0 Safety.

5.1 Many solvents used in coatings are hazardous. Precautions should be taken to avoid unnecessary inhalation and skin or eye contact. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations in regards to the performance of this test method.

5.2 User's manuals for the gas chromatograph and other related equipment should be consulted for specific precautions to be taken related to their use.

A6.0 Equipment and Supplies.

A6.1 Sampling Equipment and Supplies. The sampling equipment and supplies listed in this section are used to collect cure and other volatiles from a weighed coating sample as it is cured under controlled conditions (see Figures 1 and 2).

A6.1.1 Serum Bottle.[1,2] The serum bottle used as a curing chamber, shown schematically in Figure 1, is a disposable 125-mL bottle (Wheaton 223748, or equivalent).

A6.1.1.1 Condition serum bottles by placing them in an oven at 110°C (or the curing temperature recommended by the coating manufacturer) for at least an hour.

A6.1.1.2 Allow the bottles to cool to room temperature just prior to use.

A6.1.2 Nitrogen Inlet and Outlet Assemblies.[1,2] The nitrogen inlet and outlet assemblies are shown schematically in Figure 1 (with stainless steel unions attached). Each assembly consists of a 15-gauge needle welded to a short length of 1/4-in OD stainless steel tubing.

A6.1.3 Midget Impingers and Dispersion Tubes. Midget impingers (Fisher K37560-0000 or equivalent), shown schematically in Figure 1, have a capacity of 30 mL and graduations in 5-mL increments. Dispersion tubes (Fisher K737561-0000 or equivalent) have 18/9 spherical (or ball) joints for connection in series (see Figure 2). Wash midget impingers and dispersion tubes with warm soapy water; rinse them with warm tap water and then with organic-free or deionized water; and then dry them in an oven at 110°C.

A6.1.4 Glass Connecting Tubes. Glass connecting tubes, shown schematically in Figure 1, have 18/9 sockets at both ends and are used to connect impingers in series (see Figure 2).

A6.1.5 Glass Joints. Glass joints, shown schematically in Figure 1, are 18/9 ball and 18/9 socket joints and are used to connect sample transfer lines to the first and last impingers in the series (see Figure 2).

A6.1.6 Teflon® Tubing. Teflon® tubing used is 1/4-in OD.

A6.1.7 Digital Thermometer. A digital thermometer, which must be capable of measuring temperatures up to 200°C, is used to measure temperature inside the serum bottle during initial setting of the oven temperature.

A6.1.8 Oven. A gravity convection oven, or equivalent, equipped with a thermometer or thermocouple (for monitoring air temperature inside the oven) and with ports for nitrogen inlet and outlet lines.

A6.1.9 Stainless Steel Union Connectors. Swagelok® (or equivalent) stainless steel unions for 1/4-in OD tubing are fitted with Teflon® ferrules on one end (for connection to Teflon® tubing) and stainless steel ferrules on the other end (for connection to the nitrogen inlet or outlet assembly). The unions are shown schematically in Figure 1.

A6.1.10 Bubble Flowmeter. A 500-mL soap-film bubble flowmeter (or equivalent) is used to measure nitrogen gas flow rate over the coating sample as it is cured in the serum bottle.

A6.1.11 Ice Bath. An ice bath is used to chill at least four midget impingers connected in series (see Figure 2) for collection of cure and other volatiles.

A6.1.12 Variable Transformer. A Powerstat Variable Autotransformer, Type 116B, with inlet voltage of 120 volts and outlet voltage of 0-140 volts, or equivalent transformer is used to maintain the temperature of heat-traced sample lines (see Figure 2).

A6.2 Analysis Equipment and Supplies. The analysis equipment and supplies listed here are used to measure cure volatiles collected in impinger solutions (see Figure 2).

A6.2.1 Gas Chromatograph (GC). Any temperature-programmable GC equipped with a flame ionization detector (FID) or other detector system that yields an appropriate and reproducible response to the analytes in the injected liquid sample may be used.

A6.2.2 Recorder. An electronic data station or integrator may be used to record the gas chromatogram and associated data. If a strip chart recorder is used, it must meet the following criteria: A 1 to 10 millivolt (mV) linear response with a full-scale response time of 2 seconds or less and a maximum noise level of ±0.03 percent of full scale. Other types of recorders may be used as appropriate to the specific detector installed provided that the recorder has a full scale response time of 2 seconds or less and a maximum noise level of ±0.03 percent full scale.

A6.2.3 GC Column. A 50-m, 0.53-mm ID, 3.0-µm film thickness, DB-624 fused silica column (J&W Scientific; or equivalent column from another supplier) has been used to successfully separate the analytes. However, any column that adequately separates formaldehyde and methanol from each other and from other collected species can be used.

A6.2.4 Tubing and Tube Fittings. Tubing and tube fitting supplies are used to connect the GC with appropriate gas supply lines or cylinders.

A6.2.5 Pressure Regulators. Pressure regulators are used to regulate gas pressure between the gas supply lines or cylinders and the GC.

A6.2.6 Flow Meter. A digital or soap-film flow meter is used to measure gas flow rates.

A6.2.7 Septa. Septa are seals on a GC injection port through which liquid samples can be injected using a syringe.

A6.2.8 Liquid Charging Devices. Liquid charging devices, such as graduated microliter syringes, are used to inject liquid samples into a GC. Common sizes include syringes with 1-, 5-, and 10-µL capacities.

A6.2.9 Vials. Vials are containers that can be sealed with a septum in which samples may be prepared or stored. Sample aliquots are removed with a syringe through the vial septum for injection into a GC.

A6.2.10 Balance. A balance capable of weighing to 0.0001 g is required to determine the weights of samples and standards.

A7.0 Reagents and Standards.

A7.1 O-(2,3,4,5,6-Pentafluorobenzyl)hydroxylamine Hydrochloride (PFBHA-HCl) [57981-02-9]. PFBHA-HCl (Cat. No. 19,448-4, 98+%, Aldrich, Milwaukee, WI; or equivalent) reagent is prepared gravimetrically as a 5.0 mg/mL aqueous solution using organic free water. Solid PFBHA-HCl should be stored in a desiccator under an inert atmosphere.

A7.2 1,2-Dibromopropane [78-75-1]. 1,2-Dibromopropane (Cat. No. 14,096-1, 97%, Aldrich, Milwaukee, WI; or equivalent) is added to the extraction solvent (pentane) as an internal standard for the formaldehyde-PFBHA derivative.

A7.3 1-Propanol [71-23-8]. 1-Propanol (Cat. No. 40,289-3, 99.5+%, A.C.S. reagent, Aldrich, Milwaukee, WI; or equivalent) is used as an internal standard for the quantitation of methanol.

A7.4 Pentane [109-66-0]. Pentane (Cat. No. P399-1, HPLC Grade, Fisher Scientific, Fairlawn, NJ; or equivalent) is used as the extracting solvent for the formaldehyde-PFBHA derivative.

A7.5 Hydrochloric Acid [7647-01-0]. Hydrochloric acid (Cat. No. 32,033-1, 37% by weight in water, A.C.S. reagent, Aldrich, Milwaukee, WI; or equivalent) is used for acidification of the formaldehyde-PFBHA derivative.

A7.6 Anhydrous Sodium Sulfate [7757-82-6]. Anhydrous sodium sulfate (Cat. No. 23,931-3, 99+%,A.C.S. reagent, Aldrich, Milwaukee, WI; or equivalent) is used to dry the pentane extraction solution containing the formaldehyde-PFBHA derivative.

A7.7 Methanol [67-56-1]. Methanol (Cat. No. 44,347-6, 99.8+%, A.C.S. reagent, Aldrich, Milwaukee, WI; or equivalent) is used as an authentic standard for the quantitative measurement of methanol.

A7.8 Formaldehyde [50-00-0]. Formaldehyde (Cat. No. 25,254-9, 37% by weight in water, A.C.S. reagent, Aldrich, Milwaukee, WI; or equivalent) is used as an authentic standard for the quantitative measurement of formaldehyde.

A7.9 1-Butanol [71-36-3]. 1-Butanol (Cat. No. 27,067-9, 99.8%, HPLC grade, Aldrich, Milwaukee, WI; or equivalent) is used as the collection solvent in the third and fourth impingers during sampling. (Formaldehyde and methanol are collected in the water-filled first and second

impingers. The third and fourth impingers are therefore optional if only methanol and water are to be measured.)

A7.10 Stock Reference Standards. Stock reference standards are solutions of the reference standard materials that may be used on a daily basis to prepare calibration standards, calibration check standards, and quality control check standards. Stock reference standards may be prepared from the reference standard materials or purchased as certified solutions. The concentrations of analytes in the stock reference standards are not specified but must be adequate to prepare the calibration standards required in the method. Formaldehyde and methanol stock reference standards must be prepared separately because the commercially-available 37% formaldehyde solution used to prepare formaldehyde standards contains 10-15% methanol.

A7.10.1 Formaldehyde Stock Solution. Prepare a stock reference standard of formaldehyde by diluting a weighed amount of 37% formaldehyde solution (Section A7.8) with organic-free water. Store the well-mixed stock solution in one or more Teflon-sealed screw-cap bottles. Store, with minimal headspace, at $\leq 4^{\circ}C$ and protect from light. Prepare fresh stock reference standard solution at least monthly.

A7.10.2 Methanol Stock Solution. Prepare a stock reference standard of methanol by dissolving a weighed amount of the compound in organic-free water in a volumetric flask and diluting the solution to volume with organic free water. Store the well-mixed stock solution in one or more Teflon-sealed screw-cap bottles. Store, with minimal headspace, at $\leq 4^{\circ}C$ and protect from light. Prepare fresh stock reference standard solution at least monthly.

A7.11 Calibration Standards. Calibration standards are used to determine the response of the detector to known amounts of reference material. Calibration standards must be prepared at a minimum of three concentration levels from the stock reference standards. The lowest concentration standard should contain a concentration of analyte equivalent either to a concentration of no more than 0.01% of the analyte in a coating or to a concentration that is lower than the actual concentration of the analyte in the coating, whichever concentration is higher. The highest concentration standard should contain a concentration of analyte equivalent to slightly more than the highest concentration expected for the analyte in a coating. The remaining calibration standard should contain a concentration of analyte roughly at the midpoint of the range defined by the lowest and highest concentration calibration standards. The concentration range of the standards should thus correspond to the expected range of analyte concentrations in the prepared coating samples. Each calibration standard should also contain an appropriate amount of internal standard material (response for the internal standard material is within 25% to 75% of full scale on the attenuation setting for the particular reference standard concentration level). Calibration Standards should be stored for 1 week only in sealed vials with minimal headspace. Formaldehyde and methanol calibration standards must be prepared separately because the commercially-available 37% formaldehyde solution used to prepare formaldehyde standards contains 10-15% methanol.

A7.11.1 Formaldehyde Calibration Standards. Formaldehyde calibration standards are prepared by dilution of the formaldehyde stock solution. The calibration standards must be treated with the PFBHA derivatization solution in the same fashion as impinger samples.

A7.11.2 Methanol Calibration Standards. Methanol calibration standards are prepared by

dilution of the methanol stock solution.

A7.12 Quality Control Check Standards. Quality control check standards (QCCS) are used to determine the accuracy and precision of the analytical method. Prepare a QCCS containing methanol or formaldehyde (but not both in the same solution, for the reasons given in Section A7.10) at a concentration expected to result in a response between 25% and 75% of the limits of the calibration curve. The QCCS may be prepared from reference standard materials or purchased as certified solutions. If prepared in the laboratory, the QCCS must be prepared independently from the calibration standards.

A7.12.1 QCCS for Formaldehyde. The QCCS sample for formaldehyde must be treated with the PFBHA derivatization solution in the same fashion as impinger samples.

A7.12.2 QCCS for Methanol. The QCCS sample for methanol requires no additional treatment prior to analysis.

A8.0 Sample Collection, Preservation, Transport, and Storage.

All sample collection, preservation, transport, and storage requirements given in Section 8 of Method 311 apply in this appendix as well.

A9.0 Quality Control.

All quality control requirements given in Section 9 of Method 311 related to GC analysis shall be applicable for this method. The GC samples in this appendix are the impinger samples collected during curing of a coating sample; therefore, blanks, standards, and quality control check standards (QCCS's) shall be made up as aqueous solutions. For the formaldehyde analysis, all quality control samples shall be subjected to the PFBHA derivatization and extraction procedure prior to analysis if impinger samples will be subjected to that procedure.

A10.0 Calibration and Standardization.

All calibration and standardization requirements given in Section 10 of Method 311 related to GC analysis shall be applicable for this method. The GC samples for this method are the aqueous impinger samples collected during curing of a coating sample and therefore water will be the solvent for all stock and calibration standards. For the formaldehyde analysis, all calibration standards shall be subjected to the PFBHA derivatization and extraction procedure prior to analysis if impingers samples will be subjected to that procedure. Equations for calculations specific to this analysis are given in Section A12.

A11.0 Analytical Procedure.

A11.1 Procedures for Sample Collection. This section describes the procedures for collecting volatiles emitted from a coating sample as it cures under controlled conditions.

A11.1.1 Initial Set-Up. The apparatus used for sample collection is shown disassembled in Figure 1 and assembled in Figure 2. Sections A11.1.1.1, A11.1.1.2, and A11.1.1.3 must be done before any samples are analyzed. Nitrogen flow rate and oven temperature should then be checked (and readjusted, if necessary) at the beginning of each analysis.

A11.1.1.1 Set nitrogen flow rate. Use 1/4-in OD Teflon tubing for a dry-nitrogen supply line to the apparatus. Using a flow meter to monitor the nitrogen flow rate, adjust the nitrogen

flow through the needle of the nitrogen inlet assembly to 0.50 ± 0.05 L/min.

A11.1.1.2 Set oven temperature. The oven temperature is set to give a temperature of 110 ± 5°C (or the curing temperature recommended by the manufacturer) inside the serum bottle with 0.50 ± 0.05 L/min of nitrogen flowing through it. Set nitrogen flow rate as described in the preceding section. Remove the flow meter. Place an unsealed, empty serum bottle in the oven and place the nitrogen inlet needle in the open bottle with the point of the needle about 3/4 inch from the bottom. Run a thermocouple from outside the oven down into the serum bottle. Position the thermocouple so that it is very near to, but not touching, the bottom of the serum bottle and not directly underneath the nitrogen inlet needle. Adjust the temperature of the oven to achieve a temperature of 110 ± 5°C (or the curing temperature recommended by the manufacturer) in the bottle for one hour. Record the temperature setting of the oven required to give a temperature of 110 ± 5°C (or the curing temperature recommended by the manufacturer) in the serum bottle. The oven should be set at this temperature setting during subsequent coating analyses.

A11.1.1.3 Heat Trace Nitrogen Outlet Line. Wrap the sampling line coming out of the oven with heating tape to eliminate cold spots. The temperature of the heat-traced sampling line outside the oven should be 110 ± 5°C (or the curing temperature recommended by the manufacturer).

A11.1.2 Sample Collection. Sections A11.1.2.1 to A11.1.2.9 must be done for each analysis. Each coating should be analyzed a minimum of three times.

A11.1.2.1 With a bubble flow meter, check the nitrogen flow rate through the nitrogen inlet needle to confirm that it is 0.50 ± 0.05 L/min. If the flow rate is outside the given range, readjust it as described in Section A11.1.1.1. Record the measured flow rate.

A11.1.2.2 Measure the temperature inside the oven to confirm that it is within ± 5°C of the oven temperature measured in Section A11.1.1.2. Record the measured oven temperature.

A11.1.2.3 Four impingers arranged in series (see Figure 2) will collect most of the VOC's emitted by a coating sample as it cures. Only the first two impingers (each of which contains 25 mL organic-free water) are required to collect methanol and formaldehyde (and any other polar, water soluble compounds that might be emitted). The last two impingers (each of which contains 25 mL 1-butanol) may be used to collect less-polar, water-purgeable VOC's (styrene, for example). Referring to Figure 2, connect the impingers in series using glass connecting tubes or Teflon tubing. Connect the inlet of the first impinger to the heat-traced outlet line (see Section A11.1.1.3) and be sure there are no cold spots between the oven and the first impinger. Connect the outlet of the last impinger to a suitable vent (a hood, for example) for organic vapors. Place all impingers in an ice bath.

A11.1.2.4 Weigh an empty, dry serum bottle and cap and septum (unassembled) to ± 0.0001 g and record the weight (W_1). Add 1.5 ± 0.2 g of well-mixed coating or paint to the serum bottle, weigh the serum bottle and cap and septum again to ± 0.0001 g, and record the weight (W_2). Quickly seal the serum bottle with the septum and cap. Spread the coating sample over the inside walls of the serum bottle. This can be done by laying the bottle on its side and rolling it on a flat surface or by carefully tilting and turning the bottle by hand.

NOTE: Do not allow the coating to come into contact with the septum sealing the serum bottle where it could come into contact with the nitrogen inlet or outlet needles.

A11.1.2.5 Insert the nitrogen outlet needle through the septum in the serum bottle containing the coating sample. Insert the nitrogen inlet needle in the same fashion. Adjust the height of the end of the nitrogen inlet needle so that a flow of 0.50 ± 0.05 L/min ripples the surface of the coating or paint but does not cause the mixture to splatter excessively. Place the serum bottle in the oven.

A11.1.2.6 Check the system for leaks. With the apparatus full assembled, attach a water-filled manometer (or a 120-cm loop of clear plastic tubing with water in the bottom 1/4 of the loop) to the outlet of the last impinger. Allow just enough nitrogen into the system to displace the water in the manometer to a height difference (between the sides of the manometer) of 20 ± 2 cm. With nitrogen flow off, measure with a stopwatch the time required for the difference in water levels on the two sides of the manometer to be reduced by 10 cm or measure the change in difference in water levels after 1 minute, whichever comes first. Calculate the leak rate of the apparatus according to Equation 1.

$$\text{leak rate} = \frac{\pi d^2 h}{8t} \qquad \text{Eq. (1)}$$

where:

d = ID of manometer tube (cm)
h = change in height difference of water levels (cm)
t = time

If the leak rate is less than or equal to 10 mL/min, continue with the next section of the procedure. If the leak rate is greater than 10 mL/min but less than 20 mL/min, tighten all connectors and measure the leak rate again. If the initial leak rate is 20 mL/min or greater, or if all leak problems are not solved within 5 minutes after placing the serum bottle in the oven, discard the sample and start over with a fresh one.

A11.1.2.7 When the system passes the leak test, turn on the nitrogen gas flow through the apparatus. Measure the flow from the vent of the last impinger to ensure that the outlet flow equals the flow rate measured in Section A11.1.2.1. Leave the coating sample in the oven at 110 ± 5°C (or the curing temperature recommended by the manufacturer) with nitrogen flowing for 30 minutes.

A11.1.2.8 Formaldehyde and methanol are collected by the water in the first and second impingers. The impingers are chilled in an ice bath during the collection process. The nitrogen purge rate is 0.50 ± 0.05 L/min, and the purging time is 30 minutes.

NOTE: Breakthrough is less than 10% from the first impinger for formaldehyde and methanol when the sampling time is 30 minutes, the amount of each compound is less than 200 mg, the oven temperature is 110 ± 5°C, and the volume of water in the impingers is 25 mL.

A11.1.2.9 At the end of the 30-minute purge time, turn off the nitrogen flow and disassemble the apparatus. Take the serum bottle out of the oven and let it cool to room

temperature. Disconnect all of the impingers and measure the volume of liquid in each impinger to ± 0.1 mL. Record the volumes. Transfer the impinger solutions to separate 25-mL vials, and seal the vials with screw caps fitted with PTFE liners. Store the samples in a refrigerator at ≤ 4°C until just before they are analyzed. Weigh the serum bottle containing the nonvolatile residue to ± 0.0001 g, and record the weight (W_3).

> NOTE: The final weight of the serum bottle containing the residue is not required for calculation of the concentration of a HAP measured by this method, but this weight can be used to calculate weight percent volatiles (see NOTE at the end of Section A12.3.2).

> NOTE: The volumes of impinger solutions must be known because only a portion (aliquot) of each solution is taken for analysis.

A11.2 Procedures for Analysis. Analyze samples as quickly as possible. Methanol is analyzed by GC by direct injection of an aliquot of the impinger solution after it has been spiked with a known amount of an internal standard. Formaldehyde is converted to its PFBHA derivative; the derivative is extracted with pentane; and the pentane solution is dried, spiked with an internal standard, and analyzed by GC.

A11.2.1 Analysis for Methanol. Using a syringe, remove an aliquot from an aqueous impinger sample. Place the aliquot in a sealed vial and allow it to reach room temperature. Again using a syringe, spike the aliquot with a known amount of 1-propanol (an internal standard). Mix the solution thoroughly and then analyze by GC.

> NOTE: A Hewlett Packard 5890 Series II Gas Chromatograph with flame ionization detector (GC-FID) has been successfully used to measure methanol. A 50-m, 0.53-mm ID, 3.0 µm film thickness, DB-624 fused silica GC column was used for the separation. A split/splitless injector was used with a split ratio of 1:10. The injector temperature was 250°C. The carrier gas flow rate was 7 mL/min. The temperature program started at a column temperature of 40°C where it was held for 1 minute after injection, then increased to 120°C at a rate of 5°C/min, then increased to 200°C at a rate of 20°C/min, and held at 200°C for 5 minutes.

If the concentration of methanol is above the GC calibration range, dilute the impinger-solution aliquot before analysis.

A11.2.2 Analysis for Formaldehyde. Formaldehyde, which gives a weak FID response, is converted to its PFBHA derivative, which gives a strong FID response.

A11.2.2.1 Derivatization of Formaldehyde.[3] Using a syringe, remove an aliquot from an aqueous impinger sample. Place the aliquot in a sealed vial and allow it to reach room temperature. Using a glass pipet, add PFBHA reagent to the aliquot. Allow the solution to stand in a sealed vial at room temperature for 1 hour. Add two drops of concentrated hydrochloric acid (37%) to acidify the solution. Shake the vial and let the mixture stand for 10 minutes.

A11.2.2.2 Extraction of the Formaldehyde Derivative. In the same vial, extract the formaldehyde-PFBHA derivative with an aliquot of pentane containing a known concentration of 1,2-dibromopropane (an internal standard) by shaking the combined components for 30 seconds. The pentane extract (top layer) is removed with a Pasteur pipet, transferred to a different vial, and dried for 10 minutes over ~50 mg of anhydrous sodium sulfate.

A11.2.2.3 Analysis of the Formaldehyde-PFBHA Derivative. The dry pentane extract is analyzed for formaldehyde-PFBHA derivative by GC-FID.

NOTE: Measurement of the formaldehyde-PFBHA derivative has been successfully accomplished on the same analytical system and column described for methanol in Section A11.2.1. The temperature program for the formaldehyde-PFBHA derivative analysis started at a column temperature of 60°C, which was held for 1 minute, then increased to 120°C at a rate of °C/min, then increased to 200°C at a rate of 20°C/min, and finally held at 200°C for 2 minutes.

A12.0 Data Analysis and Calculations.

A12.1 Gas Chromatography Calculations. An analyte is considered tentatively identified if two criteria are met: (1) the sample analyte elution time is within ± 0.05 min of the average GC retention time of the same analyte in the calibration standard, and (2) either (a) the identity of the compound is confirmed by spectral matching on a GC equipped with a mass selective detector or (b) the sample analyte elution time is within ± 0.05 min of the average GC retention time of the same analyte in the calibration standard analyzed on a second, dissimilar GC column. Equations for quantitative calculations based on the internal standard approach are given in the following subsections.

A12.1.1 Response Factors for the Internal Standards. Calculate a response factor for 1-propanol (internal standard for the methanol analysis) and for 1,2-dibromopropane (internal standard for the formaldehyde-PFBHA derivative analysis) from calibration standard analysis results according to Equation 2.

$$RF_{is} = \frac{A_{is}}{C_{is}} \qquad \text{Eq. (2)}$$

where:

RF_{is} = response factor for the internal standard
A_{is} = area response for the internal standard
C_{is} = concentration of the internal standard

A12.1.2 Relative Response Factors for the HAP's. Calculate a relative response factor for methanol (relative to the internal standard, 1-propanol, used for the measurement of methanol) and for formaldehyde (relative to the internal standard, 1,2-dibromopropane, used for measurement of the formaldehyde-PFBHA derivative) for all calibration standards according to Equation 3.

$$RRF_{HAP} = \frac{A_{HAP}}{RF_{is}C_{HAP}} \quad \text{Eq. (3)}$$

where:

RRF_{HAP} = relative response factor for an individual HAP
A_{HAP} = area response for the HAP being measured
C_{HAP} = concentration of the HAP being measured
RF_{is} = response factor for the internal standard

A12.1.3 Mean Relative Response Factor. Calculate the mean relative response factor ($\overline{RRF_{HAP}}$) for the HAP in a set of calibration standards by simply averaging the relative response factors (RRF_{HAP}) calculated for each standard as shown in Equation 4.

$$\overline{RRF_{HAP}} = \sum_{i=1}^{n} RRF_{HAP}(i) \quad \text{Eq. (4)}$$

where:

$\overline{RRF_{HAP}}$ = mean relative response factor for the HAP in the calibration standards
$RRF_{HAP}(i)$ = relative response factor for the HAP in standard i
n = number of calibration standards in the set

A12.1.4 Weight of HAP in Aliquot Taken for Analysis. Calculate the weight of HAP (methanol or formaldehyde) in each aliquot according to Equation 5.

$$W_{HAP\_aliq} = \frac{A_{HAP}W_{is}}{A_{is}\overline{RRF_{HAP}}} \quad \text{Eq. (5)}$$

where:

W_{HAP_aliq} = weight of HAP in the aliquot taken for analysis
A_{HAP} = GC area response for the HAP being measured
W_{is} = weight of internal standard added to the aliquot taken for analysis (g)
A_{is} = GC area response for the internal standard added to the aliquot
$\overline{RRF_{HAP}}$ = mean relative response factor for the HAP in the calibration standards

A12.1.5 Weight of HAP in Impinger Sample. Calculate the weight of the HAP collected in the impinger according to Equation 6.

$$W_{HAP\_imp} = \frac{W_{HAP\_aliq} V_{imp}}{V_{aliq}} \quad \text{Eq. (6)}$$

where:

W_{HAP_imp} = weight of HAP in the impinger
W_{HAP_aliq} = weight of HAP in the injected sample
V_{imp} = volume of liquid in the impinger (mL)
V_{aliq} = volume of liquid aliquot taken for analysis (mL)

A12.2 Gravimetric Calculations. The weights (all expressed in grams) below must be known to calculate emissions of methanol and formaldehyde from a coating sample during curing in the serum bottle.

W_1 = weight of empty serum bottle plus septum and cap [Section A11.1.2.4]
W_2 = weight of sealed bottle with coating before heating [Section A11.1.2.4]
W_3 = weight of sealed bottle with residue after heating [Section A11.1.2.9]
$W_{methanol\_imp\_1}$ = weight of methanol in the first impinger [Equation 6]
$W_{methanol\_imp\_2}$ = weight of methanol in the second impinger [Equation 6]
$W_{formaldehyde\_imp\_1}$ = weight of formaldehyde in the first impinger [Equation 6]
$W_{formaldehyde\_imp\_2}$ = weight of formaldehyde in the second impinger [Equation 6]

A12.3 Calculation of Weight Percent of HAP's Emitted from Coating.

A12.3.1 Weight Percent Methanol. Calculate the weight percent of methanol emitted from the coating during curing by using Equation 7.

$$Wt\%_{methanol} = \left(\frac{W_{methanol\_imp\_1} + W_{methanol\_imp\_2}}{W_2 - W_1} \right) (100) \quad \text{Eq. (7)}$$

where:

$Wt\%_{methanol}$ = weight percent of methanol emitted from coating
$W_{methanol\_imp\_1}$ = weight of methanol in the first impinger
$W_{methanol\_imp\_2}$ = weight of methanol in the second impinger
W_1 = weight of empty serum bottle plus septum and cap
W_2 = weight of sealed bottle with coating before heating

A12.3.2 Weight Percent Formaldehyde. Calculate the weight percent of formaldehyde emitted from the coating during curing by using Equation 8.

$$Wt\%_{formaldehyde} = \left(\frac{W_{formaldehyde\_imp\_1} + W_{formaldehyde\_imp\_2}}{W_2 - W_1} \right)(100) \quad \text{Eq. (8)}$$

where:

$Wt\%_{formaldehyde}$ = weight percent of formaldehyde emitted from coating
$W_{formaldehyde\_imp\_1}$ = weight of formaldehyde in the first impinger
$W_{formaldehyde\_imp\_2}$ = weight of formaldehyde in the second impinger
W_1 = weight of empty serum bottle plus septum and cap
W_2 = weight of sealed bottle with coating before heating

NOTE: Weight percent total volatiles in the coating can be calculated according to the equation below.

$$Wt\%_{volatiles} = \left(\frac{W_2 - W_3}{W_2 - W_1} \right)(100)$$

where:

W_1 = weight of empty serum bottle plus septum and cap
W_2 = weight of sealed bottle with coating before heating
W_3 = weight of sealed bottle with residue after heating

A12.4 Precision and Accuracy.

A12.4.1 Calculate the mean concentration of each HAP measured for a coating according to Equation 9.

$$\overline{Wt\%_{HAP}} = \sum_{i=1}^{n} Wt\%_{HAP}(i) \quad \text{Eq. (9)}$$

where:

$\overline{Wt\%_{HAP}}$ = mean weight percent of HAP from the coating
$Wt\%_{HAP}(i)$ = weight percent of HAP from coating sample i
n = number of replicates of this coating analyzed

A12.4.2 Calculate the percent relative standard deviation (%RSD) for each HAP measured for a coating according to Equation 10.

Eq. (10)

$$\%RSD = \left(\frac{\sqrt{\frac{\sum_{i=1}^{n} \left(Wt\%_{HAP}(i) - \overline{Wt\%_{HAP}}\right)^2}{n - 1}}}{\overline{Wt\%_{HAP}}} \right) (100)$$

where:

$\%RSD$ = percent relative standard deviation

$\overline{Wt\%_{HAP}}$ = mean weight percent of HAP from the coating

$Wt\%_{HAP}(i)$ = weight percent of HAP from coating sample i

n = number of replicates of this coating analyzed

A13.0 Method Performance. [Reserved]

A14. Pollution Prevention. [Reserved]

A15. Waste Management.

All waste management requirements given in Section 16 of Method 311 apply in this appendix as well.

A16. References.

1. Max R. Peterson, R. K. M. Jayanty, Bruce A. Pate, Yvonne M. Straley, Mike W. Benson, and John R. Albritton, "Method Development for Measuring the VOC Content of Water-Based Coatings." Prepared for Work Assignment Manager Joseph E. Knoll under EPA Contract No. 68D90055, Work Assignment Nos. 28 and 40, January 1991.

2. Max R. Peterson, S. B. Tompkins, and R. K. M. Jayanty, "Evaluation of Volatilization Chamber in Water-Based Coatings Method." Prepared for Work Assignment Manager Candace Sorrell under EPA Contract No. 68D20163, Work Assignment No. I-47, August 1994.

3. William H. Glaze, Minoru Koga, and Devon Cancilla, "Ozonation Byproducts. 2. Improvement of an Aqueous-Phase Derivatization Method for the Detection of Formaldehyde and Other Carbonyl Compounds Formed by the Ozonation of Drinking Water." *Environ. Sci. Technol.*, 23, 838-847, 1988.

A17.0 Tables, Diagrams, flowcharts, and Validation Data.

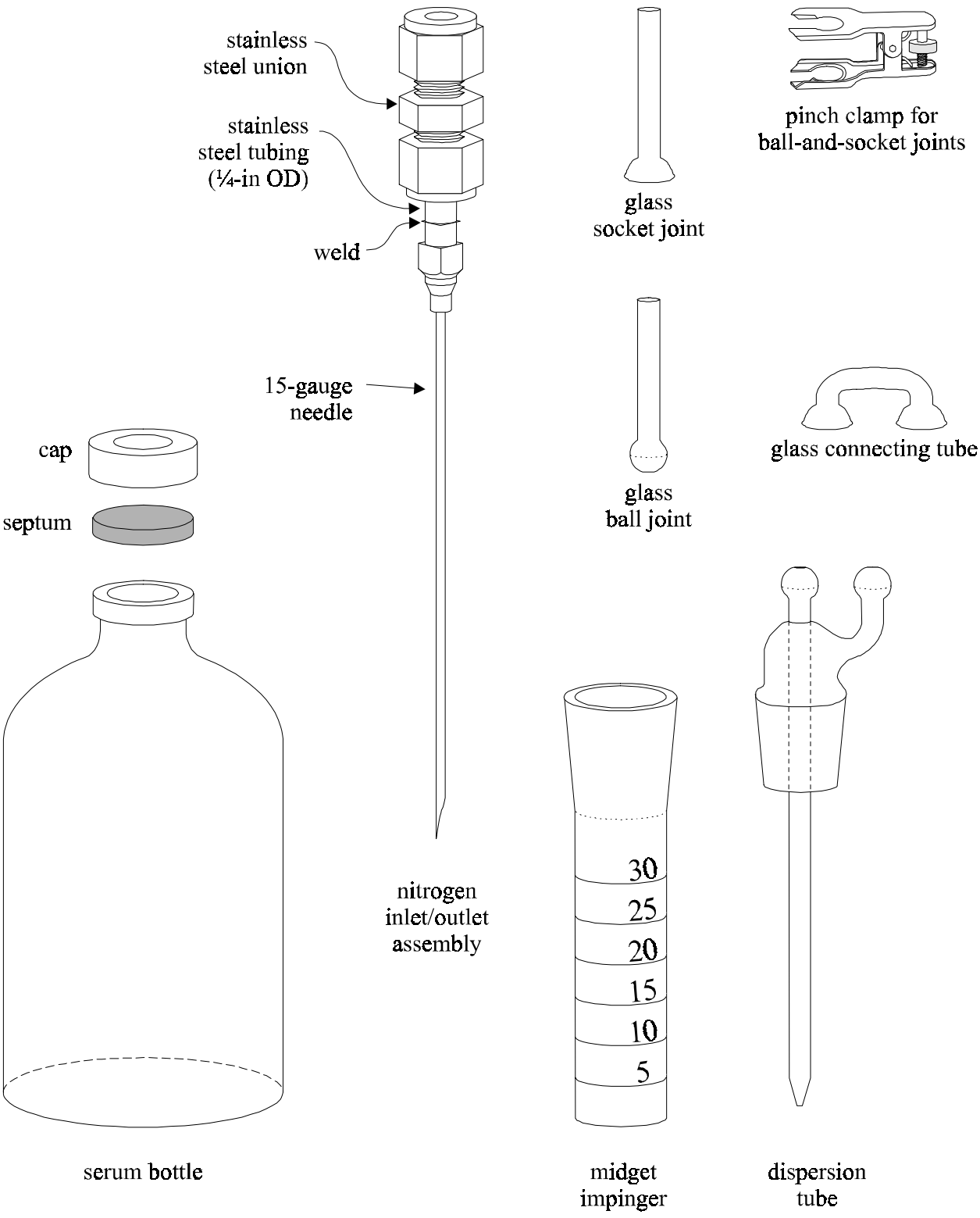

Figure 1. Components of collection apparatus for cure volatiles

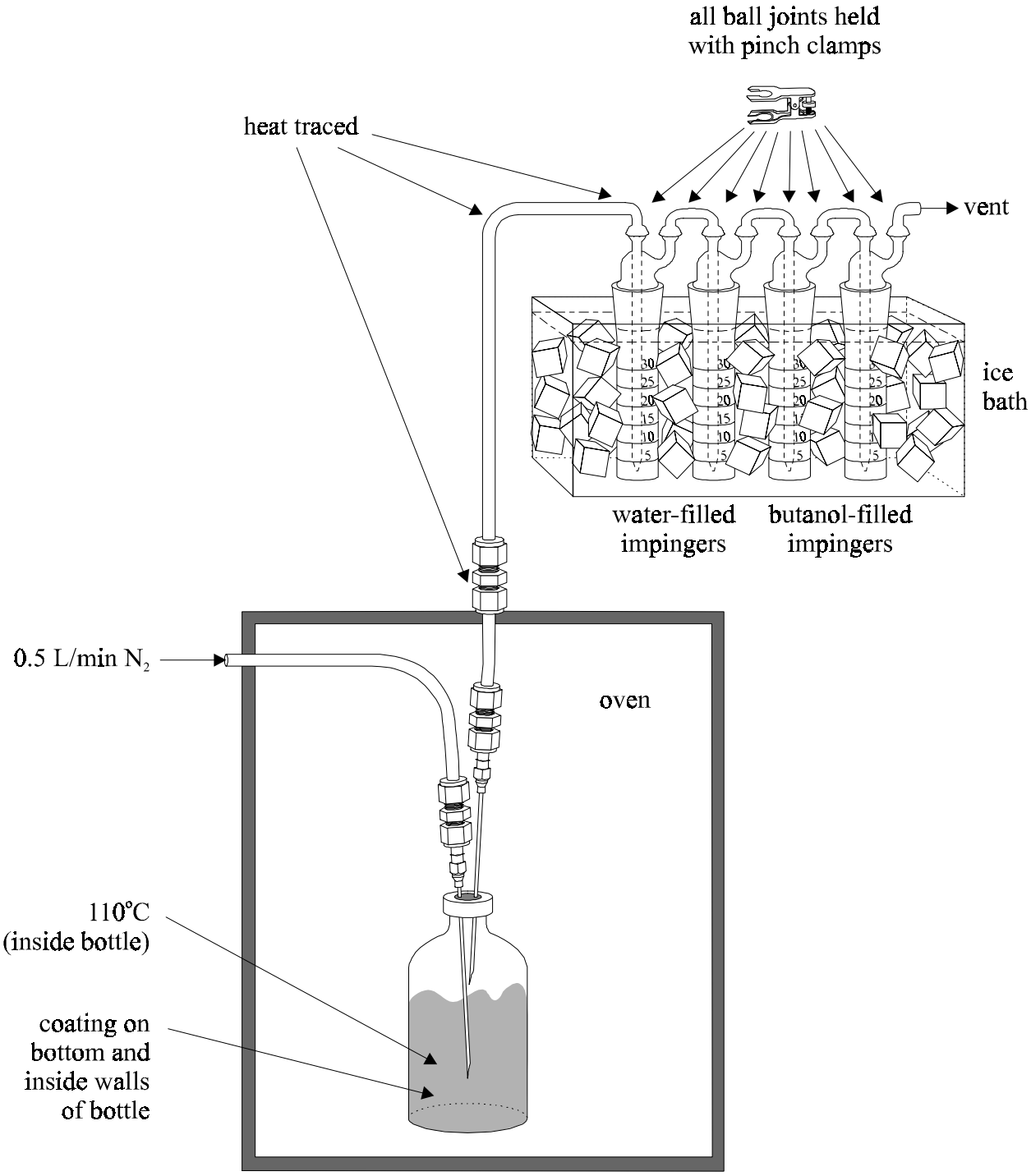

Figure 2. Assembled apparatus for collection of cure volatiles from coatings